

Ulrich Hauptmanns

Process and Plant Safety

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Preface to the German Edition

Quidquid agis prudenter agas, respice finem

Safety is a basic human need. That is why a modern society must ensure that industrial production is safe. The task of engineers dedicated to process and plant safety is to achieve this. They ensure that plants are designed for safety and built and operated safely and that people have safe work places. Only if this is fulfilled is the operation of industrial plants ethically acceptable.

Safety means that hazards are kept small. However, there is no possibility to eliminate them completely; for whatever is possible will occur with a certain probability.

In order to make technical systems safe, the probability of hazards must be reduced as far as possible. This requires a structured approach which is based on experience as well as experimental and theoretical findings. In this book, the approach for analyzing and designing safe process plants is described. Starting points are possible hazards from material properties and operating conditions. The focus is placed on the qualitative and quantitative modelling of technical systems and the simulation of physical and chemical processes during operation and accidents. The material presented is extended and complemented by a number of examples and case studies, which refer to real plants or events.

A characteristic of analyses of process and plant safety is that the interdependencies within the technical system, the influence of its components on one another and human interventions must be accounted for. A further characteristic is the stochastic nature of the processes to be analyzed, which renders it, for example, impossible to predict the moment of occurrence of an accident. These aspects are duly addressed.

Process and plant safety is interdisciplinary. Just as for building and operating a plant process, mechanical, electrical, and civil engineering as well as informatics have to be combined, plant safety needs these disciplines, too. This makes the

selection of topics difficult and shows that experts for safety, who cannot possibly have a command of all these areas of knowledge, should address safety tasks in cooperation with specialists of the areas mentioned.

The selection of topics follows that of the model curriculum “Process and Plant Safety” of ProcessNet. My gratitude goes to my colleagues, Profs. A. Schönbacher, H. W. Brenig, H. U. Moritz, and J. Schmidt as well as to Dr. O. Klais for instructive and vivid discussions when elaborating the curriculum and deciding on unavoidable omissions.

Safety needs foresight. It should not derive from trial and error as it did in the earliest days of engineering. An important tool is the elaboration of scenarios, i.e. potential developments of the future. This requires thought experiments to be performed, which must be based on a broad background of knowledge in engineering and natural sciences as well as of experimental results and the simulations of accidents.

The book provides students and practitioners with the necessary tools for analyzing processes and plants and designing them for safety. It makes use of knowledge in mathematics, physics, chemistry, as well as of thermal and fluid dynamics, as taught during the first semesters of engineering courses.

The text is based on courses which I have been offering for more than a decade and a half at the Otto-von-Guericke-Universität Magdeburg. Discussions with collaborators and students have contributed to it. I thank them for their dedication.

I gratefully acknowledge the expert advice of Professors U. Stephan and Y. Ding, and Drs. J. F. Bremen, V. Schröder, D. Jablonski, and Arizal, as well as that of Dipl.-Ing. P. Guterl and Dipl.-Stat. J. Peschke. To Dr. Arizal I am also obliged for the technical implementation of a large part of the figures. My profound gratitude is expressed to all the experts from industry who granted me access to their plants and shared their knowledge of industrial practice with me.

My thanks go to the Springer Verlag for the good co-operation and fine presentation of the book.

The author hopes that the book enables students and practitioners to acquire knowledge of modern methods of safety analysis and to contribute to the safety of processes and plants by using them. In doing so they should follow the advice from classical antiquity which I have placed in front “Whatever you do, do it with intelligence and with the outcome in mind.”

Schönebeck (Elbe), Spring 2013

Ulrich Hauptmanns

Preface to the English Edition

The preparation of the translation gave me the opportunity to correct a number of minor mistakes and to occasionally formulate concepts in a somewhat clearer language. Wherever possible, German references were replaced by English ones. All of this should be of benefit to the reader.

Schönebeck (Elbe), Spring 2014

Ulrich Hauptmanns

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Whoever demands absolute safety, ignores the law of life.

1.1 Introduction

The production of the process industry¹ often involves hazards. Their nature can be both physical and chemical. Physical hazards derive from operating conditions which may be extreme, such as very low or very high temperatures and pressures. Chemical hazards are those associated with the materials present in the process, which can be toxic, flammable, explosible, or release energy due to spontaneous² reactions. Indeed, it is the necessity to put the substances into a reactive state in order to enable one to produce the desired products that may lead to hazards.

A further complication stems from the fact that some of the properties of the substances can vary with changes of process parameters such as temperatures, pressures, or concentrations or that these changes may give rise to or favour unwanted side reactions, as was the case in the Seveso accident, where larger quantities of dioxin than usual were generated and released to the environment (cf. [1]).

In addition, dangerous properties, if not present under nominal operating conditions, may evolve upon contact of process media with auxiliary media such as coolants or lubricants. After release, reactions with substances present in the environment, e.g. the humidity of the air, may give rise to dangerous properties.

¹ The term “process industry” comprises firms from the chemical, petrochemical, pharmaceutical and food industries as well as the production of steel, cement and the like.

² “Without apparent reason” from the Latin word *sponte* “from its own accord”.

Nevertheless a concretization of the hazard potential is normally not to be expected, since the design, construction, erection, and operation of the plants are based on the state of technology, respectively safety technology³ (cf. [2]). Hence, they are supported by a broad base of experience, which, depending on the country, is reflected by the respective laws, rules, and regulations. A good overview of this topic is provided by the Guideline Plant Safety [3].

According to [3] the design of a plant has to be such that the containment of hazardous substances inside the plant, i.e. vessels, pipework, reactors etc. is ensured. This does not only result in demands on the mechanical resistance of the components of the plant, but in safety systems being introduced, which in case of undesired loads (mostly excessive temperatures and/or pressures) are to guarantee the integrity of the containment by pressure relief, emergency trips, emergency cooling etc.

If all components functioned with perfection and, in addition, the measures of safety management were perfect plants would be absolutely safe.

This is, however, not the case and cannot be achieved. Apart from the—although remote—possibility of wrong dimensioning (e.g. walls too weak) components of technical systems can fail, humans can commit errors in operating the technical system or external threats such as flood, storm or lightening may lead to failures within the plant. Thus, temperature and pressure increases or other damaging events may be triggered. In addition, it is conceivable that safety systems are not available due to component failures. Probabilities for such events may be assessed. However, the instant in time of a component failure, human error or destructive external event cannot be predicted.

Hence, despite careful design, construction and operation of plants accidents cannot totally be avoided. Whatever may happen will happen with a certain probability. Therefore the probability of an accident⁴ can only be reduced by appropriate measures. To achieve this is the objective of risk management.

³ State of safety technology: the state of development of advanced processes, installations and procedures which permit one to take for granted the practical aptitude of a measure for avoiding accidents or limiting their consequences. When determining the state of safety technology comparable processes, installations and procedures have to be considered, which have been successfully applied in practice [4] (translated by the author).

⁴ Accident: an event such as an emission, a fire or an explosion of major impact, which leads to a disturbance of the specified operation* in a site or a plant subject to this ordinance (Author's remark: this refers to the Major Accident Ordinance [4]), which leads immediately or at a later stage to a serious hazard or material damage within or outside the site involving one or several hazardous substances as listed in annex VI part 1 para I no. 4.

*Specified operation is the operation for which a plant is technically designed and appropriate. Operating regimes not covered by the valid license, posterior impositions or applicable legal requirements do not belong to the specified operation. The specified operation comprises the

- normal operation including necessary human interventions such as the taking of samples including the storage with filling, transfer and refilling procedures,
- plant commissioning and its start-up and shut-down,
- trial operation,
- maintenance, inspection, repair and cleaning work as well as
- periods of temporary stand-still [8] (translated by the author).

Table 1.1 Some accidents in the process industry [9]

Date	Place	Event	Consequences		Comment
			Work-force	Population	
June 1st, 1974	Flixborough, U.K.	Explosion of a cloud of cyclohexane	28 killed, 36 gravely injured	53 gravely injured	All buildings in a radius of 600 m destroyed, presumably an unprofessional repair
July 10th, 1976	Seveso, Italy	Release of 2,3,7,8-Tetrachlorodibenzo-dioxin		220,000 persons exposed, 736 inhabitants evacuated, >250 cases of chloracne	2,000 ha contaminated, 81,000 animals died or were forcedly slaughtered
December 2nd, 1984	Bhopal, India	Release of 23–42 t of methyl isocyanate; water used for cleaning initiated an exothermic reaction with temperature and pressure rise		16,000 persons killed, 170,000–600,000 poisoned	>4,000 animals died
October 23rd, 1989	Pasadena, U.S.A	Explosion of a cloud of isobutene, ethylene, hexane, hydrogen released during maintenance of a polyethylene reactor	23 killed, 314 injured	Housing damage in a radius of 8 km	Earthquake intensity equivalent to 2.4 t TNT, magnitude 3.5 Richter
May 13th, 2000	Enschede, Netherlands	Explosion in a fireworks depot	20 killed, among them 4 firemen	400 houses destroyed, 1,250 people homeless	Spreading of an initial fire of unclarified cause
September 21st, 2001	Toulouse, France	Explosion of 20–100 t of rejects of ammonia nitrate	22 killed	8 killed, 2,450 injured, 26,000 houses damaged	Earthquake intensity equivalent to 20–40 t TNT, magnitude 3.4 Richter, perceived up to a distance of 75 km
June 20th, 2002	Kingsville, Canada	Fire in a plastics factory		2,000 evacuated for three days, time after which the fire was extinguished	Recommendation not to allow children to play outdoors and not to consume garden vegetables

(continued)

Table 1.1 (continued)

Date	Place	Event	Consequences		Comment
			Work-force	Population	
November 28th, 2002	Mestre, Italy	Overpressure failure of a vessel containing a mixture of toluene and 2,6 diisocyanate producing a fire	4 translated by pressure wave, slightly affected	Cloud of fumes with negligible effect, bituminous emission from an outlet contaminating 8 km of beaches	A similar vessel suffers a consequential explosion (Domino effect)
January 6th, 2005	Troisdorf, Germany	Pentrite explosion during maintenance work in an explosives factory	1 killed		
March 23rd, 2005	Texas City, U.S.A.	Vapour cloud explosion in a refinery	15 killed, 170 injured	Deflagration noticed up to a distance of 8 km	Hydrocarbon release from a blow-down drum, ignition by a starting truck
December 11th, 2005	Buncefield, U.K.	Explosion (unexpectedly high overpressure) and fire in an oil storage terminal		43 injured	Overfilling of a tank from a pipeline with a subsequent release of 300 t of petrol
March 17th, 2008	Cologne, Germany	Escape of ethylene followed by fire when maintaining a pipeline inside a process plant	None	None	Fire affects nearby acrylonitrile storage, 300 t of ethylene and 1,200 t of acrylonitrile were burnt; 1,180 fire fighters involved
October 23rd, 2009	Bayamon, Puerto Rico	Fire and explosion in a fuel storage	Several persons injured including 3 rescue workers	Evacuation of 1,500 persons from their homes	Petrol cloud of 600 m diameter formed before ignition, explosion causing an earthquake of 2.8 on the Richter scale, buildings damaged in a radius >1.6 km

(continued)

Table 1.1 (continued)

Date	Place	Event	Consequences		Comment
			Work-force	Population	
November 4th, 2010	Paderno Dugagno, Italy	Explosion and violent fire in a storage of paints and spent solvents	3 killed, 4 injured	Population urged to stay indoors	Serious flaws in the safety systems
April 20th, 2011	Pardubice, Tcheque Republic	Explosion of nitroglycerine in a factory for explosives	4 presumably killed, 9 injured	Glass breakage in a radius of 4 km	Probably human error in mixing nitroglycerine and nitrocellulose

Yet, a risk remains, i.e. a probability (or more precisely an expected frequency) that a damage of a certain type and impact occurs. In a process plant this may be a fire, an explosion or a toxic release, which may affect humans or environment. It is the price to be paid for the desired product. The damage can affect employees, the population at large or both, as becomes evident from Table 1.1.

The protection of the employees is ensured by a number of laws, regulations and guidelines (cf. [5, 6]). The justified interest of the population in safety, the protection according to the Federal Pollution Control Act (BImSchG) [7], is guaranteed by the licensing procedure.

Two fundamental approaches in licensing are conceivable:

1. the license is granted solely on the basis of fulfilling the above mentioned technical requirements; risk is not assessed.
2. In addition to (1) statements on risk have to be made and certain risk criteria to be met.

The procedure according to (1) is used in the Federal Republic of Germany and that of (2), for example, in the Netherlands.

It has to be emphasized that the operating systems of a plant are dimensioned by the same procedure with both approaches. Requirements for the systems are specified, for example, the quantity of heat to be extracted from a reactor for an exothermal reaction. The corresponding calculations are performed using mathematical models reflecting the underlying laws of nature. Results in this case may be, for example, the power of the coolant pump, the necessary surface for heat transfer, or the pipe diameter. This procedure is called deterministic.

The safety design of a plant results from extensive analyses (cf. [2]) to be discussed later. The dimensioning of safety systems is also carried out deterministically. It is based on the concept of disturbances which have to be avoided,⁵ for example a cooling failure in a reactor for an exothermal reaction. This is the basis for determining the type and capacity of the safety system coping with it. Its quality and degree of redundancy may then be determined

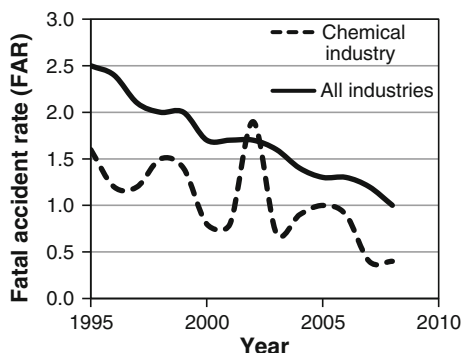
1. by indeterminate legal terms in regulations (cf. [4]) such as “reliable measuring device” or
2. probabilistically⁶ based on risk criteria.

As mentioned before, the approach according to (1) is that used so far in Germany. However, in the meantime probabilistic requirements for safety systems are derived from risk considerations in fulfilment of the standards on functional safety [10–12]. This corresponds to (2).

⁵ In the field of nuclear engineering this is referred to as “design basis accident”.

⁶ Based on probability considerations derived from the Latin word *probabilis*: assumable, likely, credible.

Fig. 1.1 Fatal accident rate FAR (fatalities per 10^8 working hours) for the chemical industry and the industry in general in Germany [16]



There is a recent tendency to measure the safety achievements by indicators (so-called key performance indicators) (cf. [13, 14]). These refer on the one hand to past performance (“lagging indicators”) and on the other to future performance (“leading indicators”).

In order to give an impression of standards achieved in the German process industry the following assessment is made. The accident statistics [15] shows that there was no fatal accident involving members of the public during 10 years of operation of the 7,800 plants subject to the Major Accident Ordinance [14]. On this basis a Bayesian zero-event statistics leads to a coarse assessment of $6.4 \times 10^{-6} \text{ a}^{-1}$ for a fatality outside a plant (vid. Example 9.4).

Figure 1.1 provides an impression of the safety performance concerning labour accidents comparing the chemical industry with figures for the industry at large.

Plant and process safety encompasses all the areas required for designing and building a process plant and implementing the corresponding processes (amongst them process, mechanical, and civil engineering). As a rule time-dependent processes have to be treated, since we are usually concerned with deviations from nominal operating conditions. The latter are considered as safe if a rigorous implementation of safety has accompanied the design and erection of a plant and is a permanent concern during its operation. The compliance with these assumptions should, of course, be checked in the context of a safety analysis.

Safety deals with stochastic events, for example the moment of occurrence of an accident, and stochastic boundary conditions (e.g. the weather at that moment). These together with lacks of knowledge about some of the phenomena to be described and imperfections in models and input data lead to uncertainties, which are normally compensated by safety factors and often lead to procedures based on conventions.

The treatment of uncertainties has substantially progressed in recent years (cf. [17–27]). However, their detailed theoretical treatment is beyond the scope of the present text, so that only procedures with particular relevance for practical applications are explained.

In what follows the physical and chemical phenomena causing the hazard potential of process plants are treated in Chaps. 2 and 3. Chapters 4–7 are dedicated to engineered and organizational measures which are devised to avoid that the hazard potential harms employees and the public at large. Chapters 8–10 deal with the determination of engineering risks. In this context the methods of plant system analysis and models for assessing accident consequences are presented. They serve to identify hazard potentials and to develop concepts for coping with them. Hence, they influence the safety design of plants and their safe operation. An important aspect of the safe design of plants is the concept of “functional safety”, which is treated in Chap. 11. Finally, Chap. 12 is devoted to the determination of appropriate distances between industrial installations and the surrounding population, which may be an additional safeguard for reducing the consequences of an accident.

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2.1 Flammability

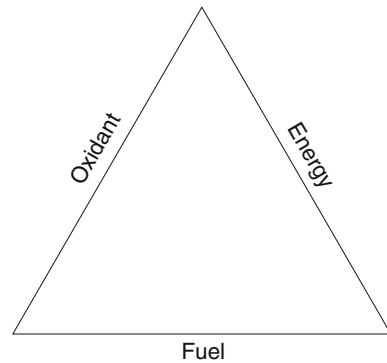
A large number of the materials handled in the process industry are flammable. They react with oxygen releasing thermal energy. In general the oxygen stems from the air but other oxidants have to be considered as well, for example hydrogen peroxide or ammonium nitrate, which easily release oxygen. Furthermore, substances like chlorine or fluorine can play the role of an oxidant.

In general combustion takes place if a flammable material enters into contact with an energy source, e.g. an electrical spark or a hot surface, and thus receives energy. If solid or liquid materials are concerned their temperature has to be raised first to such an extent that vapour is produced by vaporization or disintegration. These vapours can form flammable mixtures with air just as flammable gases. If the energy supply is sufficient a self-sustaining exothermic reaction occurs.

The conditions for a combustion process are shown in Fig. 2.1. It presents the so-called fire triangle, which comprises the necessary elements of a combustion process, namely “fuel”, “oxidant” and “energy”.

The consequence of a combustion process is either a fire or an explosion. Which of the possibilities occurs depends on the boundary conditions to be treated below. In general the approach is empirical. For example conditional probabilities (the condition is the preceding release) of 0.6 for a fire and 0.4 for an explosion after the release of a flammable gas or liquid are given in [1].

The safe handling of flammable materials requires the knowledge of their properties, which are normally described by safety parameters. These parameters are not, as a rule, constants of nature but values which are determined under fixed boundary conditions. This leads to the use of standardized measuring apparatuses (vid. [2–4]). When employing these parameters to judge real situations an eye must therefore be kept on the prevailing boundary conditions.

Fig. 2.1 Fire triangle*Example 2.1* Empirical frequencies for fires and explosions

The data bank ARIA indicates the following numbers of events as a consequence of hydrocarbon releases: $a = 1,748$ events “explosion or fire”, $b = 656$ events “explosion” and $c = 1,554$ events “fire”.

Determine the conditional probabilities (the condition is the release whose probability of occurrence is assumed here to be equal to 1) for the different events.

Solution

The sum of the numbers of events with fires and explosions amounts to

$$g = c + b = 2,210$$

However, this includes events where fire and explosion occurred jointly. Their number is

$$d = g - a = 462$$

From this we have

$b - d = 194$ events with an explosion only and

$c - d = 1,092$ events with a fire only.

Hence we obtain the following conditional probabilities:

- Only fire: $1,092/1,748 = 0.625$
- Only explosion: $194/1,748 = 0.111$
- Fire and explosion: $462/1,748 = 0.264$

If the explosion is considered the dominating event and the probability for “fire and explosion” is added to the probability for “only explosion” the result is in good agreement with that of [1]. $\square$

2.1.1 Safety Parameters for Flammable Gases and Vapours

2.1.1.1 Explosion Limits

Combustion can occur only if the mixture of fuel and oxygen lies within a certain range. This is described by the lower and upper explosion limits (LEL and UEL). In older references these limits are referred to as the lower and upper limits of flammability (LFL and UFL) (vid. [4]). They represent the volume ratio¹ of fuel vapour in air. Below the lower explosion limit the mixture is too lean, above the upper limit it is too rich for combustion to occur. The explosion limits are not fixed values. They depend on whether we deal with a mixture with air or with oxygen. Furthermore they are influenced by (vid. [4, 5]):

- pressure,
- temperature,
- direction of flame propagation,
- type and location of the source of ignition, in particular ignition energy,
- type and size of the space (closed, open, geometry),
- possibly the amount of inert gas in the mixture,
- flow regime of the gas,
- gravitational field.

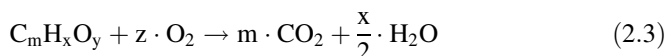
Additionally they depend, as already mentioned, on the boundary conditions of their measurement, as illustrated by Table 2.1. In general the most flammable mixture is close to but not exactly equal to the stoichiometric one [5].

The explosion limits may be calculated approximately by (vid. [6])

$$\text{LEL} = 0.55 \cdot c_{\text{st}} \quad (2.1)$$

$$\text{UEL} = 3.50 \cdot c_{\text{st}} \quad (2.2)$$

In Eqs. (2.1) and (2.2) c_{st} is the stoichiometric concentration (volume percent of fuel in air). In case of a stoichiometric equation of combustion of the form



we have

$$z = m + \frac{x}{4} - \frac{y}{2} \quad (2.4)$$

¹ Strictly speaking the indication of a volume ratio only makes sense at low pressures. At higher pressures the real gas behaviour must be taken into account; hence in that case often mass proportions (mol %) are used.

Table 2.1 Upper and lower explosion limits according to different sources

Stoff	Nabert et al. [7]		Mannan [5]		Coward and Jones [8]	
	Lower explosion limit in Vol%	Upper explosion limit in Vol%	Lower explosion limit in Vol%	Upper explosion limit in Vol%	Lower explosion limit in Vol%	Upper explosion limit in Vol%
Acetone	2.5	14.3	2.6	13	3	11
Acetylene	2.3	78–100	2.5	100	2.5	81
Ammonia	15.4	33.6	15	28	15	28
Benzene	1.2	8.6	1.4	8	1.4	7.1
n-Butane	1.4	9.3	1.8	8.4	1.9	8.5
Carbon monoxide	10.9	76	12.5	74	12.5	74
Cyclohexane	1.1	8.3	1.3	7.8	1.3	8
Ethane	2.5	15.5	3.0	12.4	3.0	12.5
Ethylene	2.3	32.4	2.7	36	3.1	32
Ethylene oxide	2.6	100	3	100	3.0	80
Hydrogen	4.0	77	4.0	75	4.0	75
Methane	4.4	17	5.0	15.0	5.3	14
Propane	1.7	10.9	2.1	9.5	2.2	9.5
Propylene	2.0	11.1	2.4	11	2.4	10.3
Styrene	1.1	6.1	1.1	6.1	1.1	6.1
Toluene	1.1	7.8	1.3	7.0	1.4	6.7

and hence

$$c_{st} = \frac{100}{1 + z/0.21} \quad (2.5)$$

However, Example 2.2 shows that the differences between calculated and measured values are considerable. Hence, whenever possible measured values are to be used.

This applies as well for the pressure dependence of the explosion limits. The following logarithmic relationship is given for the pressure dependence of the UEL (vid. [6])

$$UEL_p = UEL_{0.1\text{MPa}} + 20.6 \cdot (\log p + 1) \quad (2.6)$$

In Eq. (2.6) p denotes the absolute pressure in MPa. The equation does not represent the measured values, as is evident from Table 2.2. The values for 1 bar agree because they are introduced into the equation as the reference value $UEL_{0.1\text{MPa}}$.

Table 2.2 Dependence of the explosion limits on initial pressure (measured values from [4], calculated values (bold print) according to Eq. (2.6))

Material	LEL in vol%			UEL in vol%		
	1 bar	10 bar	100 bar	1 bar	10 bar	100 bar
Hydrogen	4.3	4.9	5.8	78.5	72.4	74
				78.5	99.1	119.7^a
Carbon monoxide	13.1	15.6	17.0	75.9	69.4	68.0
				75.9	96.5	117.1^a
Methane	4.6	5.0	4.3	16.6	21.8	44.7
				16.6	37.2	57.8
Ethane	2.7	2.7	2.7	14.1	19.3	45.2 ^b
				14.1	34.7	55.3

^asince 100 % is the maximum, the value is merely a formal result^bmeasured at an initial pressure of 50 bar

According to [4] the lower explosion limit decreases slightly with increasing initial pressure whilst the upper limit increases strongly. Exceptions from this rule are the gases hydrogen and carbon monoxide. The lower explosion limit of hydrogen at first rises slightly with increasing initial pressure and then decreases with further pressure increase. In the case of carbon monoxide the range between the explosion limits narrows at first with increasing initial pressure and remains constant with a further increase.

With an increase in temperature the range between the lower and upper explosion limits widens for all flammable gases. The relative change of the lower and upper limits is similar for many flammable gases. Hence, it may well be approximated by the following linear relationship

$$x_B(T) = x_B(T_0) \cdot [1 \pm K(T - T_0)] \quad (2.7)$$

In Eq. (2.7) $x_B(T)$ denotes the volume ratio of the gas at temperature T and $x_B(T_0)$ that at the reference temperature T_0 , e.g. ambient temperature. The positive sign applies to the upper explosion limit, the negative sign to the lower limit (vid. [4]). Factors for K are given in Table 2.3, where K_L applies to the lower limit and K_U to the upper.

The above considerations apply to a mixture of a single flammable gas and air. If several gases, e.g. I, are involved which do not react with one another, the principle of Le Chatelier is invoked and we obtain

$$\text{LEL} = \frac{1}{\sum_{i=1}^I \frac{y_i}{\text{LEL}_i}} \quad (2.8)$$

Table 2.3 Temperature coefficients K_L and K_U for selected flammable gases (vid. [9])

Flammable gas	K_L (LEL) in K^{-1}	K_U (UEL) in K^{-1}	LEL (0 °C)* in mol%	UEL (0 °C)* in mol%
Methane ^a	0.00162	0.00111	4.60	15.64
Ethane ^b	0.00124	0.00098	2.48	14.02
Propane ^b	0.00128	0.00107	1.82	10.57
Isobutane ^b	0.00149	0.00064	1.48	9.18
Hydrogen ^a	0.00162	0.00042	4.18	74.75
Carbon monoxide ^a	0.00138	0.00035	12.07	76.37

*Calculated from experimental data for use in Eq. (2.7)

^aTemperatures up to 400 °C

^bTemperatures up to 250 °C

$$UEL = \frac{1}{\sum_{i=1}^I \frac{y_i}{UEL_i}} \quad (2.9)$$

In Eqs. (2.8) and (2.9) y_i is the molar fraction of material i in the total mixture; LEL_i and UEL_i are the corresponding explosion limits.

Experience tells that this estimate agrees fairly well with the measured values of the lower explosion limit for “similar” flammable gases. The upper limit shows larger deviations. The equations should be applied with care to safety technological questions, since the deviations may lie on both the safe and the unsafe side [4].

Example 2.2 Uncertainties of the explosion limits taking propane as an example

The explosion limits of a material depend on numerous boundary conditions. Hence different measurements result in different values as shown in what follows taking the lower explosion limit of propane as an example. The following values in volumetric percent are given

x_n : 1.7; 2.1; 2.2; 2.1; 2.1; 1.7; 2.1.

Let us assume they represent $N = 7$ independent measurements (this is often not the case, since values from the same source are quoted in several references). Then the explosion limit may be assumed to be a random variable, i.e. a variable which adopts certain values with a certain probability. Random variables are described by probability distributions (vid. Appendix C). In what follows the logarithmic normal (lognormal) distribution (vid. Sect. 9.3.4) is used to represent the values

As mean value of the logarithms of the values of x_n we have

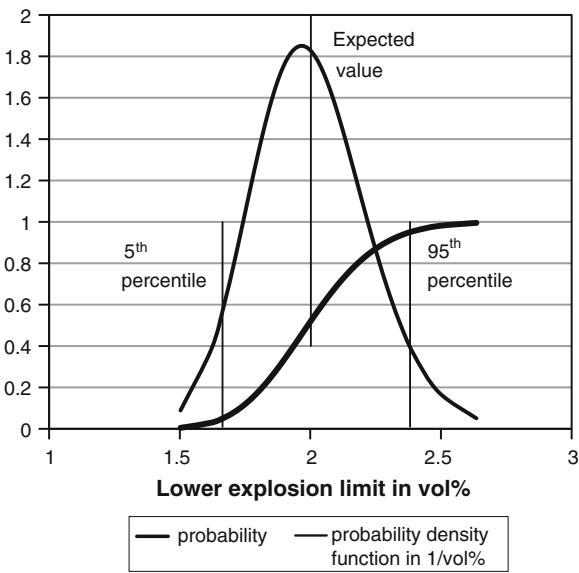
$$\mu = \frac{1}{N} \cdot \sum_{n=1}^N \ln x_n = 0.6882$$

and as the corresponding standard deviation

$$s = \left[\frac{1}{N-1} \cdot \left(\sum_{n=1}^N (\ln x_n)^2 - N \cdot \mu^2 \right) \right]^{\frac{1}{2}} = 0.1090$$

The pertinent probability distribution and probability density function, simply termed probability and probability density or pdf, are represented by Fig. 2.2.

Fig. 2.2 Probability and probability density of the lower explosion limit of propane



The percentiles are to be interpreted such that the corresponding percentage of the lower explosion limit lies below the respective percentile value. □

Example 2.3 Determination of the lower and upper explosion limits

Determine the lower and upper explosion limits of acetylene, hydrogen and ammonia for a pressure of 1 bar.

Solution

The solution is based on Eqs. (2.1)–(2.5). The results are compiled in Table 2.4.

Table 2.4 Calculation of the lower and upper explosion limits for several materials

Material	Molecular formula	z	c _{st} in vol%	LEL in vol%	UEL in vol%
Acetylene	C ₂ H ₂	2.5	7.749	4.3	27.1
Hydrogen	H ₂	0.5	29.577	16.3	100
Methane	CH ₄	2	9.502	5.2	33.3

Comparison with the measured values from Table 2.1 shows that the results are merely approximations. This underlines that it is necessary from a safety point of view to use measured values. □

Example 2.4 Temperature dependence of explosion limits

The lower and upper explosion limits of methane are to be determined for the temperatures 100, 200, 300 and 400 °C.

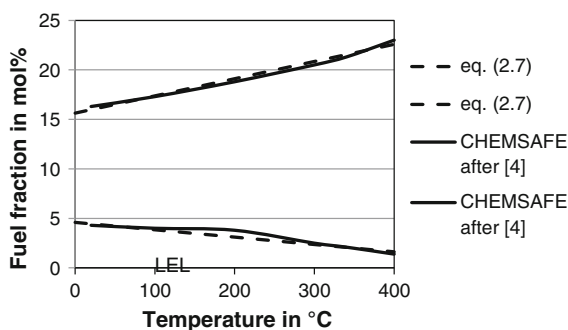
Solution

Combination of Eq. (2.7) with Table 2.3 leads to the results of Table 2.5. They are in good agreement with the measured values, as is demonstrated in Fig. 2.3.

Table 2.5 Temperature dependence of the explosion limits of methane

Methane	0 °C	100 °C	200 °C	300 °C	400 °C
LEL in mol%	4.60	3.85	3.11	2.36	1.62
UEL in mol%	15.64	17.38	19.11	20.85	22.58

Fig. 2.3 Comparison of the temperature dependence of measured and calculated explosion limits of methane



Example 2.5 Calculation of the lower and upper explosion limits of natural and petroleum gas

Natural and petroleum gas have the main components given in Table 2.6.

Table 2.6 Composition of natural and petroleum gas in mol%

	Natural gas	Petroleum gas
Methane	90	–
Ethane	6	–
Propane	2	30
Butane	–	70
Carbon dioxide	1	–
Nitrogen	1	–

Determine their lower and upper explosion limits.

Solution

According to Eqs. (2.8) and (2.9) we obtain

$$\text{LEL} = \left(\frac{0.9}{4.4} + \frac{0.06}{2.5} + \frac{0.02}{1.7} \right)^{-1} = 4.16$$

$$\text{UEL} = \left(\frac{0.9}{17} + \frac{0.06}{15.5} + \frac{0.02}{10.9} \right)^{-1} = 17.05$$

for natural gas and

$$\text{LEL} = \left(\frac{0.3}{1.7} + \frac{0.7}{1.4} \right)^{-1} = 1.48$$

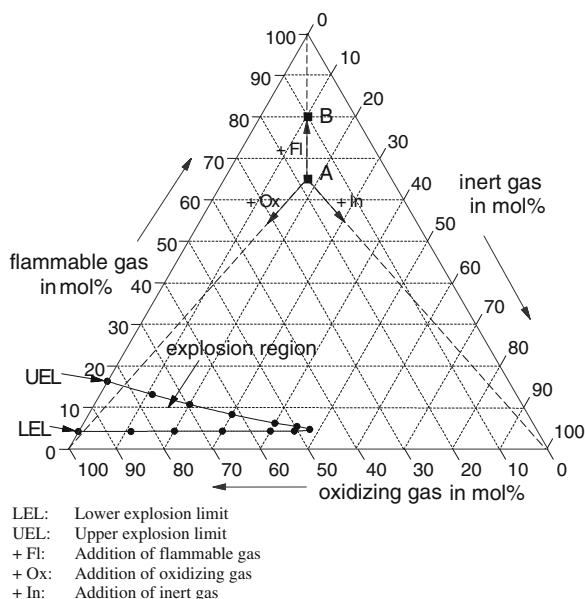
$$\text{UEL} = \left(\frac{0.3}{10.9} + \frac{0.7}{9.3} \right)^{-1} = 9.73$$

for petroleum gas.

2.1.1.2 Explosion Limits for Mixtures

Mixtures of flammable gases and oxidant were treated in the preceding Section. In practice often mixtures have to be assessed which in addition contain an inert gas. The corresponding situation is represented by Fig. 2.4. It is subsequently described following [9].

Fig. 2.4 Explosion region of a flammable gas presented in triangular coordinates [9]



The explosion limits form a boundary line enclosing all flammable compositions; the explosion range contains all flammable mixtures. Points on the sides of the triangle represent two-component systems because the fraction of the third component is zero there. Pure substances are represented by the corner points of the triangle. The fractions of the remaining two components are equal to zero there. In Fig. 2.4 the upper corner represents the pure flammable gas, the lower right corner the pure inert gas and the lower left corner the pure oxidant. If a certain amount of flammable gas, inert gas or oxidant is added to the mixture “A”, a new mixture results. If the component is added continuously, the point “A” moves along a straight line in the direction of one of the corners of the diagram (denoted by the arrows in Fig. 2.4). For example, if a certain quantity of flammable gas is added, a new composition according to point “B” is obtained after the mixture has homogenized.

2.1.1.3 Ignition Temperature

According to [7] the ignition temperature of a flammable gas or flammable liquid is determined in a standardized experimental set-up (vid. [10]). It is the lowest temperature (in °C) of the heated glass bulb, on whose concave wall the inhomogeneous gas air or vapour air mixture of the examined material (at a pressure of 1,013 mbar) is just ignited showing flames (readily ignitable mixture). Hence, it constitutes an appropriate measure for the propensity of materials to be ignited on hot surfaces. This enables one, amongst others, to assign materials to temperature classes according to safety technological criteria.

It must be emphasized that we deal with a measurement which requires no further energy source in order to produce an ignition. Table 2.7 gives ignition temperatures for selected materials.

Table 2.7 Ignition temperatures (from [7])

Material	Ignition temperature in °C	Material	Ignition temperature in °C
Acetone	535	Ethylene	425
Acetylene	305	Ethylene oxide	440
Ammonia	630	Hydrogen	560
Benzene	555	Methane	595
n-Butane	365	Propane	470
Carbon monoxide	605	Propylene	455 ^a
Cyclohexane	260	Styrene	490
Ethane	515	Toluene	545

^aValue for coarse orientation

2.1.1.4 Minimum Ignition Energy

The minimum ignition energy (MIE) is a parameter for judging the incendiarity by important sources of ignition such as electrostatic discharge and mechanical spark. It represents the smallest possible amount of energy capable of just igniting the most flammable gas/air or vapour/air mixture in such a way that a flame occurs

which is not restricted to the immediate vicinity of the igniting spark. The value of the MIE depends on both the testing apparatus and the testing procedure. It is determined on the basis of the energy of the discharge spark of a capacitor which is applied to the most flammable mixture under standard conditions (20 °C and 1,013 mbar) [11]. The most flammable mixture is considered to lie in the range of 0.9–1.4 (according to other sources 0.8–2) times the stoichiometric mixture (vid. [3]). The latter can be calculated according to Eq. (2.5).

The minimum ignition energy is determined according to

$$E = \frac{C \cdot U^2}{2} \quad (2.10)$$

In Eq. (2.10) E is the ignition energy in J, C the capacitance of the capacitor in Farad and U the voltage applied to the capacitor in V. By varying the energy E the energy amount is identified which is just sufficient to ignite the mixture under examination, the MIE.

If the ignition source is not at rest relative to the surrounding mixture, for example in the case of a flowing medium, heat is lost and the MIE increases [6]. Table 2.8 contains values of the MIE for selected materials.

Example 2.6 Ignition of hydrogen

A capacitor with a capacitance of 560 pF ($1\text{pF} = 10^{-12}\text{ F}$) is charged with a definite current of $U_0 = 220\text{ V}$. Would its discharge ignite hydrogen?

Solution

$$U(t) = U_0 \cdot \left(1 - e^{-t/\tau_0}\right)$$

describes the time-dependent voltage in the capacitor, $U(t)$, and τ_0 the time constant of the charging system. For simplicity's sake the asymptotic voltage of the capacitor is used. It amounts to U_0 and is obtained in theory for $t \rightarrow \infty$ and in practice after a period of time of approximately five times the time constant.

Table 2.8 Minimum ignition energies (MIEs) for normally ignitable materials (standard conditions) (from [3])

Material	MIE in mJ	Material	MIE in mJ
Methane	0.29–0.31	Pentane	0.22–0.28
Propylene	0.27	Benzene	0.21–0.22
Propane	0.24–0.27	Methanol	0.14
Butane	0.25–0.27	Hydrogen sulphide	0.068
Ethane	0.25	Acetylene	0.019–0.051
Heptane	0.24	Hydrogen	0.012–0.019
Hexane	0.23–0.25	Carbon disulphide	0.009–0.03

Inserting the numerical values in Eq. (2.10) we obtain

$$E = \frac{560 \cdot 10^{-12} \cdot 220^2}{2} = 0.0136 \text{ mJ}$$

Since $0.0136 \text{ mJ} > 0.012 \text{ mJ}$ (lower limit of the interval indicated in Table 2.8) the cautious analyst should expect ignition to occur.

2.1.1.5 Burning Velocity

According to [11] the burning velocity is the movement of the flame front in a homogeneous gas/air mixture per unit of time in vertical direction to the flame front into the unburnt mixture. The burning velocity is determined by heat conduction, diffusion and the flow process with the latter resulting from the expansion of the combustion gases. It depends on the initial temperature, the amount of oxygen introduced, the degree of mixture and catalytic effects (e.g. traces of steam, smoke or dust). The burning velocity is measured with respect to the unburnt gas. Hence, it differs from flame speed which is the velocity of the flame front with respect to a fixed observer. It is usually one or two orders of magnitude higher than the laminar burning velocity because of the acceleration produced by the expanding combustion products.

The burning velocity is usually determined on pre-mixed flames from a Bunsen burner in laminar flow regime (see Sect. 2.1.1.7). It is then called laminar burning velocity. In case of turbulent flow the burning velocity is many times the laminar burning velocity and does not depend on the properties of the mixture alone. Within the explosion limits the burning velocity is an appropriate parameter for describing flame propagation. Burning velocities depend on pressure and temperature [5]. Table 2.9 presents laminar burning velocities for selected substances. In some cases these velocities may be represented by polynomials, as

Table 2.9 Laminar burning velocities for selected materials

Material	v_{burn} in cm s^{-1} cit. according to [5]	v_{burn} in cm s^{-1} cit. according to [12]
Acetylene	173	155
Benzene	40.7	–
n-Butane	40.5	–
Ethane	40.1	47.6
Ethylene	68.8	73.5
n-Hexane	38.5	–
Methane	36.4	44.8
Propane	45	46.4
Hydrogen	320	325

$$v_{\text{burn}} = 4.407 \cdot \phi^3 - 150.69 \cdot \phi^2 + 308.62 \cdot \phi - 122.7 \quad (0.7 < \phi < 1.4) \quad (2.11)$$

for liquefied petroleum gas (LPG) [13] with the main components 27.65 vol% propane and 68.28 vol% butane and

$$v_{\text{burn}} = -177.43 \cdot \phi^3 + 340.77 \cdot \phi^2 - 123.66 \cdot \phi - 0.2297 \quad (0.5 < \phi < 1.4) \quad (2.12)$$

for natural gas [14].

In Eqs. (2.11) and (2.12) v_{burn} is the burning velocity in cm s^{-1} and $\phi = 1/\lambda = n_{\text{L,min}}/n_{\text{L}}$ the ratio of the molar stoichiometric requirement of air, $n_{\text{L,min}}$, and the available number of moles of air ($\phi = 1$, stoichiometric). This value is called “equivalence ratio” and is the reciprocal of the air-to-fuel ratio $\lambda = 1$.

Example 2.7 Determination of the burning velocities for petroleum gas and natural gas

Determine the burning velocity of petroleum gas and natural gas for different equivalence ratios in steps of 0.1.

Solution

Application of Eqs. Gl. (2.11) and (2.12) leads to the values of Table 2.10; they are shown in Fig. 2.5.

Table 2.10 Laminar burning velocities for petroleum gas and natural gas as a function of the mixing ratio ϕ

Material/ ϕ	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
Petroleum gas			21.0	30.0	36.2	39.6	40.3	38.3	33.5	26.1
Natural gas	1.0	9.9	19.3	28.1	35.2	39.5	39.9	35.5	25.1	7.7

Fig. 2.5 Laminar burning velocities for petroleum gas and natural gas as a function of the equivalence ratio

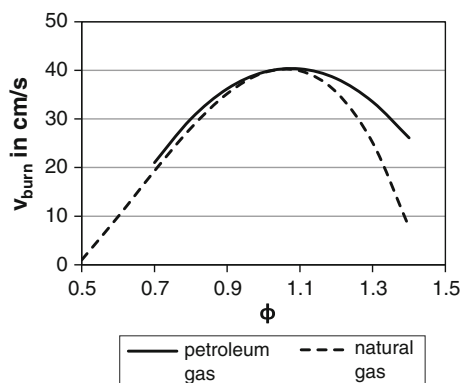


Table 2.11 Maximum experimental safe gaps (MESGs) for selected flammable materials (from [7])

Material	w_n in mm
Acetylene	0.37
Diethyl ether	0.87
1,2 Dichloroethane	1.80
Ethylene	0.65
Methane	1.14
Methanol	0.91
Propane	0.90
Carbon disulphide	0.34
Vinyl chloride	0.96
Hydrogen	0.29

2.1.1.6 Critical Slot Width and Maximum Experimental Safe Gap

Propagation of flames is hindered if they have to cross a small slot. This phenomenon is characterized by the critical slot width and the maximum experimental safe gap (MESG). According to [3] the critical slot width is the width of a slot with given length which after an explosion of the readily ignitable mixture or flammable vapour just prevents the ignition of the mixture on the other side of the slot. The critical slot “decouples” the space in which an explosion occurs from the surrounding flammable atmosphere. The MESG is the lowest value of the critical slot widths. It is measured by varying the composition of the mixture [7]. Details on the measuring process can be found in [3].

The most flammable concentration is found to lie between 0.9 and 1.4 respectively 0.8 and 2 times the stoichiometric concentration. The latter may be determined from Eq. (2.5). Table 2.11 provides MESGs for selected materials.

Example 2.8 Determination of most easily ignited concentrations

Determine the most easily ignited concentrations for the hydrocarbons from Table 2.8 and for hydrogen assuming that it occurs at 1.1 times the stoichiometric composition.

Solution

The calculations are based on Eqs. (2.3)–(2.5). The results are shown in Table 2.12.

Table 2.12 Assessment of the most easily ignited concentrations

Material	m	x	y	z according to Eq. (2.4)	$c_{st} \cdot 1.1$ in vol.% according to Eq. (2.5)
Acetylene	2	2	0	2.5	8.5
Diethyl ether	4	10	1	6	3.7
Ethylene	2	4	0	3	7.2
Methane	1	4	0	2	10.5
Methanol	1	4	1	1.5	13.5
Propane	3	8	0	5	4.4
Hydrogen	0	2	0	0.5	32.5

□

2.1.1.7 Basic Flame Types

After presenting several of the safety parameters of fire and explosion protection different types of flames are briefly discussed here. The presentation largely draws upon [15].

Basically we distinguish between pre-mixed or non pre-mixed (formerly called “diffusion flames”) flames. With pre-mixed flames the mixing between fuel and oxidant occurs before combustion with non pre-mixed flames mixing and combustion are simultaneous. A pre-mixed flame is obtained, for example, if the air supply of a Bunsen burner is opened; if it is closed the flame becomes non pre-mixed. Another example of a non pre-mixed flame is a burning candle.

Further differentiations are found in Fig. 2.6. In what follows they are briefly commented upon.

For pre-mixed flames the velocity of combustion is limited by the kinetics of the combustion process. In case of a laminar non pre-mixed flame the limitation usually stems from the diffusion velocity of air into the fuel, with turbulent non pre-mixed flames on the other hand the kinetics becomes more determining.

Laminar pre-mixed flame

The combustion velocity of a freely burning flat flame into the unburnt mixture can be described by the laminar burning velocity (vid. Sect. 2.1.1.5). In doing this different regimes of combustion can be distinguished on the basis of the equivalence ratio ϕ .

$\phi < 1$ lean (there is oxygen left after combustion)

$\phi = 1$ stoichiometric (only combustion products remain after the combustion)

$\phi > 1$ rich (fuel is left after the combustion)

If the velocity of the unburnt gas is smaller than the laminar burning velocity the flame flashes back into the outlet opening. In the opposite case blow-off occurs (slight separation from the outlet) and at even higher flow velocities the flame lifts.

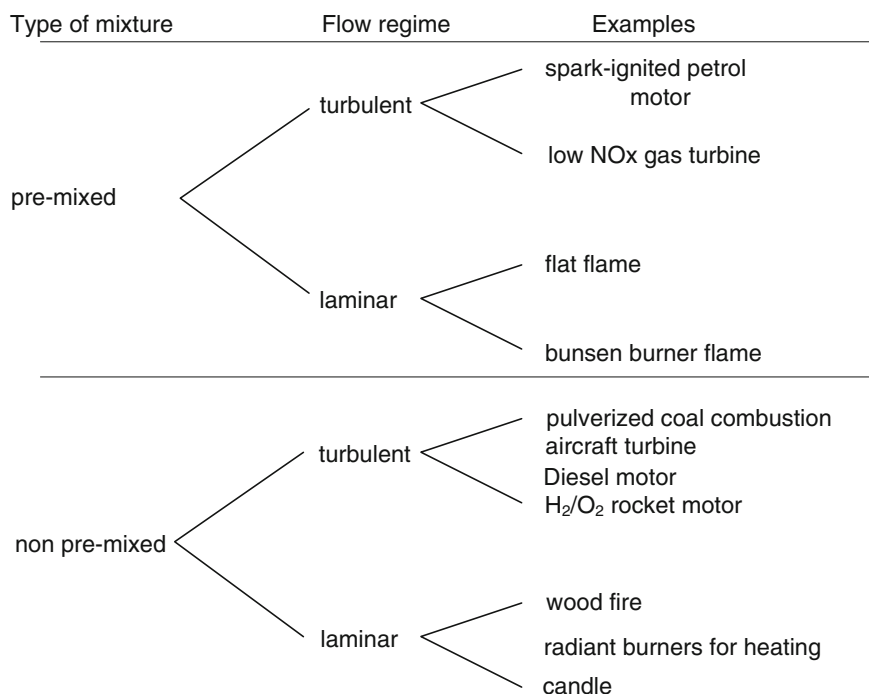


Fig. 2.6 Differentiation of flame types (according to [15])

Turbulent pre-mixed flame

The transition from laminar to turbulent flames occurs for $Re \approx 2,000$ with the Reynolds number referring to the flame. It is smaller than in the unburnt mixture because the viscosity of gases rises with increasing flame temperature. The combustion process of a turbulent pre-mixed flame can be controlled well. However, for safety reasons it is not readily applied because flammable mixtures may accumulate and hence explode.

Laminar non pre-mixed flame

Non pre-mixed flames are characterized by more complex chemical processes than pre-mixed ones and may comprise the entire spectrum $0 < \phi < \infty$. They occur if a pure fuel flows from an outlet opening and is then mixed with the surrounding air and thus with oxygen by diffusion and entrainment. Contrary to pre-mixed flames non pre-mixed flames do not propagate and hence cannot be characterized by the laminar burning velocity. For the flame length we have [16]

$$L \approx \frac{c_0}{c_{st}} \cdot \frac{\dot{V}}{4\pi D \left(1 + \frac{c_{st}}{2c_0}\right)} \quad (2.13)$$

and according to Jost (cit. in [5])

$$L \approx \frac{\dot{V}}{\pi D} \quad (2.14)$$

and according to [7]

$$L \approx \frac{\dot{V}}{2\pi D} \quad (2.15)$$

In Eqs. (2.13)–(2.15) L is the flame length in m, c_0 the concentration of the fuel at the outlet opening (fuel/air ratio: usually equal to 1, respectively 100 %), c_{st} is the corresponding stoichiometric concentration, $\dot{V}$ the volumetric flow rate in m^3s^{-1} and D the diffusion coefficient in m^2s^{-1} .

The equations suggest that the flame length at constant mixture ratio only depends on the volumetric flow rate, i.e. it is independent of the cross section of the outlet opening. With a given outlet cross section it is approximately proportional to the flow velocity. The differences between the relationships point to modelling uncertainties.

Turbulent non-premixed flame

With increasing velocity at the outlet the laminar flame becomes turbulent. The transition between the two regimes occurs at $\text{Re} \approx 2,000$. Contrary to laminar non pre-mixed flames its length does not depend on the velocity at the outlet.

Example 2.9 Determination of the lengths of non pre-mixed flames

Determine the flame lengths of non pre-mixed laminar flames for the flammable gases hydrogen, carbon monoxide and acetylene at a volumetric flow of $0.0001 \text{ m}^3\text{s}^{-1}$.

Data: $D_{\text{H}_2} = 7.1 \times 10^{-5} \text{ m}^2\text{s}^{-1}$; $D_{\text{CO}} = 2.03 \times 10^{-5} \text{ m}^2\text{s}^{-1}$; $D_{\text{C}_2\text{H}_2} = 1.62 \times 10^{-5} \text{ m}^2\text{s}^{-1}$.

Solution

The bases are Eqs. (2.13) and (2.5) as well as Eqs. (2.14) and (2.15). The resulting flame lengths are contained in Table 2.13.

Table 2.13 Flame lengths for selected gases in m

Material	c_{st} in %	Equation (2.13)	Equation (2.14)	Equation (2.15)
Hydrogen	29.58	0.33	0.45	0.22
Carbon monoxide	29.58	1.15	1.57	0.78
Acetylene	7.75	6.12	1.96	0.98

2.1.1.8 Adiabatic Flame Temperature

The adiabatic flame temperature indicates the thermal power radiated by the flame. It represents an upper limit,

- because it is determined assuming combustion without losses and
- because often the ionization and dissociation of the combustion products, which start above 1,370 °C and consume energy thus reducing the temperature, are not accounted for [5].

The adiabatic flame temperature applies to pre-mixed flames, usually in stoichiometric mixtures with oxygen from air. Non pre-mixed flames reach temperatures of appr. 1,500 K. If the oxidant is pure oxygen instead of oxygen from the air the occurring temperatures are 700–800 K higher.

The first law of thermodynamics applies to an adiabatic system (heat losses $dq = 0$) at constant pressure [17]. Accordingly the sum of the enthalpies is equal to zero. Hence, we obtain for calculating the adiabatic flame temperature

$$\sum_{i=1}^I n_i \cdot \Delta h_{in,i} + \sum_{j=1}^J m_j \cdot \Delta h_{out,j} + \Delta H_c = 0 \quad (2.16)$$

In Eq. (2.16) n_i is the number of moles of input material number i with the corresponding difference of enthalpy between its temperature (normally ambient) and the standard temperature (298.15 K), $\Delta h_{in,i}$. It is equal to zero if its initial temperature equals the standard temperature, m_j is the number of moles of combustion product j and $\Delta h_{out,j}$ the corresponding difference in enthalpy between the initial temperature and the adiabatic flame temperature of the combustion products; ΔH_c is the enthalpy of combustion of the fuel in question. For ΔH_c the net calorific value of the fuel is used, i.e. $\Delta H_c = -C_n$.

The enthalpy at the standard pressure of 101.3 kPa and at a temperature of t in K/1,000, h^0 in kJ/mol, can be obtained from [18], where the following representation is used for a number of materials

$$h^0 - h_{298,15}^0 = A \cdot t + B \cdot \frac{t^2}{2} + C \cdot \frac{t^3}{3} + D \cdot \frac{t^4}{4} - \frac{E}{t} + F - H \quad (2.17)$$

In Eq. (2.17) $h_{298,15}^0$ is the standard enthalpy (at 101.3 kPa and 298.15 K), which cancels on forming the enthalpy differences in Eq. (2.16). The relationship between enthalpy and heat capacity at constant pressure is useful for practical applications

$$h^0 - h_{298,15}^0 = \int_{298.15}^T c_p(T) dT \quad (2.18)$$

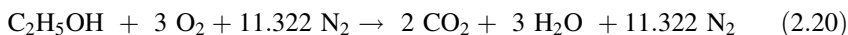
where $T = t \cdot 1,000$ is the temperature in K.

Table 2.14 contains coefficients for applying Eq. (2.17) and Table 2.15 experimentally and theoretically determined adiabatic flame temperatures for selected materials. The latter were calculated iteratively from Eq. (2.16). For this purpose the following reaction equations were used assuming air to consist of oxygen and nitrogen only so that 1 mol of oxygen is accompanied by 3.774 mol of N_2 :

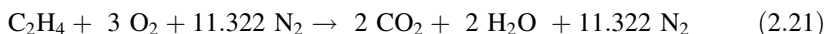
Acetylene



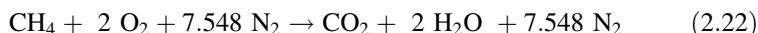
Ethanol



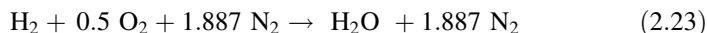
Ethylene



Methane



Hydrogen



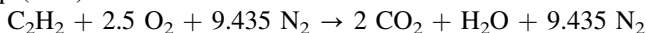
Example 2.10 Determination of the adiabatic flame temperature of acetylene

Determine the adiabatic flame temperature of acetylene for an initial temperature of 25 °C using the following mean values for the heat capacities at constant pressure. The net calorific value of acetylene, C_n , is taken from Table 2.15.

Data : $c_{p,CO_2} = 49.6 J/(mol K)$; $c_{p,H_2O} = 44.6 J/(mol K)$; $c_{p,N_2} = 33.0 J/(mol K)$

Solution

Based on Eq. (2.16) and accounting for Eq. (2.18) we obtain for the reaction Eq. (2.19)



the following enthalpy balance

$$0 = (T - 298.15) \cdot (2 \cdot 49.6 + 1 \cdot 44.6 + 9.435 \cdot 33.0) - 1,255,600$$

Solving this equation for T gives an adiabatic flame temperature of 3,056.8 K. □

Table 2.14 Coefficients for determining the enthalpy of selected materials (from [18])

Material	Temperature range in K	A	B	C	D	E	F	H
CO	298–1,300	25.56759	6.096130	4.054656	−2.671301	0.131021	−118.0089	−110.5271
	1,300–6,000	35.15070	1.300095	−0.205921	0.013550	−3.282780	−127.8375	−110.5271
CO ₂	298–1,200	24.99735	55.18696	−33.69137	7.948387	−0.136638	−403.6075	−393.5224
	1,200–6,000	58.16639	2.720074	−0.492289	0.038844	−6.447293	−425.9186	−393.5224
H ₂ O	500–1,700	30.09200	6.832514	6.793435	−2.534480	0.082139	−250.8810	−241.8264
	1,700–6,000	41.96426	8.622053	−1.499780	0.098119	−11.15764	−272.1797	−241.8264
O ₂	100–700	31.32234	−20.23531	57.86644	−36.50624	−0.007374	−8.903471	0.0
	700–2,000	30.03235	8.772972	−3.988133	0.788313	−0.007374	−11.32468	0.0
N ₂	2,000–6,000	20.91111	10.72071	−2.020498	0.146449	9.245722	5.337651	0.0
	100–500	28.98641	1.853978	−9.647459	16.63537	0.000117	−8.671914	0.0
H ₂	500–2,000	19.50583	19.88705	−8.598535	1.369784	0.527601	−4.935202	0.0
	2000–6,000	35.51872	1.128728	−0.196103	0.014662	−4.553760	−18.97091	0.0
CH ₄	298–1,000	33.066178	−11.363417	11.432816	−2.772874	−0.158558	−9.980797	0.0
	1,000–2,500	18.563083	12.257357	−2.859786	0.268238	1.977990	−1.147438	0.0
CH ₄	2500–6,000	43.413560	−4.293079	1.272428	−0.096876	−20.533862	−38.515158	0.0
	298–1,300	−0.703029	108.4773	−42.52157	5.862788	0.678565	−76.84376	−74.87310
	1,300–6,000	85.81217	11.26467	−2.114146	0.138190	−26.42221	−153.5327	−74.87310

Table 2.15 Experimental and theoretical values of the adiabatic flame temperatures for selected materials (initial temperature 25 °C)

Material	Experimental in K		Theoretical in K	C _n in kJ/mol [17]
	a	b		
Acetylene		2,598	2,903	1,255.6
Ethanol			2,288	1,234.8
Ethylene	2,248	2,253	2,561	1,322.9
Methane	2,148	2,158	2,323	802.34
Hydrogen		2,318	2,520	241.82

^aSiegel and Howell (cited according to [5])^bLewis and von Elbe (cited according to [5])

2.1.1.9 Explosions

As already mentioned the ignition of a flammable material may cause a fire or an explosion. An explosion is understood to be the sudden and violent release of energy. The violence of the explosion then depends on the rate of energy release. For example, the energy stored in a car tyre causes an explosion if the tyre bursts. On the other hand it may be gradually dissipated through a puncture. The following types of energy may lead to an explosion:

- physical energy
 - pressure energy of gases
 - strain energy of metals
 - electrical energy
 - heat energy
 - quick phase change (steam explosion)
- chemical energy
 - combustion reactions
 - dust explosions
 - runaway reactions
 - decomposition
 - polymerization
 - explosives
- nuclear energy (uncontrolled chain reaction)

In what follows explosions caused by combustion reactions are treated first. Runaway reactions, decomposition and polymerization are a subject of Chap. 3, explosives are treated in Sect. 2.5 and explosions resulting from physical energy in Sects. 10.7 and 10.9. Nuclear explosions are outside the scope of this book.

Two types of explosions due to chemical energy are distinguished

- deflagration
and
- detonation.

In a deflagration the flammable mixture burns relatively slowly. Flame propagation is mainly determined by molecular diffusion and turbulent transport processes. Mixtures of hydrocarbons and air burn in the absence of turbulence, i.e. under laminar or almost laminar conditions, with flame speeds of the order of 5–30 m/s. If there is no confinement this is too slow to produce tangible overpressures and only a flash fire is produced. That is why there is always turbulence involved in a vapour cloud explosion (turbulent flame speeds 100–300 m/s), which increases the rate of combustion and hence the overpressure [12].

A detonation is totally different. The flame front moves as a pressure wave closely followed by a combustion wave, which supplies the energy nourishing the pressure wave. A stationary detonation pressure wave reaches the velocity of sound corresponding to the hot gases. This velocity lies well above that for unburnt gases. For hydrogen-air mixtures the velocity is of the order of 2,000–3,000 m/s compared with 300 m/s in air of 0 °C.

A detonation causes a stronger pressure wave and more destruction than a deflagration. Whilst the peak pressure of a deflagration produced by a mixture of hydrocarbons and air in a confined space amounts to about 8 bar, 15–20 bar are reached following a detonation. Contrary to a deflagration a detonation does not have to occur in a confined space in order to produce such high pressures [5].

A detonation is not a stable but a fluctuating process. This finds its expression in a cellular structure of shock and reaction waves. The cell structure depends on the type of fuel and the composition of the mixture. More reactive mixtures have smaller cell sizes. Hence, cell size is a measure for the propensity of a material to detonate (cf. Table 2.16). Table 2.16 shows as well that lower ignition energies are required for a deflagration, whilst the direct triggering of a detonation requires high energies [19]. The range of concentrations in which a detonation is possible is always smaller than that for ignition (UEL–LEL) (cf. [4]). However, it becomes broader with increasing initial pressures and temperatures.

A deflagration may turn into a detonation, especially if it propagates through a pipe. Such a process is called Deflagration-Detonation-Transition (DDT). Research has not yet totally clarified its characteristics (cf. [20, 21]).

Basically it may be stated that turbulence enhancing circumstances such as obstacles, building structures, and confinements as well as high ignition energies favour the transition from deflagration to detonation. The same is true for high initial pressures and temperatures.

Table 2.16 Characteristic detonation cell sizes and ignition energies for the deflagration and detonation of selected stoichiometric fuel-air mixtures (from [19])

Flammable material	Cell size in mm	Minimum ignition energy in mJ	
		Deflagration	Detonation
Methane	300	0.28	2.3×10^{11}
Propane	55	0.25	2.5×10^9
Propylene	55	0.28	7.6×10^8
Ethylene	25	0.07	1.2×10^8
Acetylene	10	0.007	1.29×10^5

One must differentiate as well between confined and unconfined explosions. Typical confinements are vessels and pipework as well as buildings. Unconfined explosions (outdoors) exhibit other characteristics than confined ones (vid. Sect. 10.6.3).

2.1.1.10 Maximum Pressure and Maximum Rate of Pressure Rise

Deflagration

The strength of an explosion is characterized by its maximum pressure and its maximum rate of pressure rise. The standardized methods for measuring these parameters are described in [22].

The maxima of the explosion parameters depend on the vessel volume. Whilst the maximum pressures of conventional fuels (flammable vapours) may generally be constant and only dependent on vessel volume the maximum rate of pressure rise may adopt very different values depending on the type of fuel and vessel volume.

The volume dependence of the maximum rate of pressure rise of a flammable gas or vapour can be described by the cube root law

$$\frac{dp}{dt_{\max}} \cdot V^{1/3} = K_G = \text{const.} \quad (2.24)$$

In Eq. (2.24) the unit of the vessel volume has to be compatible with that of K_G , i.e. m^3 for the K_G values from Table 2.17, which additionally also contains maximum pressures; $dp/dt_{\max}$ then results in bar s^{-1} .

Table 2.17 Characteristic values for the explosion of flammable gases and vapours (5-l sphere for explosion tests, ignition energy $E = 10 \text{ mJ}$, standard conditions) from [3]

Flammable Material	$p_{\max}$ in bar	K_G in bar m s^{-1}
Butane	8.0	92
Ethane ^a	7.8	106
Ethylbenzene ^a	7.4	96
Methane	7.1	55
Methyl alcohol ^a	7.5	75
Propane	7.9	100
Carbon disulphide	6.4	105
Hydrogen sulphide	7.4	45
Hydrogen	6.8	550

^aExtrapolated value

Example 2.11 Maximum rates of pressure rise for the deflagration of methane and hydrogen

Determine the maximum rates of pressure rise for vessel sizes between 5 l and 10 l in steps of 1 l for methane and hydrogen.

Solution

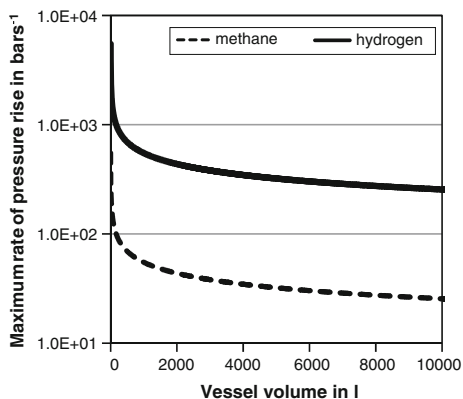
Using Eq. (2.24) in conjunction with Table 2.17 we obtain $\frac{dp}{dt}_{\max} = \frac{55}{V^{1/3}}$ for methane and $\frac{dp}{dt}_{\max} = \frac{550}{V^{1/3}}$ for hydrogen

The results for the maximum rates of pressure rise in bar s^{-1} are given in Table 2.18 and in Fig. 2.7 for an even larger range of volumes.

Table 2.18 Maximum rates of pressure rise for deflagrations of methane and hydrogen in bar s^{-1}

Flammable material	5 l	6 l	7 l	8 l	9 l	10 l
Methane	321.6	302.7	287.5	275.0	264.4	255.3
Hydrogen	3,216	3,027	2,875	2,750	2,644	2,553

Fig. 2.7 Maximum rates of pressure rise for methane and hydrogen as a function of vessel volume

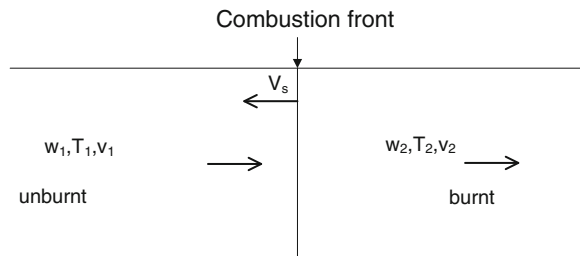


□

Detonation

A detonation is usually modelled as a one dimensional shock wave (vid. [5, 23, 24]). For this purpose a coordinate system is used which moves with the combustion front (velocity $V_s = -w_1$ in the coordinate system of an outside observer, also called laboratory system, vid. Figure 2.8). The following relations are used in the model in order to relate the state after the detonation (subscript 2) with that before the detonation (subscript 1):

Fig. 2.8 Schematic for deriving the equations governing a detonation



Conservation of mass flux

$$\frac{w_1}{v_1} = \frac{w_2}{v_2} \quad (2.25)$$

Conservation of momentum

$$p_1 + \frac{w_1^2}{v_1} = p_2 + \frac{w_2^2}{v_2} \quad (2.26)$$

Conservation of energy

$$h_2 + \frac{w_2^2}{2} - \left(h_1 + \frac{w_1^2}{2} \right) = C_n \quad (2.27)$$

Inserting Eqs. (2.25) and (2.26) in Eq. (2.27) we have

$$h_2 - h_1 - C_n = \frac{1}{2}(p_2 - p_1) \cdot (v_1 + v_2) \quad (2.28)$$

Additionally the ideal gas equation of state is invoked

$$p \cdot v = R \cdot T \quad (2.29)$$

Equation (2.28) establishes a relationship between pressure and specific volume (enthalpy is related via heat capacity and Eq. (2.29) with pressure and specific volume). It is called Hugoniot equation or Hugoniot shock adiabat and consists of thermodynamic quantities only.

The foregoing equations use the following nomenclature:

- w : velocity of gases relative to the combustion front in m/s
- p : pressure in Pa
- v : specific volume in kg/m³
- h : enthalpy in J/kg
- C_n : net calorific value (heat of reaction) in J/kg
- M : molar mass of the flammable gas

R_m : universal gas constant $R_m = 8.3145$ (J/mol K)

R : mass basis gas constant $R = R_m / M$ in J/(kg K)

The following relations apply

$$h_2 = \sum_{j=1}^J \frac{y_j}{M_j} \cdot \Delta h_{out,j} \quad \text{and} \quad h_1 = \sum_{i=1}^I \frac{y_i}{M_i} \cdot \Delta h_{in,i} \quad (2.30)$$

In Eq. (2.30) y denotes the molar fractions and M the molar masses.

From Eqs. (2.26) and (2.25) we obtain the velocity of the shock wave D

$$D = w_1 + V_1 = v_1 \cdot \left(\frac{p_2 - p_1}{v_1 - v_2} \right)^{\frac{1}{2}} \quad (2.31)$$

since V_1 , the velocity of the unburnt gas moving into the combustion front, is equal to zero.

A detonation is characterized by the rapid change of pressure accompanying the combustion process. This change is derived from Eqs. (2.26) and (2.25) giving

$$p_2 - p_1 = \left(\frac{w_1}{v_1} \right)^2 (v_2 - v_1) \quad (2.32)$$

Equation (2.32) connects the state before the combustion (1) with that after the combustion (2); it is called Rayleigh line. From Eq. (2.32) we have for its gradient

$$\frac{p_2 - p_1}{v_2 - v_1} = - \left(\frac{w_1}{v_1} \right)^2 = - \left(\frac{w_2}{v_2} \right)^2 \quad (2.33)$$

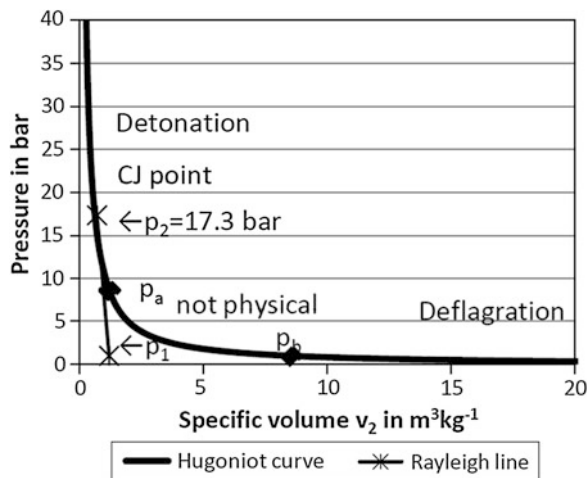
The solution for the detonation pressure has to satisfy Eqs. (2.28) and (2.33). This condition leads to an infinite number of solutions. According to Chapman and Jouguet one has to choose the one for which the Rayleigh line is a tangent to the Hugoniot curve (point CJ in Fig. 2.9). Entropy becomes a maximum at this point (vid. [23]).

Figure 2.9 shows the Hugoniot curve for the stoichiometric combustion of hydrogen. It is based on the evaluation of Eq. (2.28) and serves for some more general explanations.

The curve consists of three regions: explosions with pressures after combustion $p_2 > p_a$, which is characteristic of detonations, and $p_2 < p_b$, which means deflagration. In between there is a physically non permissible region, which is characterized by the fact that the corresponding pairs of values (v_2, p_2) lead to imaginary solutions for the velocities according to Eq. (2.31).

For $p_2 > p_a$ the combustion front moves with supersonic velocity and for $p_2 < p_b$ with subsonic velocity. The differentiation has to be based on the velocity

Fig. 2.9 Hugoniot curve and Rayleigh line between (p_1, v_1) and (p_2, v_2) for the stoichiometric combustion of hydrogen (CJ-Chapman-Jouguet point with the corresponding pressure $p_2 = p_{CJ}$)



of sound applicable to the pertinent temperature T_2 and gas composition, which is obtained from

$$c_2 = \sqrt{\kappa_2 \cdot p_2 \cdot v_2} = \sqrt{\kappa_2 \cdot R_2 \cdot T_2} \quad (2.34)$$

In Eq. (2.34) R_2 is the mass basis gas constant for the gas mixture after the combustion in $J/(kg \cdot K)$ and κ_2 the corresponding heat capacity ratio.

Example 2.12 Simplified determination of detonation pressure and velocity for hydrogen

Determine the detonation pressure and the corresponding velocity for hydrogen. The initial pressure for the detonation is $p_1 = 1$ bar and the initial temperature $T_1 = 298.15$ K.

Data:

Mean values for the heat capacities: $c_{p,H_2O} = 44.6$ $J/(mol \cdot K)$; $c_{p,N_2} = 33.0$ $J/(mol \cdot K)$

Molar masses: hydrogen $M_{H_2} = 2.016$ g/mol, oxygen $M_{O_2} = 31.998$ g/mol, nitrogen $M_{N_2} = 28.013$ g/mol, steam $M_{H_2O} = 18.015$ g/mol.

Solution

According to Zeldovich (vid. [5]) the detonation pressure p_2 may be approximated by

$$p_2 \approx 2 \cdot p_v \quad (2.35)$$

where p_v is the pressure after an isochoric combustion. Because of

$$c_v = c_p - R$$

we obtain

$$c_{v,H_2O} = 44.6 \text{ J}/(\text{mol K}) - 8.3145 \text{ J}/(\text{mol K}) = 36.29 \text{ J}/(\text{mol K})$$

$$c_{v,N_2} = 33.0 \text{ J}/(\text{mol K}) - 8.3145 \text{ J}/(\text{mol K}) = 24.69 \text{ J}/(\text{mol K})$$

By using the reaction Eq. (2.23) and C_n from Table 2.15 for the isochoric heat-up we arrive at

$$(T_2 - T_1) \cdot (n_{H_2O} \cdot c_{v,H_2O} + n_{N_2} \cdot c_{v,N_2}) = C_n \quad (2.36)$$

Solving Eq. (2.36) for the temperature T_2 gives

$$\begin{aligned} T_2 &= \frac{H_u}{n_{H_2O} \cdot c_{v,H_2O} + n_{N_2} \cdot c_{v,N_2}} \\ &+ T_1 = \frac{241,820 \frac{\text{J}}{\text{mol}}}{1 \text{ mol} \cdot 36.29 \frac{\text{J}}{\text{mol K}} + 1.887 \text{ mol} \cdot 24.69 \frac{\text{J}}{\text{mol K}}} \\ &+ 298.15 \text{ K} = 3,215.9 \text{ K} \end{aligned}$$

The corresponding pressure is

$$p_v = p_1 \cdot \left(\frac{T_2}{T_1} \right) = 100,000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot \left(\frac{3215.9 \text{ K}}{298.15 \text{ K}} \right) = 10786181.5 \frac{\text{kg m}}{\text{m}^2 \text{s}^2}$$

According to Eq. (2.35) the pressure of the shock wave is

$$p_2 \approx 2 \cdot 10786181.5 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} = 21572363 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \approx 21.6 \text{ bar}$$

Using the ideal gas equation of state Eq. (2.31) provides the corresponding detonation velocity

$$D = w_1 + V_1 = v_1 \cdot \left(\frac{p_2 - p_1}{v_1 - v_2} \right)^{\frac{1}{2}}$$

where

$$v_1 = \frac{R_m \cdot T_1}{p_1 \cdot M_{\text{reactants}}} \quad \text{and} \quad v_2 = \frac{R_m \cdot T_2}{p_2 \cdot M_{\text{products}}}$$

From Eq. (2.23) we obtain with $n_{\text{reactants}} = n_{H_2} + n_{O_2} + n_{N_2} = 1 + 0.5 + 1.887 = 3.387$ the following molar mass for the mixture of reactants

$$M_{\text{reactants}} = \frac{n_{\text{H}_2}}{n_{\text{reactants}}} \cdot M_{\text{H}_2} + \frac{n_{\text{O}_2}}{n_{\text{reactants}}} \cdot M_{\text{O}_2} + \frac{n_{\text{N}_2}}{n_{\text{reactants}}} \cdot M_{\text{N}_2}$$

$$= 0.2952 \cdot 2.016 \frac{\text{g}}{\text{mol}} + 0.1476 \cdot 31.998 \frac{\text{g}}{\text{mol}} + 0.5571 \cdot 28.013 \frac{\text{g}}{\text{mol}} = 20.930 \frac{\text{kg}}{\text{kmol}}$$

and for the mixture of reaction products with $n_{\text{products}} = n_{\text{H}_2\text{O}} + n_{\text{N}_2} = 1 + 1.887 = 2.887$

$$M_{\text{products}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{products}}} \cdot M_{\text{H}_2\text{O}} + \frac{n_{\text{N}_2}}{n_{\text{products}}} \cdot M_{\text{N}_2}$$

$$= 0.3464 \cdot 18.015 \frac{\text{g}}{\text{mol}} + 0.6536 \cdot 28.013 \frac{\text{g}}{\text{mol}} = 24.5497 \frac{\text{kg}}{\text{kmol}}$$

Hence, we obtain the velocity of the shock wave as

$$D = \frac{R_m \cdot T_1}{p_1 \cdot M_{\text{reactants}}} \cdot \left(\frac{p_2 - p_1}{\frac{R_m \cdot T_1}{p_1 \cdot M_{\text{reactants}}} - \frac{R_m \cdot T_2}{p_2 \cdot M_{\text{products}}}} \right)^{\frac{1}{2}} = \frac{8314.5 \frac{\text{J}}{\text{kmol K}} \cdot 298.15 \text{ K}}{100000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot 20.93 \frac{\text{kg}}{\text{kmol}}}$$

$$\cdot \left(\frac{\frac{21572363 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} - 100000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2}}{\frac{8314.5 \frac{\text{J}}{\text{kmol K}} \cdot 298.15 \text{ K}}{100000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot 20.93 \frac{\text{kg}}{\text{kmol}}} - \frac{8314.5 \frac{\text{J}}{\text{kmol K}} \cdot 3215.9 \text{ K}}{21572363 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot 24.5497 \frac{\text{kg}}{\text{kmol}}}} \right)^{\frac{1}{2}} = 5154.1 \frac{\text{m}}{\text{s}}$$

However, the result lies considerably above the value to be expected from Table 2.19. $\square$

Example 2.13 Numerical calculation of the detonation pressure for selected reactions

Determine the detonation velocities and pressures for the following flammable gases: methane (CH_4), hydrogen (H_2), ethylene (C_2H_4), acetylene (C_2H_2) in air and acetylene with 2.5 mol of oxygen.

Solution

The calculation is performed using Eqs. (2.28) and (2.33). The enthalpies are determined on the basis of Eq. (2.17) in conjunction with Table 2.14. Rearranging Eq. (2.28) we have

$$h_2 - h_1 - C_n - \frac{1}{2}(p_2 - p_1) \cdot (v_1 + v_2) = 0$$

Invoking the ideal gas equation of state the value of T_2 satisfying the above equation for an assumed value of p_2 is determined via bisection (vid. [25]). This

gives a value for v_2 , too. Stepwise modification of p_2 and a renewed search for T_2 enables one to calculate the Hugoniot curve (cf. Fig. 2.9).

The gradient of the Hugoniot curve may now be approximated by the quotient of differences

$$\frac{p_2^i - p_2^{i-1}}{v_2^i - v_2^{i-1}}$$

The superscript i refers to the present value of p_2 , the superscript $i-1$ to the preceding one; the analogue applies to v_2 . The calculation was performed for $p_2^i - p_2^{i-1} = 30 \text{ kgm}/(\text{m}^2\text{s}^2)$, a step width which proved adequate.

The gradient of the Rayleigh line is (vid. Gl. (2.33))

$$\frac{p_2^i - p_1}{v_2^i - v_1}$$

By setting both gradients equal to each other the Chapman-Jouguet point is found. In doing this one requires that the modulus of the relative deviation of both values for the gradient is smaller than a predetermined upper limit ε , i.e.

$$\left| \frac{\frac{p_2^i - p_2^{i-1}}{v_2^i - v_2^{i-1}} - \frac{p_2^i - p_1}{v_2^i - v_1}}{\frac{p_2^i - p_1}{v_2^i - v_1}} \right| < \varepsilon$$

where ε is a small number, e.g. 10^{-5} . Table 2.19 contains the results. Mathematically more sophisticated procedures for finding the Chapman-Jouguet point are described in [23] and [24].

The differences between the calculated values and those from the literature are probably due to the more recent material parameters used and to accounting for the change in the number of moles caused by the reaction.

Table 2.19 Detonation pressures and velocities for selected reactions (final state: thermodynamic equilibrium)

Reaction	Pressure p_2 in bar	Pressure p_2 in bar (calculated)	Detonation velocity w_1 in m/s	Detonation velocity w_1 in m/s (calculated)
$\text{CH}_4 + \text{air}$	17.4 [26]	18.5	1,803 [26]	1,901
$\text{H}_2 + \text{air}$	15.8 cit. in [27]	17.3	1,968 cit. in [27]	1,997
$\text{C}_2\text{H}_4 + \text{air}$	18.2 cit. in [27]	20.4	1,822 cit. in [27]	1,962
$\text{C}_2\text{H}_2 + \text{air}$		24.5		2,038
$\text{C}_2\text{H}_2 + 2.5 \text{ O}_2$		34.0		2,341

2.2 Chemically Unstable Materials: Decomposition and Polymerization

Decomposition and polymerization of materials which release energy are considered as hazardous; they are treated following [28]. The groups of materials with propensity to decomposition at ambient temperature are

- organic peroxides and
- self-reactive materials.

Materials are called self-reactive, if they have a propensity to violent exothermic decomposition at temperatures above ambient or by contact with impurities. These are mostly materials with sensitive nitrogen-nitrogen groups in the molecule.

Organic peroxides are materials which contain the bivalent peroxy-(O–O-) structural element and may be regarded as derivatives of hydrogen peroxides with one or both hydrogen atoms replaced by organic rests. They can already decompose exothermically at ambient temperature. The decomposition may be caused by heat, contact with impurities (e.g. acids and heavy metal compounds), friction or impact.

Whilst materials decompose by breaking up into smaller entities, the uncontrolled polymerization leads to the formation of large molecules, the polymers, and to a temperature rise if the heat of reaction is not removed sufficiently. The rate of heat removal decreases the larger the molecules become during the progressing polymerization. Table 2.20 provides an overview of the quantities of heat released by the aforementioned reactions, which by the way can also act as sources of ignition.

2.3 Flammable Liquids

Flammable liquids are classified in [29]. The properties of the liquids which form the basis for classification are given in Table 2.21.

The parameters flash point and fire point are used for characterizing flammable liquids.

2.3.1 Flash Point

The flash point of a liquid is the lowest temperature in °C corrected to 101.3 kPa of a flammable liquid in an open or closed cup at which vapours develop in such a quantity that under defined measuring conditions in the cup a vapour-air mixture is

Table 2.20 Heats of decomposition and polymerization of selected unstable materials (after [28])

Material	
<i>Peroxides</i>	<i>Heat of decomposition in kJ/mol</i>
Alkyl hydroperoxide	≈ 180
Dialkyl peroxide	170–180
Peroxydicarboxylic acids	80–90
Diacyl peroxide	120–130
<i>Self-reactive materials</i>	
Azobenzene	145.8
Azodicarbonamide	49.9
4-Nitrosophenol	147.7
Phenyldiazonium chloride	210.9
<i>Polymerizing materials</i>	<i>Heat of polymerization in kJ/mol</i>
Acrylic acid	67
Ethyl acrylate	80
Methyl acrylate	80
Methacrylic acid	42
Methyl methacrylate	59
Styrene	71
Vinyl acetate	88

Table 2.21 Classification of flammable liquids [29]

Characteristic	Flammable liquid		
	Category 1	Category 2	Category 3
Flash point	<23 °C	<23 °C	≥23 °C and ≤60 °C ^a
Initial boiling point	≤35 °C	>35 °C	
Hazard statement	H 224 extremely flammable liquid and vapour	H 225 highly flammable liquid and vapour	H 226 flammable liquid and vapour
Signal word	Danger	Danger	Warning
Past hazard class according to VbF	AI and B	AI and B	AII

^aFor the purpose of this regulation ([29]) gas oil, Diesel fuel and heating oils with a flashpoint between 55 and 75 °C may be considered as belonging to category 3

formed above the liquid surface which is just ignitable by an igniter from the outside [6]. There are several measuring methods (vid. [30]). Table 2.22 gives values for selected liquids.

Table 2.22 Characteristic parameters for flammable liquids (after [7])

Flammable liquid	Flash point in °C (closed cup)	Boiling point in °C	Categorization
Styrene	31	145	H 226
Chlorobenzene	28	132	H 226
Ethyl alcohol	12	78	H 225
Methanol	11	65	H 225
Petrol	< -20	60	H 224
Diethyl ether	< -20	35	H 224
Diesel fuel	>55	>155	may be assigned to H224 (cf. Table 2.21)

2.3.2 Fire Point

The fire point can provide information on fire hazards, for example after the spill of a flammable liquid, whilst the flash point indicates the existence of an explosive atmosphere.

The flash point implies that the ignited vapour goes out shortly after ignition, whereas the fire point is obtained by heating the liquid such that the fire continues after ignition (vid. [3]). Table 2.23 shows a comparison between the flash points and the fire points of selected materials.

2.4 Dusts

Materials which are flammable in solid state can explode if they are present as dusts, i.e. in the form of fine particles which can be whirled up and mixed with air. Then they behave similarly to exploding gases. Their propensity to explode is influenced by a number of factors. In [5] the following are named:

- chemical composition;
- particle size;
- moisture content;
- oxygen concentration;
- inert gas;
- admixed inert dust concentration.

Safety parameters are used to describe the combustion behaviour; they characterize the behaviour of

- deposited dust and
- dust dispersed in air

Table 2.23 Comparison of flash points and fire points (from [3])

Liquid	Boiling temperature in °C	Flash point in °C (closed cup)	Flash point in °C (open cup)	Fire point in °C
Toluene	110	6	14	18
Ethylene glycol	135	43	62	62
2-Butoxyethylacetate	192	88	98	98
Hexadecane	280	135	142	152

In what follows a few safety parameters are discussed; a detailed treatment including the measuring apparatuses is given in [3].

2.4.1 Self-Ignition

Flammable dusts already show a tendency to self-ignition at relatively low ambient temperatures, since a slow reaction with the oxygen of the air on the particle surfaces produces heat even at ambient temperature. Whether the final temperature reached lies below or above the self-ignition temperature (characterized by the equilibrium between heat production and removal) depends on the ratio of heat removal to the environment and heat production. The final temperature rises if the environmental temperature is increased, for example in an oven. The temperature at which the heat production is just larger than its removal is called self-ignition temperature. Apart from the properties of the material this temperature depends on the geometry of the bulk powder, which influences heat removal. More details on the theory of self-heating and self-ignition are found in Sect. 4.5.1.1.

2.4.2 Glow Temperature

The glow temperature is the lowest temperature, for which a dust layer with a thickness of 5 mm is ignited. It is determined under well-defined testing conditions on a hot plate (vid. [31]). The glow temperature decreases with increasing layer thickness. Additionally, grain size and bulk powder density influence the heat balance and hence the glow temperature. Table 2.24 contains values for selected materials.

2.4.3 Explosion Limits

Dust-air mixtures are flammable only within a certain range of concentrations just like gas-air mixtures. This range is marked by the lower explosion limit (LEL) and the upper explosion limit (UEL).

Table 2.24 Glow temperatures for selected materials [32]

Material	Maximum particle size in μm	Main particle size in μm	Bulk powder density in kg/l	Glow temperature in $^{\circ}\text{C}$
Phosphorus (red)	150	30–50	0.99	305
Iron powder	500	100–150	1.6	240
Rye flour	200	30–50	0.31	325
Wood dust (beech)	150	70–100	0.22	315
Charcoal	20	1–2	0.36	340
Naphthalene	300	80–100	0.53	Melts
Polyvinyl chloride	10	4–5	0.55	Carbonizes

The lower limit is of special practical interest. For many technical dusts it lies between 15 and 60 g/m^3 ; the UEL is very high, viz. 2–6 kg/m^3 . Investigations have shown that the LEL is largely independent of the ignition energy employed [3].

The temperature dependence of the LEL is described by [3]

$$\text{LEL}(T) = \text{LEL}(T_0) \cdot [1 - 0.0027 \cdot (T - T_0)] \quad (2.37)$$

In Eq. (2.37) $\text{LEL}(T)$ is the lower explosion limit at temperature T and $\text{LEL}(T_0)$ that at the reference temperature T_0 . Table 2.25 gives values for selected materials.

2.4.4 Minimum Ignition Energy

The minimum ignition energy (MIE) is the smallest quantity of energy stored in a capacitor which is sufficient to ignite the most flammable mixture of dust and air. The test is carried out under standardized conditions (vid. [33]). Table 2.26 gives values for selected materials.

Materials are categorized according to their minimum ignition energy

$\text{MIE} \geq 10 \text{ mJ}$: normally sensitive to ignition

$3 \text{ mJ} \leq \text{MIE} \leq 10 \text{ mJ}$: especially sensitive to ignition

$\text{MIE} \leq 3 \text{ mJ}$: extremely sensitive to ignition

Table 2.25 Lower explosion limits for selected materials and the ratio UEL/LEL at standard conditions [11]

Type of dust	LEL in gm^{-3}	UEL/LEL
Aluminum	35	172
Magnesium	25	223
Zirconium	45	544
Lignite	35	20

Table 2.26 Particle size and minimum ignition energy (MIE) for selected dusts [3]

Type of dust	Particle size in μm	MIE in mJ
Activated carbon	<10	500×10^3
Chicory	40	100
Pea flour, green	27	100
Sewage sludge (76 % organic)	89	50
Wax	<20	5
Lycopodium	32	2
Aluminum	<10	≈ 0.1

2.4.5 Limiting Oxygen Concentration (LOC)

The limiting oxygen concentration (LOC) is the maximum oxygen concentration of a flammable dust with air and an inert gas for which there is no self-sustaining propagation of flames for any fuel concentration. Fuel concentration is varied by varying the concentration of inert gas. The determination takes place under standardized test conditions (vid. [34]).

The oxidizing medium usually is air; yet substances like chlorine may serve as well. Oxygen concentrations higher than that of air (21 vol%) raise the combustion velocity and ignitability. The converse is also true. This offers possibilities for preventing dust explosions by reducing the O_2 contents by mixing with an inert material. In industry carbon dioxide, nitrogen, noble gases or inert dusts like calcium carbonate (CaCO_3) are used for this purpose [35]. Table 2.27 gives details.

Table 2.27 Limiting oxygen concentrations for inserting dust clouds in an O_2/N_2 atmosphere [35]

Dust type	Median of the particle diameter in μm	Maximum O_2 concentration on inerting with N_2 in vol%
Aluminum	22	5
Soot	<10	12
Charcoal	42	12
Wood	27	10
Cornstarch	17	9
Organic pigments	<10	12
Herbicides	10	12

2.4.6 Maximum Pressure and Maximum Rate of Pressure Rise

The maximum pressure, $p_{\max}$, and the maximum rate of pressure rise, $(dp/dt)_{\max}$, in closed vessels, frequently spherical ones with volumes of 20 l or 1 m³, characterize the strength of a dust explosion. The maximum strength is determined in a series of experiments by systematically varying the concentration of dust. The value may differ for the two vessel sizes. It was found that for vessels larger than 1 m³ the maximum explosion pressure virtually does not change. However, the maximum rate of pressure rise varies, as for flammable gases (cf. Sect. 2.1.1.10), according to

$$\frac{dp}{dt_{\max}} \cdot V^{1/3} = K_{st} = \text{const.} \quad (2.38)$$

Hence, the maximum rate of pressure rise decreases with increasing vessel volume. The pertinent measuring procedures are standardized in [36] and [37]. Table 2.28 shows values for selected dust-air mixtures.

Based on the value of K_{st} dusts are categorized in classes [38]. These classes serve to support the design of constructive protection measures for equipment. They are shown in Table 2.29.

Table 2.28 Maximum explosion pressures and K_{st} for selected dusts [3]

Type of dust	Particle size in μm	$p_{\max}$ in bar	K_{st} in bar ms^{-1}
Activated carbon	<10	7.3	72
Chicory	40	8.5	157
Pea flour, green	27	9.1	109
Sewage sludge (76 % organic)	89	7.5	71
Wax	<20	8.4	185
Lycopodium	32	7.0	134
Aluminum	<10	11.4	625

Table 2.29 Categorization of dusts in explosion classes according to the value of K_{st}

K_{st} in bar ms^{-1}	Dust explosion class
0	0
0–200	1
200–300	2
>300	3

Example 2.14 Determination of the maximum rate of pressure rise of dust explosions

The maximum rate of pressure rise of dust explosions of sewage sludge and aluminum are to be compared for vessel volumes between 1 and 20 m³.

Solution

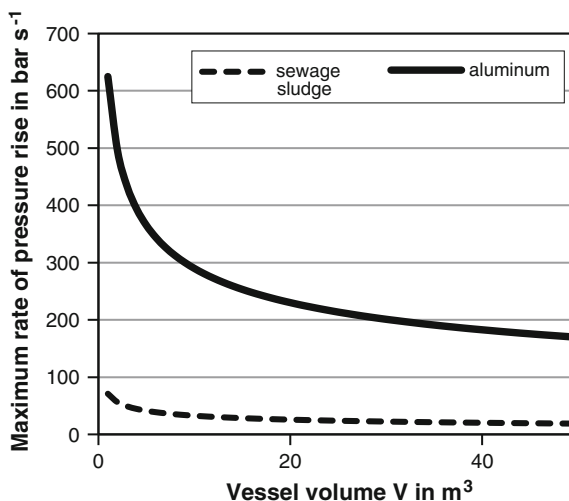
Using Eq. (2.38) and Table 2.28 we obtain $\frac{dp}{dt}_{\max} = \frac{71}{V^{1/3}}$ for sewage sludge and for aluminum $\frac{dp}{dt}_{\max} = \frac{625}{V^{1/3}}$

Table 2.30 shows the results for varying vessel volumes and Fig. 2.10 provides the corresponding graphical representation.

Table 2.30 Maximum rate of pressure rise for explosions of sewage sludge and aluminum dusts as a function of vessel volume

V in m ³	(dp/dt) _{max} in bar s ⁻¹ · sewage sludge	(dp/dt) _{max} in bar·s ⁻¹ aluminum
1	71	625
2	56.35	496.06
3	49.23	433.35
4	44.72	393.73
5	41.52	365.5
6	39.07	343.95
7	37.12	326.73
8	35.5	312.5
9	34.13	300.47
10	32.96	290.1
11	31.93	281.03
12	31.01	273
13	30.2	265.8
14	29.46	259.3
15	28.79	253.43
16	28.18	248.03
17	27.62	243.07
18	27.09	238.48
19	26.61	234.22
20	26.16	230.25

Fig. 2.10 Maximum rate of pressure rise for dust explosions as a function of vessel volume



2.5 Explosives

A material capable of an exothermic reaction such that gases and vapours are generated and released so rapidly that they cause destruction in their surroundings is called explosive. An explosion can occur only if the material has a big positive energy of formation or a large negative energy of decomposition. Such materials have a certain chemical structure. Since they are organic and mostly have reactive groups with available oxygen an intermolecular oxidation of their flammable part may occur. Examples for oxidizing reactive groups are nitro-, nitroso- and peroxy groups. Organic compounds containing acidic, acetylene or diazonium groups can also be strong explosives. Furthermore explosive mixtures can be produced by mixing inorganic oxidizing substances with flammable materials. Well known examples are: mixtures of potassium nitrate, sulphur and charcoal (black powder), of ammonium nitrate and fuel oil (ANFO) as well as nitrating mixtures containing potassium nitrate and oxidizing substances with hydrogen peroxide [39]. In [40] instructions are given for identifying materials which may potentially be explosive because they contain reactive groups. Explosible materials are categorized according to intended use and the type of handling hazard.

If the energy contents of a material is such that an explosion, the initiation of an explosion (by a small impact or a weak spark), a propellant (characterized by slow combustion) or a pyrotechnic effect can occur we are dealing with an explosive [40].

The characteristic of explosives is that they contain the oxygen required for combustion. Hence, they do not need an oxygen supply from outside and can therefore ignite even under water.

Explosives are characterized by a number of parameters [41], among them

- energy of formation;
- enthalpy of formation;
- brisance or shattering power;
- explosion energy;
- loading density;
- oxygen balance;
- nitrogen content;
- volume of explosion gases;
- thermal sensitivity;
- impact sensitivity;
- friction sensitivity;
- thermal stability.

Some of them are described below largely following [41]

2.5.1 Brisance

Brisance is the destructive fragmentation effect of a charge on its immediate vicinity. The relevant parameters are the detonation rate and the loading density (compactness) of the explosive, as well as the gas yield and the heat of explosion. Brisance is a measure for the time required to build up the maximum explosion pressure.

2.5.2 Loading Density

Loading density is understood to be the ratio between the mass of explosive and the volume available for the detonation. It depends on the production process, e.g. casting or pressing.

2.5.3 Oxygen Balance

The oxygen balance is the quantity of oxygen, expressed in percent mass, released by complete conversion of the explosive. If all the oxygen bonded in the explosive is not sufficient to convert the explosible material completely, the oxygen balance is negative. In the converse case it is positive (cf. Table 2.31).

2.5.4 Maximum Pressure

The blast wave produced by an explosion is caused by two mechanisms, the heating of the reaction products and the change in mole number. If an explosion progresses so fast that the volume at first remains unchanged and we deal with ideal gases the maximum pressure, p_s , is obtained as follows [42]

Table 2.31 Characteristics of selected explosives [41]

Substance	Molar mass in g	Chemical formula	Loading density in g/cm ³	Oxygen balance in %	Detonation velocity v_D in m/s ^a
Trinitrotoluene (TNT)	227.1	C ₇ H ₅ N ₃ O ₆	0.82–1.07	−74	6,900 for $\rho = 1.6$ g/cm ³
Ammonium-nitrate	80.0	NH ₄ NO ₃	0.82–1.6 ^b	+20	–
Hexogen (cyclonite)	222.1	C ₃ H ₆ N ₆ O ₆		−21.6	8,750 for $\rho = 1.76$ g/cm ³
Trinitrobenzene	213.1	C ₆ H ₃ N ₃ O ₆		−56.3	7,300 for $\rho = 1.71$ g/cm ³
Nitroglycerin	227.1	C ₃ H ₅ N ₃ O ₉		+3.5	7,600 for $\rho = 1.59$ g/cm ³

^aThis is the detonation velocity under confinement (e.g. in a drilling hole) contrary to the detonation velocity in the open

^bDepending on the mixture, e.g. with TNT

$$p_s = \frac{p_a \cdot n_e \cdot T_e}{n_a \cdot T_a} \quad (2.39)$$

In Eq. (2.39) p is the pressure in Pa or bar, T the temperature in K, n the number of moles; the subscript “a” refers to the state before the explosion and “e” to that afterwards.

According to [43] the maximum pressure may also be obtained from

$$p_s = 9.9792 \cdot 10^{-10} \cdot \rho \cdot v_D^2 \quad (2.40)$$

In Eq. (2.40) ρ is the density in kg/m³ and v_D the detonation velocity in m/s (vid. Table 2.31). The maximum pressure, p_s , then results in bar.

2.5.5 Explosion Energy

The amount of energy released in an explosion depends on the initial and final states of the reaction. Yet it is difficult to determine the final state because the hot reaction products still undergo reactions during cooling. Explosives with a positive oxygen balance (rich in oxygen) will produce CO₂ and H₂O after the reaction; in case of a negative oxygen balance CO and H₂ will be encountered.

The following quantities are of interest:

- heat of combustion;
- energy of explosion;
- heat of explosion.

The heat of explosion is equal to the difference of the internal energies before and after the explosion, ΔU . The heat of combustion is the difference of the internal energies in case of stoichiometric combustion. The explosion energy equals the work done by the expansion of the gases, i.e.

$$w = - \int_1^2 p dV \quad (2.41)$$

In Eq. (2.41) 1 denotes the state before the explosion and 2 that afterwards. The sign is negative, if work is transferred out of the system boundaries and positive if it is introduced into the system; p is the pressure and V the volume.

The evaluation of the integral requires one to know the changes of pressure and volume during the explosion. Therefore it is difficult to be evaluated. It is easier to relate the thermodynamic states before and after the reaction with each other. This is achieved with the help of Helmholtz's free energy f . We have (cf. [5])

$$du = dw + dq \quad (2.42)$$

and using the relationship between heat and entropy $dq = Tds$

$$du = dw + Tds \quad (2.43)$$

Helmholtz's free energy is defined as

$$f = u - Ts \quad (2.44)$$

whence one obtains

$$df = du - Tds - sdT \quad (2.45)$$

In an isothermal process ($dT = 0$) the entire energy change is transformed into work. This gives

$$df = du - Tds \quad (2.46)$$

Inserting Eq. (2.43) in Eq. (2.46) we obtain

$$df = dw \quad (2.47)$$

Helmholtz's energy represents the maximum amount of work which a system can exert on its surroundings. Hence, it constitutes an upper bound for the work done by the explosion. Helmholtz's free energy is not normally found in tables. Therefore calculations based on Eq. (2.46) make use of the internal energy and entropy differences. We then have

$$du \approx \Delta u = (\Delta u_f^0)_P - (\Delta u_f^0)_R \quad (2.48)$$

which is the difference between the internal energies of formation of the reaction products $(\Delta u_f^0)_P$ and of the reactants $(\Delta u_f^0)_R$ at standard conditions, and

$$ds \approx \Delta s = s_P - s_R \quad (2.49)$$

which is the difference of the corresponding entropies. For the entropy we have

$$s = s^0 - R \cdot \sum_{(i)} n_i \cdot \ln \frac{n_i}{n} \quad (2.50)$$

In Eq. (2.50) s^0 is the entropy at standard conditions, n_i is the number of moles of the substance i and n the total number of moles. Since important contributions to the entropy are only made by the gaseous reaction products, the pressures $p_i = n_i/n$ are the partial pressures of product i in the mixture. The sum term in Eq. (2.50) constitutes the entropy increase caused by the irreversible mixing process (vid. [5]). Obviously it is only relevant if the mole numbers before and after the reaction differ substantially.

Application of the above considerations to the detonation of TNT leads to the following result (vid. [5])



In the first place the differences of the internal energies are formed. The necessary information is given in Table 2.32

Table 2.32 Thermodynamic properties of selected substances [6]

Substance	ΔU_f^0 in kJ/mol	ΔH_f^0 in kJ/mol	s^0 in kJ/(mol K)	ΔH_c^0 kJ/mol
C	0	0	0.00574	–
CO	–111.9 ^a	–110.53	0.197556	–283
CO ₂	–393.8 ^a	–393.51	0.213667	–
H ₂ O	–240.8 ^a	–241.814	0.188724	–
H ₂	0	0	0.130571	–241.82
N ₂	0	0	0.1915	–
O ₂	0	0	0.205043	–
Acetylene		228.2	0.20081	–1257
Ethylene	49.86 ^b	52.51	0.2192	–1323
TNT	–49.74 ^a	67.07*	0.27	–3295.9
Nitroglycerin	–349.71 ^a	–370.83*		–1529 ^c

^aFrom [41]; ^bcalculated; ^cfrom [18]

Table 2.33 Characteristics of selected explosives (from [41]), values behind the oblique bar from ([44])

Substance	Molar mass in g	Chemical formula	Explosion energy in kJ/kg (H ₂ O _{liq.})	Explosion energy in kJ/mol (H ₂ O _{liq.})
Trinitrotoluene (TNT)	227.1	C ₇ H ₅ N ₃ O ₆	4,564/4,520	1,036.5/1,026.5
Ammonium nitrate	80.0	NH ₄ NO ₃	2,479	198.3
Hexogen (cyclonite)	222.1	C ₃ H ₆ N ₆ O ₆	5,647/5,360	1,254.2/1,190.5
Trinitrobenzene	213.1	C ₆ H ₃ N ₃ O ₆	3,876	826.0
Nitroglycerin	227.1	C ₃ H ₅ N ₃ O ₉	6,671	1,515.0

$$\Delta u = 1 \cdot 0 + 6 \cdot (-111,9) + 2,5 \cdot 0 + 1,5 \cdot 0 - 1 \cdot (-49,74) = -621,66 \frac{\text{kJ}}{\text{mol}}$$

$$= -2738,6 \frac{\text{kJ}}{\text{kg}}$$

The result is the heat of explosion, for which -2710 kJ kg^{-1} is found in [5]. Still to be added is the term describing the expansion work. Based on Eqs. (2.49) and (2.50) we have

$$ds = 1 \cdot 0.00574 + 6 \cdot 0.197556 - 8.3145 \cdot 10^{-3} \cdot 6 \cdot \ln \frac{6}{10} + 2.5 \cdot 0.130571 - 8.3145 \cdot 10^{-3} \cdot 2.5 \cdot \ln \frac{2.5}{10}$$

$$+ 1.5 \cdot 0.1915 - 8.3145 \cdot 10^{-3} \cdot 1.5 \cdot \ln \frac{1.5}{10} - 1 \cdot 0.27 = 1.6127 \frac{\text{kJ}}{\text{mol K}} = 7.103 \frac{\text{kJ}}{\text{kg K}}$$

We obtain the explosion energy according to Eq. (2.46)

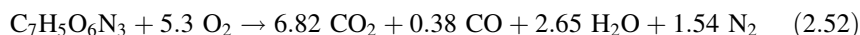
$$dw = df = du - Tds = -2738,6 - 298,15 \cdot 7,1013 = -4855,9 \frac{\text{kJ}}{\text{kg}}$$

In [5] the explosion energy is stated to be $-4,850 \text{ kJ kg}^{-1}$. The heat of combustion is determined in Example 2.15.

Details on selected other explosives are provided in Table 2.33

Example 2.15 Determination of the heat of combustion of TNT

Determine the heat of combustion of TNT. A look at Table 2.31 shows that TNT has a negative oxygen balance. Therefore the decomposition reaction is substoichiometric. Hence, the products may still react with oxygen and then release heat. If this is accounted for, the following equation of reaction can be established [45]



Solution

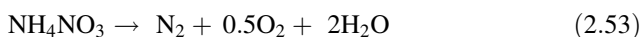
The difference of the internal energies is

$$\begin{aligned}\Delta u &= 6.8 \cdot (-393.8) + 0.38 \cdot (-111.9) + 2.65 \cdot (-240.8) + 1.54 \cdot 0 - 1 \cdot (-49.74) - 5.3 \cdot 0 \\ &= -3408.22 \frac{\text{kJ}}{\text{mol}} = -15014.19 \frac{\text{kJ}}{\text{kg}}\end{aligned}$$

In [5] $-1,5132 \text{ kJ/kg}$ is given as heat of combustion.

Example 2.16 Generation of gaseous reaction products

Determine the volume of gas produced by the explosion of 1 kg of ammonium nitrate (molar mass 80.04) (water is usually considered as being in gaseous state although the molar standard volume of $22.414 \text{ m}^3 \text{ kmol}^{-1}$ refers to 0°C and 101.325 kPa).

*Solution*

Calculation of the number of moles in 1 kg of ammonium nitrate:

$$N = \frac{1,000 \text{ g}}{80.04 \frac{\text{g}}{\text{mol}}} = 12.49$$

According to the reaction Eq. (2.53) 1 mol of ammonium nitrate reacts to form 3.5 mol of product. Hence we have

$$V = 12.49 \cdot 3.5 \text{ mol} \cdot 22.414 \cdot 10^{-3} \frac{\text{m}^3}{\text{mol}} = 0.979 \text{ m}^3$$

□

Example 2.17 Calculation of the peak overpressure of an explosion of TNT

We consider an explosion of TNT according to the reaction Eq. (2.51) at an initial temperature of $T_a = 298.15 \text{ K}$.



Determine the maximum pressure of its detonation.

Solution

The entire heat release calculated as the difference between the energies of formation of the products and the reactants must be equal to $c_v \Delta T$.

$$\Delta u_{\text{TNT}} = \int_{T_0}^{T_e} (1 \cdot c_C + 6 \cdot c_{v,\text{CO}} + 2,5 \cdot c_{v,\text{H}_2} + 1,5 \cdot c_{v,\text{N}_2}) dT$$

The specific heat capacity of graphite is taken as the constant value $c_C = 8.5 \text{ J/(mol K)}$. All the other heat capacities depend on temperature. In order to determine them recourse is had to the information of Sect. 2.1.1.8. Use is made of the facts that the integral of c_p over temperature is the enthalpy and that the relationship

$$c_v = c_p - R_m$$

holds between the heat capacities with $R_m = 8.3145 \text{ J/(mol K)}$ being the universal gas constant. Hence we have

$$\Delta u_x(T_e) = h_x^0(T_e) - h_{x,298,15}^0 - R_m \cdot (T_e - 298,15)$$

with x representing the respective material. Using Eq. (2.51) the temperature T_e is found iteratively from the transcendental equation

$$\Delta u_{\text{TNT}} = 1 \cdot c_C \cdot (T_e - T_0) + 6 \cdot \Delta u_{\text{CO}} + 2.5 \cdot \Delta u_{\text{H}_2} + 1.5 \cdot \Delta u_{\text{N}_2}$$

This is done using a root finding method (vid. [24]). With the above results and the help of Table 2.32 $T_e = 2,665.6 \text{ K}$ is obtained. Then we obtain according to Eq. (2.39)

$$p_s = \frac{1 \text{ bar} \cdot 10 \cdot 2665.6 \text{ K}}{1 \cdot 298.15 \text{ K}} = 89.4 \text{ bar}$$

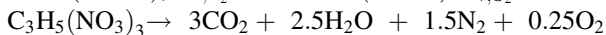
Using Eq. (2.40) and the data from Table 2.31 we have

$$p_s = 9.9792 \cdot 10^{-10} \cdot 1600 \cdot 6900^2 = 76.02 \text{ bar}$$

□

Example 2.18 Calculation of the maximum pressure of the explosion of nitroglycerin

Nitroglycerin explodes according to the reaction equation given below. The following mean heat capacities are to be used: $c_{v,\text{CO}_2} = 51.03 \text{ J/(mol K)}$, $c_{v,\text{H}_2\text{O}} = 43.12 \text{ J/(mol K)}$, $c_{v,\text{N}_2} = 27.34 \text{ J/(mol K)}$, $c_{v,\text{O}_2} = 30.08 \text{ J/(mol K)}$.



Solution

$$\begin{aligned} \Delta u_{\text{Nitroglycerin}} &= 3 \cdot (-393.8) + 2.5 \cdot (-240.8) + 1.5 \cdot 0 + 0.25 \cdot 0 - (-349.71) \\ &= -1433.68 \text{ kJ/mol} \end{aligned}$$

Using this value and following the procedure of Example 2.17 one obtains

$$T_e = 4633.5 \text{ K}$$

Equation (2.39) gives the maximum pressure

$$p_s = \frac{1 \text{ bar} \cdot 7.25 \cdot 4633.5 \text{ K}}{1 \cdot 298.15 \text{ K}} = 112.7 \text{ bar}$$

Using Eq. (2.40) and the data from Table 2.31 we obtain

$$p_s = 9.9792 \cdot 10^{-10} \cdot 1590 \cdot 7600^2 = 91.65 \text{ bar}$$

2.6 Toxic Materials

Toxic materials or poisons are substances which can harm health. Their impact depends on the type of material and exposure, which may range between short time exposures to high concentrations and long-term exposures to low concentrations during an entire working life. Toxic substances can enter the body through the following routes of exposure:

- inhalation;
- ingestion;
- external contact with skin resorption.

The following effects are then to be expected:

- irritations, allergies
 - respiratory tract,
 - skin,
 - eyes;
- narcosis;
- asphyxiation
 - simple,
 - chemical;
- systemic damage, harm to the bodily control functions;
- cell mutations;
- cancer;
- genetic damage.

2.6.1 Limiting Long-Term Exposure

The physician K.B. Lehmann observed in the course of his factory inspections and as a result of animal and other experiments in the years 1884 to 1886 that there exists an airborne concentration for any substance below which no occupational disease develops. This is true independently of the time of exposure. This realization led to the development of the MAK values (MAK: maximum occupational

Table 2.34 AGW values for selected materials of frequent use in the process industry [47]

Material	Workplace threshold value	
	ml m ⁻³ (ppm)	mg m ⁻³
Ammonia	20	14
Chlorine	0.5	1.5
Carbon monoxide	30	35
Carbon dioxide	5,000	9,100
Phosgene	0.1	0.41
Mercury	–	0.02
Sulphur dioxide	1	2.5
Vinyl acetate	5	18

exposure concentration; similar to OEL: occupational exposure limits in the U.K. and TLV: threshold limit values in the U.S.A.) [46].

These values nowadays are only of historical interest. Instead the Technical Rules for Hazardous Materials are used [47]. They contain threshold values for occupational exposure.² Table 2.34 gives the corresponding values for selected materials, which are frequently used in the process industry. The values apply to a working life with a five-day week and 8 h of daily work. They are called workplace threshold values (AGW). Additionally, there is a transgression factor catering for short-time exposure to higher concentrations (vid. [47]).

For practical applications it is often necessary to convert ppm into mg m⁻³ and vice versa. This is done by

$$C^* = \frac{1000 \cdot \frac{Z \cdot R_m \cdot T}{p}}{M} \cdot C \frac{\text{mg}}{\text{m}^3} \quad (2.54)$$

In Eq. (2.54) Z is the compressibility factor, R_m the universal gas constant in J/(mol K), T the temperature in K and M the molar mass of the respective material in g/mol.

Fixing thresholds below which no impact is to be expected encounters limitations in the case of carcinogenic substances. This is why recently a probability-related concept was proposed for such substances (vid. [49] and Sect. 8.2).

² The workplace threshold value (AGW) is the limiting value for a time-averaged concentration of a substance in the air at the workplace related to a given time period of reference. It indicates the concentrations for which acute or chronic harmful effects on health are not generally to be expected (Para. 3, Sect. 6 Hazardous Materials Ordinance [48]).

2.6.2 Limiting Short-Term Exposure

2.6.2.1 Threshold Values

During an accident large quantities of toxic materials may be released. Specific threshold values were developed for the resulting concentrations, since the threshold values for work life exposure are inappropriate. Among them figure AEGLs (Acute Exposure Guideline Levels) [50], ERPGs (Emergency Response Planning Guidelines) [51], TEELs (Temporary Emergency Exposure Levels) [52] and EEIs (Emergency Exposure Indices) [53]. These values are specifically devised for emergency planning.

The SEL (Seuil d'Effet Létal) [54] and DTL (Dangerous Toxic Load) [55] values are mainly targeted at land-use planning. Only the ACUTEX method of the European Community [56] provides values for land-use and emergency planning.

2.6.2.2 Probit Relations

Whilst threshold values merely enable one to take “good” or “bad” decisions a probit (“probability unit”)-relation allows one to assess the probability of a certain consequence, e.g. death, occurring due to a causative factor such as toxic exposure. For example, we have for the exposure to chlorine

$$Y = -17,1 + 1,69 \cdot \ln \left(\int_0^t C(t')^{2,75} \cdot dt' \right) \quad (2.55)$$

In Eq. (2.54) $C(t')$ denotes the variation with time of the chlorine concentration. Generally the time integral over a concentration is called dose. However, if an exponent $\neq 1$ is applied to the concentration we speak of load, e.g. in this case toxic load.

Probit relations are formulated such that they adopt the value $Y = 5$ for a damage probability of 0.5. This corresponds to the lethal dose 50, LD_{50} , a value at which 50 % of the affected individuals are expected to die.

The probability of damage then results from

$$P_{\text{damage}} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} \exp\left(-\frac{x^2}{2}\right) dx = \phi(Y-5) \quad (2.56)$$

in Eq. (2.56) ϕ standard normal distribution (cf. [57]).

The advantage of using a probit relation is the higher degree of realism. The probability of damage usually grows with an increasing intensity of the damage-causing factor. The application of probit relations therefore is an appropriate way to make knowledge from areas like medicine and toxicology available and practicable for the engineer.

Appendix B gives probit relations for a number of materials used in the process industry. They are based on observations of accidents, experiments with animals and expert judgment. Hence, they are relations affected by uncertainties. However, no assessment of their magnitude is usually indicated.

Example 2.19 Calculation of probabilities of death and uncertainties

Calculate the probabilities of death for those substances, where several probit relations are given in Appendix B. The calculations are to be based on a concentration of 5,000 ppm and an exposure during 30 min. They reveal that uncertainties affect the probit relations.

Solution

The calculations are based on Eqs. (2.55) and (2.56). In conjunction with the equations of Appendix B the following results are obtained

<i>Ammonia</i>		
(B3a)	$Y = 6.4$	$P_{\text{death}} = 0.92$
(B3b)	$Y = 5.6850$	$P_{\text{death}} = 0.7533$
(B3c)	$Y = 1.9058$	$P_{\text{death}} = 9.9 \times 10^{-4}$
<i>Chlorine</i>		
(B7a)	$Y = 28.232$	$P_{\text{death}} = 1.0$
(B7b)	$Y = 44.575$	$P_{\text{death}} = 1.0$
(B7c)	$Y = 10.595$	$P_{\text{death}} = 1.0$
(B7d)	$Y = 8.3717$	$P_{\text{death}} = 0.9996$
<i>Hydrogen fluoride</i>		
(B11a)	$Y = 9.5099$	$P_{\text{death}} = 1.0$
(B11b)	$Y = 7.6551$	$P_{\text{death}} = 0.9960$
(B11c)	$Y = 4.1043$	$P_{\text{death}} = 0.1852$
(B11d)	$Y = 14.104$	$P_{\text{death}} = 1.0$
<i>Phosgene</i>		
(B17a)	$Y = 33.584$	$P_{\text{death}} = 1.0$
(B17b)	$Y = 24.661$	$P_{\text{death}} = 1.0$

□

Example 2.20 ERPG values and probabilities of death

Using the probit equations of Appendix B the probabilities of death are to be determined which correspond to the ERPG values³ of Table 2.35. An exposure time of one hour is to be used, which is the reference duration for the ERPG values.

³ ERPG-1: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odour. ERPG-2: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action. ERPG-3: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing or developing life-threatening health effects.

Table 2.35 ERPG values [51] and corresponding probabilities of death

Substance	ERPG-1			ERPG-2			ERPG-3			Probability of death			Eq.
	ppm			ppm			ppm			ERPG-1	ERPG-2	ERPG-3	
Acrolein	0.05			0.15			1.5			0	0	5.6×10^{-9}	(B1)
Acrylonitrile	10			35			75			0	4.9×10^{-12}	2.1×10^{-4}	(B2)
Ammonia	25			150			750			0	0	5.7×10^{-7}	(B3a)
Benzene	50			150			1,000			0	0	0	(B4)
Bromine	0.1			0.5			5			0	0	1.3×10^{-13}	(B5)
Hydrogen cyanide	n.a.			10			25			–	0	1.1×10^{-16}	(B6)
Chlorine	1			3			20			0	0	0.1	(B7a)
Hydrogen chloride	3			20			150			0	8.7×10^{-15}	1.4×10^{-4}	(B8)
Ethylene oxide	n.a.			50			500			–	4.2×10^{-6}	1.6×10^{-2}	(B9)
Fluorine	0.5			5			20			0	1.3×10^{-8}	2.6×10^{-3}	(B10)
Hydrogen fluoride	2			20			50			0	0	0	(B11a)
Formaldehyde (>90 %)	1			10			40			0	1.5×10^{-9}	1.0×10^{-2}	(B12)
Carbon disulphide	1			50			500			0	0	1.1×10^{-16}	(B13)
Carbon monoxide	200			350			500			1.1×10^{-16}	3.7×10^{-10}	6.6×10^{-7}	(B14)
Methanol	200			1,000			5,000			1.6×10^{-7}	2.6×10^{-5}	1.4×10^{-3}	(B15)
Fuming sulphuric acid 65 %	2			10			120			0	0	6.4×10^{-3}	(B16)
Phosgene	n.a.			0.5			1.5			–	0	0	(B17a)
Phosphine	n.a.			0.5			5			–	5.9×10^{-5}	6.1×10^{-2}	(B18)
Hydrogen sulphide	0.1			30			100			0	1.1×10^{-8}	4.7×10^{-4}	(B19)
Sulphur dioxide	0.3			3			25			0	0	5.4×10^{-8}	(B20)
Toluene	50			300			1000			4.3×10^{-10}	8.3×10^{-6}	1.0×10^{-3}	(B21)

n.a.: not appropriate

Solution

The solutions are based on Eqs. (2.55) and (2.56). In conjunction with the equations from Appendix B we obtain the results of Table 2.35. $\square$

Example 2.21 Toxic exposure in a building

If toxic gases are released in residential areas part of them penetrates into the buildings. Nevertheless a building may afford shelter, a circumstance which should be accounted for when assessing the possible number of persons killed or injured following a release. The extent to which a building provides protection depends on its air exchange rate, which in turn depends on the following factors:

- topographic situation,
- building quality,
- wind speed,
- wind direction,
- difference between temperatures indoors and outdoors.

According to [58] an air exchange rate of $k = 0.5$ to 0.8 per hour may be assumed if the windows are closed. The time variation of the concentration inside the building is regarded as proportional to the difference between the concentrations of the toxic substance inside the building, $c_i(t)$, and in its surroundings, $c_s(t)$. We then have

$$\frac{dc_i}{dt} = k \cdot (c_s - c_i) \quad (2.57)$$

If c_s is considered as constant and the initial condition $c_i(t = 0) = 0$, i.e. no toxic material inside the building at the beginning of the release, Eq. (2.57) has the following solution

$$c_i(t) = c_s \cdot [1 - \exp(-k \cdot t)] \quad (2.58)$$

However, with a real accident the concentration in the surroundings varies with time. This can approximately be described for releases close to the ground of gases which are lighter than air by (vid. Sect. 10.5)

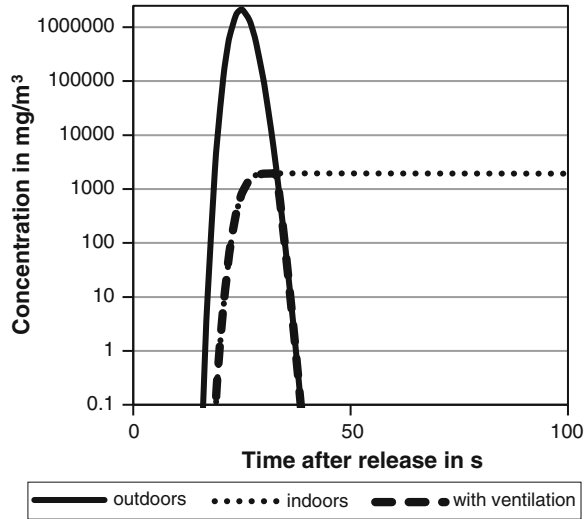
$$c_s(t, x_1, y_1, z_1) = \frac{2 \cdot Q}{(4\pi Kt)^{3/2}} \cdot \exp\left(-\frac{(x_1 - ut)^2 + y_1^2 + z_1^2}{4Kt}\right) \quad (2.59)$$

Table 2.36 Probabilities of death after a puff release of CO for different building qualities and mitigation strategies

Wind speed	$u = 2 \text{ ms}^{-1}; K = 0.5833 \text{ m}^2 \text{ s}^{-1}$				$u = 4 \text{ ms}^{-1}; K = 1.167 \text{ m}^2 \text{ s}^{-1}$		$u = 10 \text{ ms}^{-1}; K = 2.917 \text{ m}^2 \text{ s}^{-1}$	
Air exchange rate	Windows permanently closed	Windows opened when outside concentration lower than inside	Windows permanently closed	Windows opened when outside concentration lower than inside	Windows permanently closed	Windows opened when outside concentration lower than inside	Windows permanently closed	Windows opened when outside concentration lower than inside
0.7 h^{-1}	0.9998	0	0.8449	0	0.0007	0	0	0
3 h^{-1a}	0.9998	0	0.8438	0	0.0090	0	0	0

^aThis simulates a building of bad quality

Fig. 2.11 Time variation of the concentration after a toxic release outdoors and indoors without and with ventilation after the outdoor concentration drops below the indoor concentration ($u = 4 \text{ ms}^{-1}$)



The quantities in Eq. (2.59) have the following meaning:

- Q : released mass of toxic gas in kg
- x_1 , y_1 , and z_1 : coordinates of the building in m, assuming that the point of release is the origin of the coordinate system
- K is a parameter characterizing the atmospheric and topological conditions in the surroundings of the point of release, the eddy coefficient in m^2s^{-1}
- u the wind speed in m/s in the direction of x-axis, which is oriented in such a way that it connects the point release with the location of the building

Whilst it makes sense to seek shelter in a building and to close its windows immediately after the release it is preferable in the long term to open the windows and leave the building, when the outside concentration drops below the concentration inside the building.

The inhomogeneous linear differential Eq. (2.59) is solved numerically using the Runge-Kutta method of second order with variable time steps (cf. [25]).

Scenario for the calculation

Owing to tank failure there is a puff (instantaneous) release of 10,000 kg of CO. A building stands at a distance of 100 m in the direction of the wind. Determine the time-dependent concentrations and probabilities of death.

Solution

Equation (2.57) in conjunction with Eq. (2.59) is applied. The probability of death is calculated using the probit from Eq. (B14). The following input data is used:

$Q = 10,000 \text{ kg}$; $x_1 = 100 \text{ m}$; $y_1 = 0 \text{ m}$; $z_1 = 6 \text{ m}$

The results are shown in Table 2.36 and in Fig. 2.11. □

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Many of the reactions used in the process industry are exothermic and therefore have to be cooled (vid. Table 3.1). If cooling is insufficient or even fails the reaction temperature rises. This rise can be accompanied by gas releases and the evaporation of the substances involved. As a consequence pressure may build up and the reactor may be destroyed (cf. [1, 2]). The reaction experiences a “runaway”. In this context it is recommended to examine the possibility of secondary reactions, for example decompositions, which may occur because of the rising temperature and may be even more destructive than the runaway of the original reaction [1].

Whilst the previous chapter was concerned with the properties of materials only, a runaway implies a coupling with the equipment in which the reaction takes place. Hence, equipment properties have to be accounted for as well. They furnish the boundary conditions for modelling. Therefore reaction kinetics and reactor models are now briefly reviewed. Details can be found in [4] and [5].

3.1 Formal Kinetics Description of Chemical Reactions

The velocity of reactions in principle depends on the number of collisions per unit of time between the reactants. It may be assessed with the methods of physical chemistry. Yet, for practical applications it is determined experimentally. The experimental results are then evaluated using simplified model concepts. For this reason we speak of formal kinetics.

A relatively general representation of the rate of reaction of homogeneous gas and liquid reactions is

$$r = k \cdot c_1^{m_1} \cdot c_2^{m_2} \quad (3.1)$$

In Eq. (3.1) r is the rate of reaction in $\text{mol}/(\text{m}^3 \text{ s})$, c_1 the concentration of the first feed material in mol/m^3 and c_2 that of the second; k is the rate constant with the unit $\text{s}^{-1} (\text{mol}/\text{m}^3)^{-(m_1+m_2-1)}$. The latter depends on temperature. The order of

Table 3.1 Enthalpies of reactions of standard chemical processes [3]

Reaction	ΔH_r (kJ/mol)	Reaction	ΔH_r (kJ/mol)
Neutralization (HCl)	-55	Hydrogenation (nitroaromatics)	-560
Neutralization (H ₂ SO ₄)	-105	Hydrogenation (alkenes)	-200
Diazotization	-65	Amination	-120
Sulphonation	-150	Combustion (hydrocarbons)	-900
Nitration	-130	Diazo decomposition	-140
Epoxidation	-100	Nitro decomposition	-400
Polymerization (styrene)	-60		

the reaction is $m_1 + m_2$. Due to the adaptation process mentioned non integer or negative orders may occur.

For heterogeneously catalyzed reactions Eq. (3.1) is used as well. Besides the following relationship is employed

$$r = \frac{k \cdot c_1^{m_1} \cdot c_2^{m_2}}{(1 + K_1 \cdot c_1 + K_2 \cdot c_2)^{m_3}} \quad (3.2)$$

In Eq. (3.2) K_1 and K_2 are the equilibrium constants of the reaction; r now has the unit s^{-1} (mol/m²), which in the heterogeneous case applies for Eq. (3.1) as well (cf. [4]).

The dependence of the rate constant on temperature is crucial for safety considerations. It is described by the Arrhenius equation

$$k = k_0 \cdot \exp\left(-\frac{E}{R_m \cdot T}\right) \quad (3.3)$$

In Eq. (3.3) k_0 is the pre-exponential factor with the same unit as the rate constant, E the apparent energy of activation in J/mol, R_m the universal gas constant and T the absolute temperature.

3.2 Reactor Models

The complicated interactions between the chemical reaction and the transport processes for mass, energy and momentum, which occur simultaneously, are described by the corresponding laws of conservation. We have [4]

$$\frac{\partial c_i}{\partial t} = -\text{div}(\vec{u} \cdot c_i) + \text{div}(D_i^e \cdot \text{grad } c_i) + \sum_j v_{i,j} \cdot r_j \quad (3.4)$$

Equation (3.4) expresses that the variation with time of the concentration of substance i (left hand side of the equation) is caused by forced convection (for example by stirring) (first term on the right hand side), the effective diffusion (second term on the right hand side) and the chemical transformation (third term on the right hand side). D_i^e is the effective diffusion coefficient in $\text{m}^2 \text{s}^{-1}$ of substance i and v_{ij} the stoichiometric coefficient of substance i in reaction j (negative sign for feed materials and positive sign for products); $\vec{u}$ is the velocity vector of the flow in ms^{-1} .

For process safety problems normally space-independent solutions of Eq. (3.4) are used. However, for some cases, for example stirrer failure or the correct placing of measuring sensors, accounting for space dependence is desirable. Space independence leads to the concept of “ideal stirring”, i.e. at any point inside the reactor we have the same temperature and concentrations (ideal reactor). This is assumed in subsequent sections.

Equation (3.4) is complemented by the enthalpy balance

$$\frac{\partial(\rho \cdot \bar{c}_p \cdot T)}{\partial t} = -\text{div}(\rho \cdot \bar{c}_p \cdot T \cdot \vec{u}) + \text{div}(\lambda^e \cdot \text{grad}T) + \sum_j r_j \cdot (-\Delta H_{R,j}) \quad (3.5)$$

The time variation of enthalpy per m^3 (left hand side of the equation) is caused by forced convection (first term on the right hand side), the effective heat transfer (second term on the right hand side) and the heat release caused by the chemical reaction (third term on the right hand side); λ^e is the effective coefficient of thermal conductivity of the mixture of substances in $\text{W}/(\text{m K})$, ρ is its density in kg/m^3 , $\bar{c}_p$ the corresponding heat capacity at constant pressure in $\text{J}/(\text{kg K})$ and $\Delta H_{R,j}$ the enthalpy of reaction of reaction j in J/kg (with a negative sign for exothermic reactions).

3.2.1 Ideal Batch Reactor

A batch reactor is initially filled with all reagents. During the reaction no substances are introduced into or removed from the reactor. Additionally, it is normally assumed that the volume remains constant during reaction.

Equation (3.4) then becomes

$$\frac{dc_i}{dt} = \frac{1}{V} \cdot \frac{dn_i}{dt} = \sum_j v_{ij} \cdot r_j \quad (3.6)$$

In Eq. (3.6) n_i denotes the number of moles of substance i and, v_{ij} the stoichiometric number of component i in reaction j (positive for created substances and negative for removed ones), V the volume of the reacting mixture in m^3 .

Introducing the conversion X

$$X = \frac{n_{i,0} - n_i}{n_{i,0}} = \frac{c_{i,0} - c_i}{c_{i,0}} \quad (3.7)$$

and assuming a single reaction ($i = 1$) Eq. (3.6) yields

$$dt = -n_{1,0} \cdot \frac{dX}{V \cdot v_1 \cdot r} = -c_{1,0} \cdot \frac{dX}{v_1 \cdot r} \quad (3.8)$$

where the subscript 0 denotes the initial state of the quantity in question.

If Eq. (3.8) is integrated it enables one to calculate the time until a certain degree of conversion, X^* , is reached

$$t_{X^*} = -n_{1,0} \int_0^{X^*} \frac{dX}{v_1 \cdot r \cdot V} = -c_{1,0} \int_0^{X^*} \frac{dX}{v_1 \cdot r} \quad (3.9)$$

The enthalpy balance follows from Eq. (3.5)

$$\frac{d(\rho \cdot \bar{c}_p \cdot T)}{dt} = \sum_j r_j \cdot (-\Delta H_{R,j}) \quad (3.10)$$

Equation (3.10) holds for an adiabatic system, which does not exchange heat with its surroundings. Multiplying Eq. (3.10) with the reactor volume V and assuming for simplicity's sake that the material coefficients

- do not depend on temperature,
- their change due to the reaction may be neglected,

and that only one reaction takes place, we write instead of Eq. (3.10)

$$(\bar{C}_w + m \cdot \bar{c}_p) \frac{dT}{dt} = r \cdot V \cdot (-\Delta H_R) \quad (3.11)$$

Equation (3.6) with $v = -1$ yields

$$\frac{dc}{dt} = \frac{1}{V} \cdot \frac{dn}{dt} = -r \quad (3.12)$$

In Eq. (3.11) C_w is the thermal capacity of the reactor in J and m the mass of its contents in kg.

Inserting Eq. (3.11) in Eq. (3.10) we obtain

$$(\bar{C}_w + m \cdot \bar{c}_p) \frac{dT}{dt} = \frac{dn}{dt} \cdot (-\Delta H_R) \quad (3.13)$$

The solution of Eq. (3.13) with the initial conditions $T(0) = T_0$ and $n(0) = n_0$ is

$$T(t) - T_0 = \frac{n_0 - n(t)}{C_w + m \cdot c_p} (-\Delta H_R) \quad (3.14)$$

The maximum final temperature is reached if all of the reactant is consumed, i.e. $n(t) = 0$. The result is the adiabatic temperature rise ΔT_{ad}

$$\Delta T_{ad} = \frac{n_0 \cdot (-\Delta H_R)}{\bar{C}_w + m \cdot \bar{c}_p} \quad (3.15)$$

The adiabatic temperature rise is proportional to the enthalpy of reaction and to the initial quantity of the reactant.

According to [6] the normal operation of a reactor is considered to be safe, if $\Delta T_{ad} < 50$ K holds for the reaction occurring during normal operation and if there are no thermal instabilities of the reagents, the reacting mixture or the products in the temperature range $[T, T + \Delta T_{ad}]$. However, this criterion should be used with care, since the time behaviour should be accounted for as well in assessing safety. Additionally, the uncertainties of the calculation should be observed [7].

If a secondary reaction exists whose starting temperature is reached before the reactants are used up, the temperature rise after cooling failure may be even higher than ΔT_{ad} . This leads to the concept of criticality classes, which is amply discussed in [1].

So far it was assumed that there is no reactor cooling. In order to account for it Eq. (3.10) is extended to yield

$$\frac{d(\rho \cdot \bar{c}_p \cdot T)}{dt} = \sum_j r_j \cdot (-\Delta H_{R,j}) - U \cdot F \cdot (T - T_0) \quad (3.16)$$

In Eq. (3.16) U is the overall coefficient of heat transfer in $W/(m^2 \text{ K})$, F the area of the heat exchanger in m^2 and T_0 in K the temperature on the secondary side of the heat exchanger. The latter is considered to be constant in time; the model is extended in Example 3.5.

Example 3.1 Adiabatic temperature rise

A reactor contains a mass of $m = 970$ kg, its volume is $V = 0.63 \text{ m}^3$ and the initial concentration of the reactant is $c_0 = 250 \text{ mol/m}^3$. The average thermal capacity of the reaction mixture amounts to $\bar{c}_p = 2,000 \text{ J/(kg K)}$ and that of the reactor to $\bar{C}_w = 6,500 \text{ J/K}$. The enthalpy of reaction is $-\Delta H_R = 27,437 \text{ kJ/mol}$. Calculate the adiabatic temperature rise.

Solution

Equation (3.15) yields

$$\Delta T_{ad} = \frac{n_0 \cdot (-\Delta H_R)}{\bar{C}_w + m \cdot \bar{c}_p} = \frac{250 \frac{\text{mol}}{\text{m}^3} \cdot 0.63 \text{ m}^3 \cdot 27,437 \frac{\text{J}}{\text{mol}}}{6,500 \frac{\text{J}}{\text{K}} + 970.2 \text{ kg} \cdot 2,000 \frac{\text{J}}{\text{kg K}}} = 22.23 \text{ K}$$

□

Example 3.2 Final temperature of an adiabatic temperature rise

A reactor contains a mixture of a mass of 1,650 kg; 150 kg thereof is the reactant, which has a thermal capacity of $c_p = 2,428 \text{ J/(kg K)}$ and an enthalpy of reaction of $-\Delta H_R = 1,465.4 \text{ kJ/kg}$. The second material has a thermal capacity of $c_p = 1,717 \text{ J/(kg K)}$. The thermal capacity of the reactor amounts to $\bar{C}_w = 10,000 \text{ J/K}$. The temperature of reaction is $T_R = 293.15 \text{ K}$.

What are the adiabatic temperature rise and the corresponding final temperature?

Solution

Starting point is Eq. (3.15), which is multiplied by M/M , with M being the molar mass of the reactant. Thus, the numerator is changed to mass related quantities. This yields

$$\Delta T_{ad} = \frac{150 \text{ kg} \cdot 1,465,400 \frac{\text{J}}{\text{kg}}}{10,000 \frac{\text{J}}{\text{K}} + 150 \text{ kg} \cdot 2,428 \frac{\text{J}}{\text{kg K}} + 1,500 \text{ kg} \cdot 1,717 \frac{\text{J}}{\text{kg K}}} = 74.52 \text{ K}$$

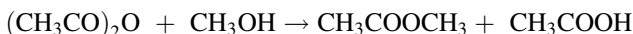
and hence a final temperature of

$$T = T_R + \Delta T_{ad} = 293.15 \text{ K} + 74.52 \text{ K} = 367.67 \text{ K} \hat{=} 94.52^\circ \text{C}$$

□

Example 3.3 Determination of the time of reaction

The example reaction to be used is the exothermic esterification of acetic anhydride and methanol. Methyl acetate and acetic acid are then formed. The reaction takes place according to the following reaction equation



The corresponding kinetic equation is of second order. It is [vid. Eqs. (3.1), (3.3) and (3.12)]

$$\frac{dc_1}{dt} = -k_0 \cdot \exp\left(-\frac{E}{R_m T}\right) \cdot c_1 \cdot c_2 = -r \quad (3.17)$$

The following data and denominations are used:

$k_0 = 8.966 \times 10^6 \text{ m}^3/(\text{kmol s})$, $E = 73,752 \text{ kJ/kmol}$, concentration of acetic anhydride c_1 and that of methanol c_2 . The initial concentrations are $c_{1,0} = 0.8591 \text{ kmol m}^{-3}$ and $c_{2,0} = 21.4777 \text{ kmol m}^{-3}$. The thermal capacity of the mixture is $c_p = 2.31 \text{ kJ/kg}$, its density is $\rho = 832.8 \text{ kg m}^{-3}$, and the enthalpy of reaction is $-\Delta H_R = 60,744.44 \text{ kJ/kmol}$. The reaction temperature is $T_R = 293.15 \text{ K}$.

Determine the time required for reaching a degree of conversion of $X^* = 0.99$ for an isothermal reaction and compare the result with that of an adiabatic reaction.

Solution

In the first place the abbreviation of Eq. (3.7) is inserted in the kinetics Eq. (3.17). This yields

$$\frac{dX}{dt} = k_0 \cdot \exp\left(-\frac{E}{R_m T}\right) \cdot (1 - X) \cdot (c_{2,0} - c_{1,0} \cdot X) \quad (3.18)$$

Integration of Eq. (3.18) for the fixed reaction temperature T_R leads to

$$t_{0,99} = \int_0^{0,99} \frac{\exp\left(\frac{E}{R_m T_R}\right)}{k_0 \cdot (1 - X) \cdot (c_{2,0} - c_{1,0} \cdot X)} \cdot dX \quad (3.19)$$

After some rearrangements Eq. (3.19) can be solved analytically (cf. [8]). This gives

$$\begin{aligned} t_{0,99} &= \frac{\exp\left(\frac{E}{R_m T_R}\right)}{k_0} \int_0^{0,99} \frac{dX}{c_{1,0} \cdot X^2 - X \cdot (c_{1,0} + c_{2,0}) + c_{2,0}} \\ &= \frac{\exp\left(\frac{E}{R_m T_R}\right)}{k_0 \cdot \sqrt{-\Delta}} \cdot \left(\ln \frac{2 \cdot c_{1,0} \cdot 0,99 - c_{1,0} - c_{2,0} - \sqrt{-\Delta}}{2 \cdot c_{1,0} \cdot 0,99 - c_{1,0} - c_{2,0} + \sqrt{-\Delta}} - \ln \frac{-c_{1,0} - c_{2,0} - \sqrt{-\Delta}}{-c_{1,0} - c_{2,0} + \sqrt{-\Delta}} \right) \\ &= 74,860.5291 \text{ s} \cdot (7.78365 - 3.2189) = 94.92 \text{ h} \end{aligned}$$

where

$$\Delta = 4 \cdot c_{1,0} \cdot c_{2,0} - (-c_{1,0} - c_{2,0})^2 = -425.1267 \frac{\text{kmol}^2}{(\text{m}^3)^2}$$

For an adiabatic reaction process we have

$$t_{0,99} = \int_0^{0,99} \frac{\exp\left(\frac{E}{R_m (T_R + \Delta T_{ad} X)}\right)}{k_0 \cdot (1 - X) \cdot (c_{2,0} - c_{1,0} \cdot X)} \cdot dX \quad (3.20)$$

In Eq. (3.20) the relation

$$T(t) = T_0 + X \cdot \Delta T_{ad} \quad (3.21)$$

is used, which can easily be derived from Eq. (3.14) in conjunction with Eqs. (3.7) and (3.15).

Numerical evaluation of Eq. (3.20) then leads to 15.96 h, where $\Delta T_{ad} = 27.13 \text{ K}$. The shorter period of time is not surprising, since the adiabatic

process produces higher temperatures than the isothermal one. This increases the rate of reaction according to Eqs. (3.1) and (3.3). $\square$

Example 3.4 Variation with time of the temperature of a reaction

A cylindrical stirred reactor has the following properties:

Reaction enthalpy per unit mass of the mixture	$q = \left(-\Delta H_R \frac{c \cdot V}{m}\right) = 169.5 \frac{\text{J}}{\text{kg}}$
Pre-exponential factor	$k_0 = 1,715,745.53 \text{ s}^{-1}$
Volume	$V = 0.63 \text{ m}^3$
Density of the reactor contents	$\rho = 1,540 \text{ kg/m}^3$
Mean thermal capacity of the reactor contents	$\bar{c}_p = 2,000 \text{ J/(kg K)}$
Overall heat transfer coefficient	$U = 1,400 \text{ W/(m}^2 \text{ K)}$
Area for heat transfer (jacket + coil)	$F = 7 \text{ m}^2$
Apparent energy of activation	$E = 34,392.9 \text{ J/mol}$
Reaction temperature	$T_R = 288.15 \text{ K}$

Determine the temperature on the coolant side, T_0 , and the variation with time of the reactor temperature after cooling failure. The thermal capacity of the reactor and heat transfer to the surroundings are to be neglected. Both assumptions are on the safe side (conservative).

Solution

Equation (3.16) is simplified by assuming constant material properties and a single reaction. Furthermore it is assumed that the reaction is of zero order [$m_1 = m_2 = 0$ in Eq. (3.1)], i.e. the reactant is not used up. Hence, we obtain

$$\rho \cdot V \cdot \bar{c}_p \cdot \frac{dT}{dt} = q \cdot \rho \cdot V \cdot k_0 \cdot \exp\left(-\frac{E}{RT}\right) - U \cdot F \cdot (T - T_0) \quad (3.22)$$

Due to the assumption of a reaction of order 0 the concentration of the reactant is constant and a decrease with time according to Eq. (3.12) does not have to be assessed. This is conservative because in reality the consumption of the reactant would reduce the reaction rate.

The temperature on the cooling side during stationary operation ($dT/dt = 0$) is

$$\begin{aligned}
 T_0 &= T_R - \frac{q \cdot k_0 \cdot \exp\left(-\frac{E}{R \cdot T_R}\right) \cdot \rho \cdot V}{U \cdot F} \\
 &= 288.15 \text{ K} - \frac{169.5 \frac{\text{J}}{\text{kg}} \cdot 1,715,745.53 \text{ s}^{-1} \cdot 6.1056 \cdot 10^{-7} \cdot 1,540 \frac{\text{kg}}{\text{m}^3} \cdot 0.63 \text{ m}^3}{1,400 \frac{\text{W}}{\text{m}^2 \text{ K}} \cdot 7 \text{ m}^2} \\
 &= 288.15 \text{ K} - 16.78 \text{ K} = 271.37 \text{ K} \triangleq -1.78^\circ \text{C}
 \end{aligned}$$

In order to simulate cooling failure the second term on the right hand side of Eq. (3.22) is set equal to 0. This yields

$$\frac{dT}{dt} = \frac{q \cdot k_0 \cdot \exp\left(-\frac{E}{RT}\right)}{\bar{c}_p} \quad (3.23)$$

This non-linear homogeneous differential equation of first order cannot be solved analytically. Therefore a numerical approach is used. A simple integration scheme is

$$T_i = T_{i-1} + \frac{q \cdot k_0 \cdot \exp\left(-\frac{E}{RT_{i-1}}\right)}{\bar{c}_p} \cdot \Delta t \quad (3.24)$$

The results shown in Figs. 3.1 and 3.2 were obtained with the scheme of Eq. (3.24) with $\Delta t = 0.01$ s and a Runge-Kutta integration of second order with variable step size (cf. [9]). The difference between the two procedures may be neglected in this case. It is obvious that the thermal explosion (runaway) leaves but little time for emergency interventions.

Fig. 3.1 Variation with time of the reaction temperature after cooling failure (*dotted line* simple integration)

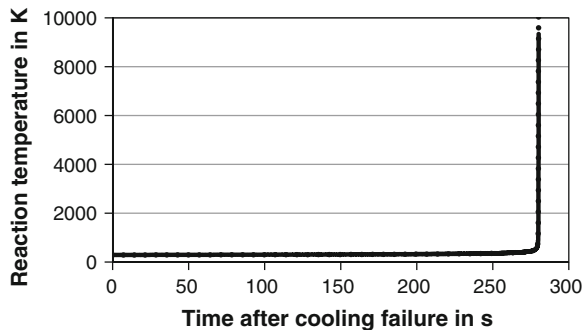


Fig. 3.2 Variation with time of the reaction temperature after cooling failure (detail)

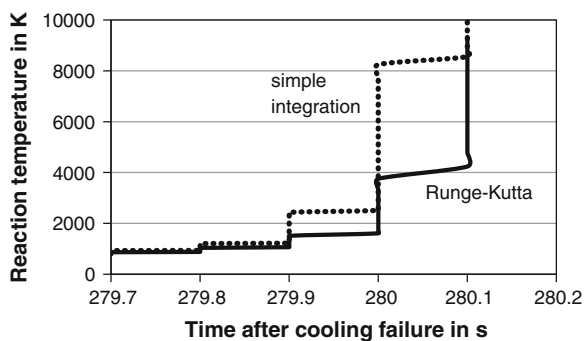
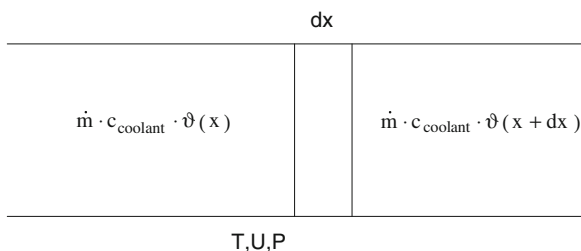


Fig. 3.3 Schematic for deriving the heat balance for a heat exchanger



Example 3.5 Partial failure of reactor cooling and the Semenov diagram

Extending example 3.4 the heat exchanger is now treated explicitly. It is modelled as a circular pipe with perimeter P . The thickness of its walls is neglected for simplicity's sake (Fig. 3.3). The inlet temperature of the coolant (a mixture of water and methanol) amounts to $\vartheta_e = -5^\circ\text{C}$. Its thermal capacity is $c_{\text{coolant}} = 3,600 \text{ J/(kg K)}$. This modified model enables one to analyze partial cooling failure which may occur, for example, if the coolant circuit control valve remains stuck in a position of partial opening.

The heat balance for a pipe-shaped heat exchanger for constant reaction temperature T is

$$\dot{m} \cdot c_{\text{coolant}} \cdot \vartheta(x + dx) - \dot{m} \cdot c_{\text{coolant}} \cdot \vartheta(x) = P \cdot k \cdot [T - \vartheta(x)] \cdot dx \quad (3.25)$$

Using the abbreviation $\theta = T - \vartheta$ and developing $\vartheta(x + dx)$ in a Taylor series, of which only the first two terms are retained, we have

$$-\frac{d\theta}{dx} \cdot dx = \frac{P \cdot k}{\dot{m} \cdot c_{\text{coolant}}} \cdot \theta \cdot dx \quad (3.26)$$

Integration of Eq. (3.26) over x leads to

$$\theta(x) = A \cdot \exp\left(-\frac{P \cdot k}{\dot{m} \cdot c_{\text{coolant}}} \cdot x\right) = T - \vartheta \quad (3.27)$$

With the initial condition

$$\vartheta(0) = \vartheta_e \quad (3.28)$$

we have

$$\vartheta(x) = T - (T - \vartheta_e) \cdot \exp\left(-\frac{P \cdot k}{\dot{m} \cdot c_{\text{coolant}}} \cdot x\right) \quad (3.29)$$

The thermal power removed equals the product of the coolant mass flow with the coolant thermal capacity and the difference between the coolant outlet and inlet temperatures, i.e. $\vartheta(L) - \vartheta(0)$. This gives

$$\dot{q}_{\text{cooling}} = \dot{m} \cdot c_{\text{coolant}} \cdot (T - \vartheta_e) \cdot \left[1 - \exp\left(-\frac{k \cdot F}{\dot{m} \cdot c_{\text{coolant}}}\right) \right] \quad (3.30)$$

In Eq. (3.30) $P \cdot L = F$ equals the surface area of the pipe. Hence, Eq. (3.30) may be applied to heat exchangers of any geometry with surface area F . Differing geometric designs only impact the overall coefficient of heat transfer U .

First the coolant mass flow required for stationary operation is determined. A look at Eq. (3.22) shows that the cooling power has to be equal to

$$\begin{aligned} \dot{q}_{\text{cooling}} &= U \cdot F \cdot (T - T_0) = 1,400 \frac{\text{W}}{\text{m}^2 \text{K}} \cdot 7 \text{ m}^2 \cdot (288.15 \text{ K} - 271.37 \text{ K}) \\ &= 164,444 \text{ W} \end{aligned}$$

Solving this equation by bisection (cf. [9]) gives

$$\dot{m} = 7.52 \frac{\text{kg}}{\text{s}}$$

Using the procedure of Example 3.4 the results of Figs. 3.4 and 3.5 are obtained.

Figure 3.4 illustrates the fact that for coolant mass flows below that required for stationary operation runaway occurs. Only the starting time of the runaway reaction depends on the degree of mass flow reduction.

Figure 3.5 shows that heat generation increases exponentially with rising temperature [vid. Eq. (3.3)], whilst cooling only experiences a linear increase. This leads to the following states. S marks the point of stable operation: a temperature increase enhances cooling and thus causes the system to return to point S. I marks the point of unstable operation: a temperature increase leads to stronger

Fig. 3.4 Variation with time of the temperature after partial cooling failure

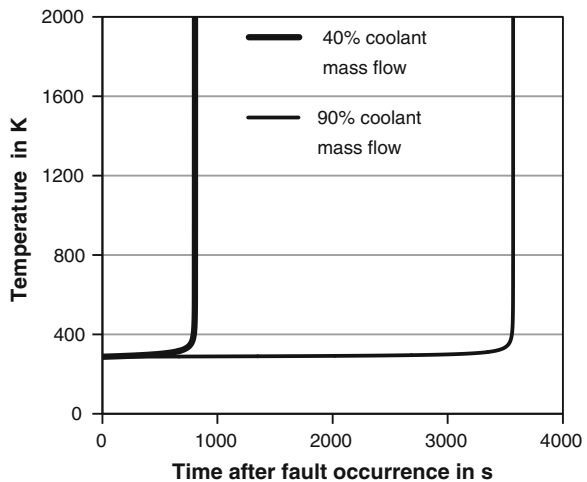
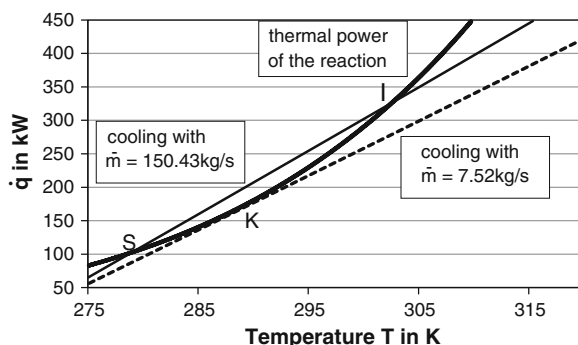


Fig. 3.5 Representation of the process in the Semenov diagram (thermal power $\dot{q}$ as a function of temperature T)



cooling, but that increase is not sufficient to make the system return to point I; runaway occurs. K marks the point of critical operation (it results from the assessment of the necessary coolant mass flow for stationary operation). Obviously this should not be the maximum possible coolant mass flow. There must still be a reserve to compensate random variations, e.g. of material composition, environmental temperature, and thus to avoid runaway. $\square$

3.2.2 Continuous Stirred Tank Reactor

In order to model a continuously operating reactor a feed and a removal term with a volumetric flow of $\dot{V} \text{ m}^3 \text{ s}^{-1}$ are added to Eq. (3.6). It is supposed that the volume of the reactor contents does not change. Differences in composition are expressed via the concentrations $c_{i,\text{in}}$ and c_i in mol m^{-3} . In line with the assumption of an ideally stirred reactor, the composition of the substances flowing out of the reactor is the same as that inside the reactor. We obtain

$$V \cdot \frac{dc_i}{dt} = \dot{V} \cdot c_{i,\text{in}} - \dot{V} \cdot c_i - V \cdot \sum_j v_{i,j} \cdot r_j \quad (3.31)$$

The heat balance is treated analogously. Equation (3.16) is extended by a term representing enthalpy feed ($\dot{V} \cdot \rho_{\text{in}} \cdot c_{p,\text{in}} \cdot T_{\text{in}}$) and one for enthalpy removal ($-\dot{V} \cdot \rho \cdot c_p \cdot T$), i.e.

$$\rho \cdot \bar{c}_p \cdot \frac{dT}{dt} = \dot{V} \cdot \rho_{\text{in}} \cdot c_{p,\text{in}} \cdot T_{\text{in}} - \dot{V} \cdot \rho \cdot c_p \cdot T + \sum_j r_j \cdot (-\Delta H_{R,j}) - U \cdot F \cdot (T - T_0) \quad (3.32)$$

Example 3.6 Determination of material concentrations for the stationary operation of a reactor

The nitration of hexamethylenetetramine (hexamine) takes place in a continuous stirred tank reactor (CSTR). The following data apply

Volume	$V = 0.63 \text{ m}^3$
Feed and removal volumetric flow	$\dot{V} = 0.79 \cdot 10^{-3} \text{ m}^3/\text{s}$
Concentration of hexamine in feed	$c_{1,0} = 985.1 \text{ mol/m}^3$
Molar mass of hexamine	$M_1 = 140.19 \text{ kg kmol}^{-1}$
Concentration of nitric acid in feed	$c_{2,0} = 20,908.7 \text{ mol/m}^3$
Molar mass of nitric acid	$M_2 = 63.01 \text{ kg kmol}^{-1}$
Pre-exponential factor	$k_0 = 1,715,745.53 \text{ s}^{-1}$
Apparent energy of activation	$E = 34,392.9 \text{ J/mol}$
Order of the reaction	$m_1 + m_2 = 10.958 \text{ (} m_1 = 9.958 \text{)}$
Thermal capacity of hexamine	$c_{p,1} = 1.256 \text{ kJ/(kg K)}$
Feed temperature of hexamine	$T_{1,0} = 293.15 \text{ K}$
Thermal capacity of nitric acid	$c_{p,2} = 1.989 \text{ kJ/(kg K)}$
Feed temperature of nitric acid	$T_{2,0} = 277.15 \text{ K}$
Overall coefficient of heat transfer	$U = 1,400 \text{ W/(m}^2 \text{ K)}$
Area for heat transfer (jacket + coil)	$F = 7 \text{ m}^2$
Enthalpy of reaction	$\Delta H_r = -247.3 \text{ kJ mol}^{-1}$
Reaction temperature	$T_R = 288.15 \text{ K}$

Reaction and heat release are described below in a simplified manner for the stationary state. Subscript “1” denotes hexamine and “2” nitric acid.

- Hexamine

$$F_1 = \dot{V} \cdot c_{1,\text{in}} - \dot{V} \cdot c_1 - V \cdot (-r) = 0$$

- Nitric acid

$$F_2 = \dot{V} \cdot c_{2,\text{in}} - \dot{V} \cdot c_2 - V \cdot (-10 \cdot r) = 0$$

- Heat balance

$$\begin{aligned} &\dot{V} \cdot (c_{1,0} \cdot c_{p,1} \cdot T_{1,0} + c_{2,0} \cdot c_{p,2} \cdot T_{2,0} - c_1 \cdot c_{p,1} \cdot T - c_2 \cdot c_{p,2} \cdot T) \\ &+ (-\Delta H_r) \cdot (-r) \cdot V - U \cdot F(T_R - T_C) = 0 \end{aligned}$$

- Reaction rate

$$-r = k_0 \cdot \exp\left(-\frac{E}{R \cdot T_R}\right) \cdot c_2^{m_2} \cdot c_1^{m_1}$$

Determine the equilibrium concentrations of hexamine and nitric acid as well as the coolant temperature T_c , which is considered to be constant on the entire heat transfer area.

Solution

The non-linear system of equations consisting of the two reaction equations F_1 and F_2 can be solved iteratively with an extension of Newton's rule (cf. [2-9]), which yields

$$\vec{F}(\vec{x} + d\vec{x}) \approx \vec{F}(\vec{x}) + \vec{J} \cdot d\vec{x} = 0$$

where we have

$$\vec{F} = \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} \quad d\vec{x} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad \text{and } \vec{J} \text{ the Jacobian } \vec{J} = \begin{pmatrix} \frac{\partial F_1}{\partial c_1} & \frac{\partial F_1}{\partial c_2} \\ \frac{\partial F_2}{\partial c_1} & \frac{\partial F_2}{\partial c_2} \end{pmatrix}.$$

The iterative evaluation leads to $c_1 = 260 \text{ mol m}^{-3}$ and $c_2 = 13,657.3 \text{ mol m}^{-3}$.

The coolant temperature results, if the heat balance is solved for T_c , i.e.

$$T_c = T_R - \frac{\dot{V} \cdot (c_{1,0} \cdot c_{p,1} \cdot M_1 \cdot T_{1,0} + c_{2,0} \cdot c_{p,2} \cdot M_2 \cdot T_{2,0} - c_1 \cdot c_{p,1} \cdot M_1 \cdot T - c_2 \cdot c_{p,2} \cdot M_2 \cdot T) + (-\Delta H_r) \cdot (-r) \cdot V}{U \cdot F}$$

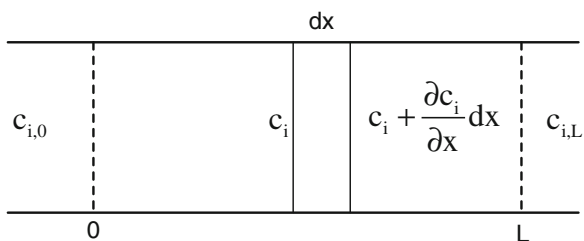
$$\begin{aligned} T_c &= 288.15 \text{ K} - \frac{247.3 \text{ kJ mol}^{-1} \cdot 1,715,745.53 \text{ s}^{-1} \cdot \exp\left(-\frac{34,392.9 \text{ J mol}^{-1}}{8,3145 \text{ J (mol K)}^{-1} \cdot 288.15 \text{ K}}\right) \cdot 0.63 \text{ m}^3}{1.4 \text{ kW (m}^2 \text{ K)}^{-1} \cdot 7 \text{ m}^2} \\ &\quad - \frac{0.79 \cdot 10^{-3} \text{ m}^3 \text{ s}^{-1} \cdot \left(985.1 \text{ mol m}^{-3} \cdot 1.256 \text{ kJ (kg K)}^{-1} \cdot 0.1409 \text{ kg mol}^{-1} \cdot 293.15 \text{ K}\right)}{1.4 \text{ kW (m}^2 \text{ K)}^{-1} \cdot 7 \text{ m}^2} \\ &\quad + \frac{20,908.7 \text{ mol m}^{-3} \cdot 1.989 \text{ kJ (kg K)}^{-1} \cdot 0.06301 \text{ kg mol}^{-1} \cdot 227.15 \text{ K}}{1.4 \text{ kW (m}^2 \text{ K)}^{-1} \cdot 7 \text{ m}^2} \\ &\quad + \frac{0.79 \cdot 10^{-3} \text{ m}^3 \text{ s}^{-1} \cdot \left(260 \text{ mol m}^{-3} \cdot 1.256 \text{ kJ (kg K)}^{-1} \cdot 0.1409 \text{ kg mol}^{-1} \cdot 288.15 \text{ K}\right)}{1.4 \text{ kW (m}^2 \text{ K)}^{-1} \cdot 7 \text{ m}^2} \\ &\quad + \frac{13,657.3 \cdot \text{mol m}^{-3} \cdot 1.989 \text{ kJ (kg K)}^{-1} \cdot 0.06301 \text{ kg mol}^{-1} \cdot 288.15 \text{ K}}{1.4 \text{ kW (m}^2 \text{ K)}^{-1} \cdot 7 \text{ m}^2} \\ &= 288.15 \text{ K} - 15.90 \text{ K} - 52.10 \text{ K} + 40.83 \text{ K} = 260.98 \text{ K} \triangleq -12.17^\circ \text{C} \end{aligned}$$

□

3.2.3 Tubular Flow Reactor

In order to calculate the concentration profile in an ideal tubular flow reactor (TFR) (vid. Fig. 3.6) with a cross sectional area of $F = \pi R^2$ the equation of conservation is established. In doing this it is assumed that there are no

Fig. 3.6 Schematic for deriving the material balance of a tubular flow reactor



concentration gradients in the radial direction and that the volume of the mixture remains unchanged, so that the velocity of flow through the reactor u in ms^{-1} is constant. We then have

$$S \cdot \frac{\partial c_i}{\partial t} dx = [c_i(x + dx, t) - c_i(x, t)] \cdot u \cdot S + S \cdot dx \cdot \sum_j v_{i,j} \cdot r_j \quad (3.33)$$

In Eq. (3.33) $c_i(x + dx, t)$ is developed in the x -direction according to Taylor and only the first two terms are retained, i.e. $c_i(x + dx, t) \approx c_i(x, t) + \frac{\partial c_i}{\partial x} dx$. We then obtain after dividing by $S \cdot dx$

$$\frac{\partial c_i}{\partial t} = \frac{\partial(c_i \cdot u)}{\partial x} + \sum_j v_{i,j} \cdot r_j \quad (3.34)$$

In the non-stationary regime the concentration changes as a function of space and time. The latter does not figure if we limit ourselves to the stationary case. We thus obtain

$$\frac{d(c_i \cdot u)}{dx} = \frac{d\dot{n}_i}{dV} = \frac{d(c_i \dot{V})}{S dx} = \sum_j v_{i,j} \cdot r_j \quad (3.35)$$

If the conversion of the key component 1 is introduced,

$$\frac{dX}{dV} = -\frac{v_1 \cdot r}{\dot{n}_{1,0}} = -\frac{v_1 \cdot r}{\dot{V}_0 \cdot c_{1,0}} \quad (3.36)$$

holds. Integration of Eq. (3.36) leads to

$$V = -\dot{n}_{1,0} \cdot \int_0^{X_L} \frac{dX}{v_1 \cdot r} \quad (3.37)$$

where L is the length of the reactor. The hydrodynamic residence time is

$$\tau = \frac{V}{\dot{V}_0} = -c_{1,0} \cdot \int_0^{X_L} \frac{dX}{v_1 \cdot r} \quad (3.38)$$

Assuming that there is but one stoichiometrically independent reaction and that the flow velocity u is constant (no change of the volume of the mixture or the reactor cross section) we obtain

$$u \cdot \frac{\partial c_i}{\partial X} + v_i \cdot r_i = 0 \quad (3.39)$$

The heat balance of the tubular flow reactor is

$$-m \cdot \bar{c}_p \cdot \frac{\partial T}{\partial V} + \sum_j r_j \cdot (-\Delta H_{R,j}) + \frac{d\dot{q}}{dV} = \left(\frac{dC_W}{dV} + \rho \cdot \bar{c}_p \right) \frac{\partial T}{\partial t} \quad (3.40)$$

If there is only one stoichiometrically independent reaction and the operation is stationary, we have instead of Eq. (3.40)

$$-m \cdot \bar{c}_p \cdot \frac{dT}{dV} + r \cdot (-\Delta H_R) + \frac{d\dot{q}}{dV} = 0 \quad (3.41)$$

Example 3.7 Determination of the volume of an ideal tubular flow reactor

The reaction of Example 3.3 is to take place in a TFR under adiabatic conditions. The volumetric flow amounts to $\dot{V}_0 = 1 \text{ m}^3 \text{ h}^{-1}$. What is the necessary volume of the reactor? It is assumed that the adiabatic temperature rise is constant in the entire reactor and amounts to $\Delta T_{ad} = 27.13 \text{ K}$.

Solution

Inserting Eq. (3.17) in Eq. (3.38) we have

$$\tau = \frac{V}{\dot{V}_0} = \int_0^{X_L} \frac{\exp\left(\frac{E}{R_m \cdot (T_R + \Delta T_{ad} \cdot X)}\right)}{k_0 \cdot (1 - X) \cdot (c_{2,0} - c_{1,0} \cdot X)} \cdot dX$$

Comparison with Eq. (3.20) shows that the conversion in both reactor types is the same if the reaction time t_R is equal to the mean hydraulic residence time; t_R was calculated in Example 3.3 as 15.96 h. Hence, we have

$$\frac{V}{\dot{V}_0} = 15.96 \text{ h}$$

and thus

$$V = 15.96 \text{ m}^3$$

□

3.3 Autocatalytic Reactions

With an autocatalytic reaction the product acts as a catalyst for the reaction, which is thus accelerated. This can be true, for example, for decomposition processes (vid. Sect. 2.2). Autocatalytic reactions may exhibit oscillating behaviour.

A number of formal kinetic models exist to describe autocatalytic reactions (cf. [1]). In what follows only the simplest model, the Prout-Tompkins model, is described following [1]. It is based on the reaction equation



The reaction of Eq. (3.42) is modelled by the following kinetic equation

$$\frac{dc_1}{dt} = -r = -k \cdot c_1 \cdot c_2 \quad (3.43)$$

In Eq. (3.43) the subscript “1” denotes material A and “2” material B.

Example 3.8 Autocatalytic Reaction

On the basis of the data from [1]:

Apparent activation energy	$E = 97,211 \text{ J mol}^{-1}$
Total energy release	$Q = 456,000 \text{ J}$
Concentration times the pre-exponential factor	$c_{1,0} \cdot k = 1.3238 \cdot 10^{-4} \text{ s}^{-1}$
Reaction temperature	$T_r = 363.15 \text{ K}$
Concentration	$c_{1,0} = 5.7380 \cdot 10^{-3} \text{ mol cm}^{-3}$
Total thermal capacity	$C_p = 1,200 \text{ J K}^{-1}$

the following topics are to be addressed:

1. Reformulation of Eq. (3.43) using the conversion according to Eq. (3.7)
2. Determination of the variation with time of the conversion, if the conversion at $t = 0$ amounts to 10^{-6} , and of the time-dependent generation of the thermal power
3. Time until the maximum rate of conversion
4. Time behaviour of the corresponding adiabatic process.

Solution

(1)

$$X = \frac{c_{1,0} - c_1}{c_{1,0}}$$

and hence

$$c_1 = c_{1,0} \cdot (1 - X) \quad \text{and}$$

$$c_2 = c_{2,0} - (c_{1,0} - (1 - X) \cdot c_{1,0}) + 2 \cdot (c_{1,0} - (1 - X) \cdot c_{1,0}) = c_{2,0} + c_{1,0} \cdot X$$

as well as

$$\frac{dX}{dt} = \frac{dc_1}{dt} \cdot \frac{-1}{c_{1,0}} \quad \text{and} \quad \text{hence} \quad \frac{dc_1}{dt} = -c_{1,0} \cdot \frac{dX}{dt}$$

If we set $c_{2,0} = 0$ (substance B is only generated by the reaction; however, a minimum concentration must be available at the beginning of the reaction, which is neglected for mathematical simplicity), we have

$$\frac{dX}{dt} = k \cdot (1 - X) \cdot c_{1,0} \cdot X \quad (3.44)$$

Equation (3.44) is a non-linear differential equation. Its solution for the isothermal case ($T_r = \text{const.}$) is achieved by setting

$$X = \gamma \cdot \frac{u'}{u} \quad (3.45)$$

which converts Eq. (3.44) into

$$\gamma \cdot \frac{u'' \cdot u - u'^2}{u^2} = k \cdot c_{1,0} \cdot \left(\gamma \cdot \frac{u'}{u} - \gamma^2 \cdot \frac{u'^2}{u^2} \right) \quad (3.46)$$

By comparing both sides of the equation it is evident that the quadratic terms cancel if

$$\gamma = \frac{1}{c_{1,0} \cdot k} \quad (3.47)$$

holds. Hence, there remains

$$\frac{u''}{u'} = k \cdot c_{1,0} \quad (3.48)$$

with the solution

$$u' = A \cdot \exp(c_{1,0} \cdot k \cdot t) \quad \text{and} \quad u = \frac{A}{c_{1,0} \cdot k} \cdot \exp(c_{1,0} \cdot k \cdot t) + B \quad (3.49)$$

The constants of solution in Eq. (3.49), A and B, are determined from the boundary conditions. Inserting Eqs. (3.47) and (3.49) in Eq. (3.45) we obtain

$$X = \frac{1}{1 + \frac{B}{A} \cdot c_{1,0} \cdot k \cdot \exp(-c_{1,0} \cdot k \cdot t)} \quad (3.50)$$

(2)

From Eq. (3.50) and the data of the problem statement we obtain the ratio B/A

$$\frac{B}{A} = \frac{10^6 - 1}{1.3238 \cdot 10^{-4} \text{ s}^{-1}} = 7.5540 \cdot 10^9 \text{ s}$$

and hence

$$X = \frac{1}{1 + 7.5540 \cdot 10^9 \text{ s} \cdot 1.3238 \cdot 10^{-4} \text{ s}^{-1} \cdot \exp(-1.3238 \cdot 10^{-4} \text{ s}^{-1} \cdot t)} \quad (3.51)$$

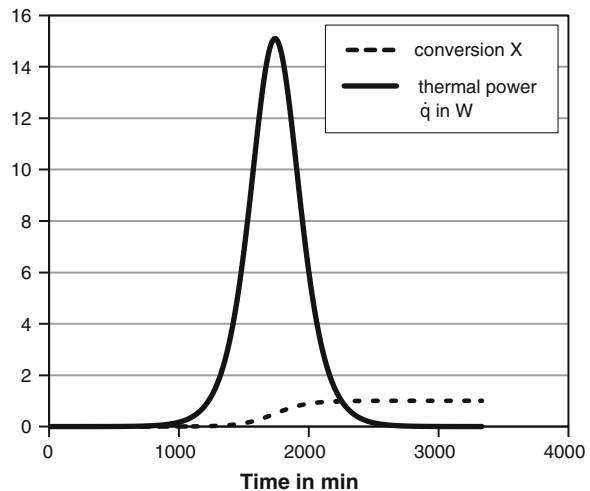
The thermal power is

$$\dot{q} = \frac{dX}{dt} \cdot Q \quad (3.52)$$

In Eq. (3.52) Eqs. (3.44) and (3.45) were used.

The variations with time of the preceding quantities are shown in Fig. 3.7.

Fig. 3.7 Variation with time of conversion and thermal power for an isothermal autocatalytic reaction



(3)

Equation (3.44) is the basis. The maximum rate of conversion is obtained as follows

$$\frac{dX}{dt} = \dot{X} = k \cdot (1 - X) \cdot c_{1,0} \cdot X \quad (3.53)$$

From Eq. (3.53) we have the necessary condition for the maximum with respect to t

$$\begin{aligned} \frac{d}{dt} \dot{X} &= \frac{d\dot{X}}{dX} \cdot \frac{dX}{dt} = (k \cdot (-1) \cdot c_{1,0} \cdot X + k \cdot (1 - X) \cdot c_{1,0}) \cdot (k \cdot (1 - X) \cdot c_{1,0} \cdot X) \\ &= 0 \end{aligned} \quad (3.54)$$

This leads to

$$X = \frac{1}{2}$$

Inserting this value in Eq. (3.51) we obtain

$$\begin{aligned} t^* &= \frac{1}{-1.3238 \cdot 10^{-4} \text{ s}^{-1}} \cdot \ln \frac{1}{7.5540 \cdot 10^9 \text{ s} \cdot 1.3238 \cdot 10^{-4} \text{ s}^{-1}} \\ &= 104,362.5 \text{ s} \hat{=} 1,739.4 \text{ min} \end{aligned}$$

This can be seen as well from Fig. 3.7. It is the isothermal induction time, which implies that the heat generated is removed.

(4)

In order to address this topic the non-linear system of equations consisting of Eq. (3.44) and the following extension of Eq. (3.52) has to be solved numerically, e.g. using the Runge-Kutta method.

$$C_p \cdot \frac{dT}{dt} = \frac{dX}{dt} \cdot Q \quad (3.55)$$

The results obtained with the data of the problem statement are shown in Figs. 3.8 through 3.10.

From Figs. 3.8, 3.9, and 3.10 it is evident that autocatalytic reactions are capable of strong temperature rises. The thermal induction time is all the shorter the higher the reaction temperature before cooling failure. These statements hold as well for autocatalytic reactions of other orders than the one of second order treated here.

Fig. 3.8 Variation with time of the temperature after cooling failure with a reaction temperature of $T_R = 343.15\text{ K}$

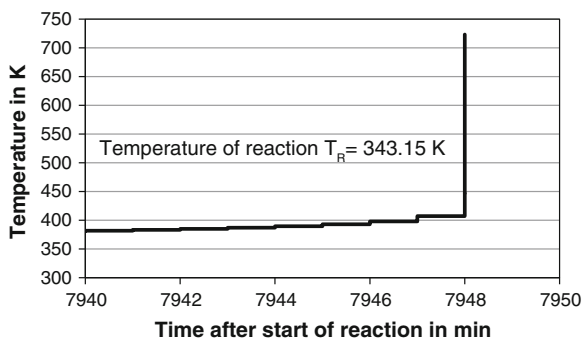


Fig. 3.9 Variation with time of the temperature after cooling failure with a reaction temperature of $T_R = 363.15\text{ K}$

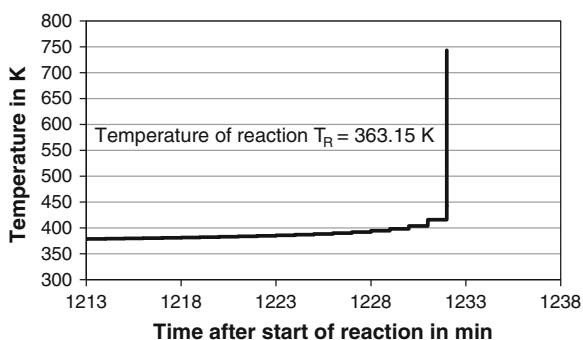
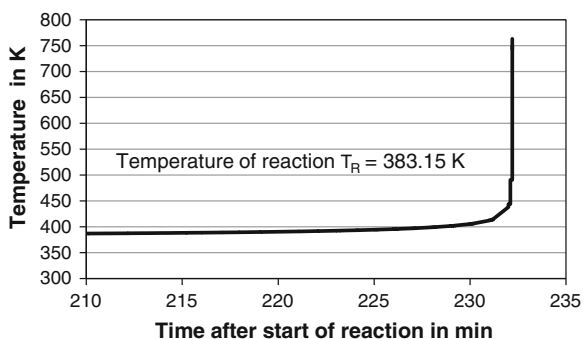


Fig. 3.10 Variation with time of the temperature after cooling failure with a reaction temperature of $T_R = 383.15\text{ K}$



□

3.4 Polymerization

On the basis of the detailed treatment in [2] some peculiarities of polymerization reactions are briefly described here (vid. Sect. 2.2). Frequently such reactions are characterized by high values of the specific heats of reaction (appr. 500–3,500 kJ/kg).

This leads to high adiabatic temperature rises, which lie in the range of 250–1,800 K. Furthermore, instantaneous increases of the reaction rate and hence the thermal power are possible. This is known as the gel or Tromsdorf effect.

So far it was assumed that the material properties do not change during the reaction process. This is frequently almost true, but not in the case of polymerizations. Most of all viscosity is expected to increase. This influences process safety in the following way

- heat removal changes due to changes of the heat transfer coefficient;
- increase of the thermal power introduced into the reactor by the stirrer.

Both aspects have to be accounted for in cases of planned as well as undesired polymerizations.

3.5 Extreme Process Conditions

Chemical processes can require extremely high or low pressures or temperatures or both in order to work efficiently. These are accompanied by specific, mostly physical hazards.

3.5.1 High Pressures

According to [10] the following pressure ranges are distinguished

- pressures up to 250 bar;
- pressures of several 1,000 bar;
- pressures above 8,000 bar.

Most process plants work in the range of up to 250 bar. Higher pressures are accompanied by higher energies. The characteristic quantity is the product of the maximum permissible pressure (PS) in bar and the volume exposed to it (V) in l, the energy

$$E = PS \cdot V \quad (3.56)$$

Specific requirements concerning design manufacture and conformity assessment for vessels, piping, equipment with safety functions (safety accessories) and equipment under pressure (pressure accessories) have to be fulfilled if the maximum permissible pressure (PS) is above 0.5 bar [11, 12]. The requirements are graded depending on the category to which equipment has to be assigned, as shown in Table 3.2. One of the measures from the corresponding category has to be chosen; details are provided in [11].

The amount of stored energy affects the consequences of equipment failure (vid. Sect. 10.9.2.1)

Table 3.2 Categories and consequences from the pressure equipment directive [11]

Category	PS·V in bar l	Obligations
I	$25 \leq \text{PS} \cdot V < 50$	Internal production control
II	$50 \leq \text{PS} \cdot V < 200$	Internal manufacturing checks with monitoring of the final assessment
		Production quality assurance
		Product quality assurance
III	$200 \leq \text{PS} \cdot V < 1,000$	EC design examination + production quality assurance
		EC design examination + product verification
		EC type-examination + product quality assurance
		EC type-examination + conformity to type
		Full quality assurance
IV	$1,000 \leq \text{PS} \cdot V$	EC type-examination + production quality assurance
		EC design examination + product verification
		EC unit verification
		Full quality assurance with design examination and special surveillance of the final assessment

Example 3.9 Category assignment for a buffer tank according to the pressure equipment directive

A buffer tank for compressed air has a volume of 0.9 m³; the maximum permissible pressure is 2.5 MPa. To which category is it to be assigned?

Solution

According to Eq. (3.56) we have

$$E = 25 \text{ bar} \cdot 900 \text{ l} = 22,500 \text{ bar} \cdot \text{l} \stackrel{\Delta}{=} 2,250 \text{ kJ}$$

Hence, the tank is inscribed in category IV of Table 3.2. □

3.5.2 Low Pressures

There are numerous processes, respectively process steps which operate at pressures below atmospheric or where processes like unwanted condensation may produce underpressure. In general underpressure is a smaller problem than overpressure. Yet, there is the possibility of ingress of air and consequent reactions with the contents of the equipment. For example, ingress of air into a distillation column may cause an explosion [13]. Furthermore one must observe that the stability of vessels and such like is reduced by underpressure because manufacturing flaws (slight distortions) may be enhanced. With overpressure, on the other hand, they are compensated (“the vessel is blown up”).

3.5.3 High Temperatures

High temperatures together with high pressures increase the energy content of the equipment. High temperatures generally reduce the strength of materials and enhance the propensity to corrosion. Furthermore, hot equipment may constitute an unwanted source of ignition. Cyclic loads during start-up and shut-down induce thermal stress (all the more the higher the operating temperatures) and thus shorten the lifetime of structural materials.

3.5.4 Low Temperatures

Numerous processes in the process industry take place at low temperatures, for example in the food industry. An important area is the refrigerated storage of gases which are liquefied at low temperatures and hence occupy a smaller volume than in gaseous state. With process temperatures $< 77\text{ K}$ and insulation damage air is decomposed into reactive oxygen and cold nitrogen, which moves at ground level and impedes breathing thus leading to death.

Example 3.10 Cooling failure in a refrigerated storage

The cooling equipment of a cylindrical vessel for the refrigerated storage of liquefied nitrogen fails. It is assumed that the relief equipment (breather valve protecting against under and overpressure following temperature variations) fails at the same time. The failure pressure of the vessel amounts to 1.2 bar (0.12 MPa). The following questions are to be answered.

What are the masses of liquid and gas as well as the gas content before and after the pressure rise?

How much thermal energy is introduced into the vessel until its failure pressure is reached?

How much time elapses before the failure pressure is reached?

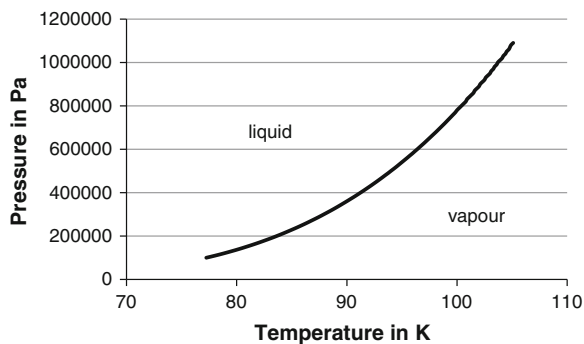
Data:

Volume	$V = 53.29\text{ m}^3$
Radius	$R = 1.42\text{ m}$
Storage pressure	$p_1 = 1\text{ bar}$
Degree of filling	$\varphi = 0.9$
Average heat supply from the environment	$\dot{Q} = 0.74\text{ kW}$.

Thermodynamic quantities

Initial state “1”

Density of the liquid phase	$\rho_{\text{fl},1} = 808.41\text{ kg m}^{-3}$
Density of the vapour phase	$\rho_{\text{g},1} = 4.37\text{ kg m}^{-3}$
Enthalpy of the liquid phase	$h_{\text{fl},1} = -122.25\text{ kJ kg}^{-1}$
Enthalpy of the gas phase	$h_{\text{g},1} = 77.07\text{ kJ kg}^{-1}$.

Fig. 3.11 Vapour pressure curve for nitrogen

Final state “2”

Density of the liquid phase $\rho_{fl,2} = 801.07 \text{ kg m}^{-3}$

Density of the gas phase $\rho_{g,2} = 5.14 \text{ kg m}^{-3}$

Enthalpy of the liquid phase $h_{fl,2} = -119.01 \text{ kJ kg}^{-1}$

Enthalpy of the gas phase $h_{g,2} = 78.25 \text{ kJ kg}^{-1}$.

Solution

According to the vapour pressure curve for nitrogen (vid. Fig. 3.11) the temperature of $T_1 = 77.24 \text{ K}$ corresponds to the storage pressure of 1 bar (100,000 Pa). Owing to heat transfer from the environment the temperature inside the vessel increases and the pressure rises according to the vapour pressure curve.

Vessel contents “liquid”

$$m_{fl} = V \cdot \varphi \cdot \rho_{fl} = 53.29 \text{ m}^3 \cdot 0.9 \cdot 808.41 \text{ kg m}^{-3} = 38,772.15 \text{ kg}$$

Vessel contents “vapour”

$$m_g = V \cdot (1 - \varphi) \cdot \rho_g = 53.29 \text{ m}^3 \cdot (1 - 0.9) \cdot 4.37 \text{ kg m}^{-3} = 23.29 \text{ kg}$$

Vapour quality

$$x_1 = \frac{m_g}{m_g + m_{fl}} = \frac{23.29 \text{ kg}}{23.29 \text{ kg} + 38,772.15 \text{ kg}} = 6.00 \cdot 10^{-4}$$

Total mass

$$m = m_g + m_{fl} = 23.29 \text{ kg} + 38,772.15 \text{ kg} = 38,795.44 \text{ kg}$$

From this follows that $m_g = x_1 \cdot m$ and $m_{fl} = (1 - x_1) \cdot m$.

The change of state is isochoric since the volume does not change. The average specific volume of the vessel contents is $v = V/m = 53.29 \text{ m}^3/38,795.44 \text{ kg} = 1.3736 \text{ m}^3/\text{kg}$. It applies for any state on the vapour pressure curve, i.e.

$$v = x \cdot v_g + (1 - x) \cdot v_{fl}$$

In order to relate state “2” with state “1” we have

$$x_2 = \frac{v - v_{fl,2}}{v_{g,2} - v_{fl,2}} = \frac{\frac{V}{m} - \frac{1}{\rho_{fl,2}}}{\frac{1}{\rho_{g,2}} - \frac{1}{\rho_{fl,2}}} = \frac{\frac{53.29 \text{ m}^3}{38,795.44 \text{ kg}} - \frac{1}{801.07 \text{ kg m}^{-3}}}{\frac{1}{5.14 \text{ kg m}^{-3}} - \frac{1}{801.07 \text{ kg m}^{-3}}} = 6.48 \cdot 10^{-4} \quad (3.57)$$

Hence we obtain

$$m_{fl,2} = (1 - x_2) \cdot m = 0.999352 \cdot 38,795.44 \text{ kg} = 38,770.30 \text{ kg of liquid nitrogen and}$$

$$m_{g,2} = x_2 \cdot m = 6.48 \cdot 10^{-4} \cdot 38,795.44 \text{ kg} = 25.14 \text{ kg of gaseous nitrogen}$$

According to the vapour pressure curve the temperature has risen to 78.82 K. The first law of thermodynamics applies to the vaporization process

$$Q_{1,2} + W_{1,2} = u_2 - u_1 = h_2 - h_1 - (p_2 V_2 - p_1 V_1)$$

Since there is no change in volume, we have $W_{1,2} = 0$ and $V_1 = V_2 = V$. Hence, we obtain

$$Q_{1,2} = m \cdot (h_2 - h_1) - (p_2 - p_1) \cdot V = m \cdot [(1 - x_2) \cdot h_{fl,2} + x_2 \cdot h_{g,2} - (1 - x_1) \cdot h_{fl,1} - x_1 \cdot h_{g,1}] - (p_2 - p_1) \cdot V$$

Insertion of the numerical values of the problem statement yields

$$\begin{aligned} Q_{1,2} &= 38,795.44 \text{ kg} \cdot [(1 - 6.48 \cdot 10^{-4}) \cdot (-119.01 \text{ kJ kg}^{-1}) + 6.48 \cdot 10^{-4} \cdot 78.25 \text{ kJ kg}^{-1} \\ &\quad - (1 - 6.00 \cdot 10^{-4}) \cdot (-122.25 \text{ kJ kg}^{-1}) - 6.00 \cdot 10^{-4} \cdot 77.07 \text{ kJ kg}^{-1}] \\ &\quad - (120,000 \text{ Pa} - 100,000 \text{ Pa}) \cdot 53.29 \text{ m}^3 = 126,016.61 \text{ kJ} - 1,065.8 \text{ kJ} = 124,950.81 \text{ kJ} \end{aligned}$$

In order to reach the final stated “2”(failure) the rate of heat introduced into the vessel has to equal the change of internal energy $Q_{1,2}$. This enables one to calculate the time required until failure

$$t_E = \frac{Q_{1,2}}{\dot{Q}} = \frac{124,950.81 \text{ kJ}}{0.74 \text{ kW}} = 168,852.45 \text{ s} \hat{=} 46.9 \text{ h}$$

This time would be sufficient to repair the relief equipment or to carry out emergency measures such as emptying the vessel in a controlled way.

As may be inferred from Fig. 3.12 the result depends essentially on the quality of the vessel insulation.

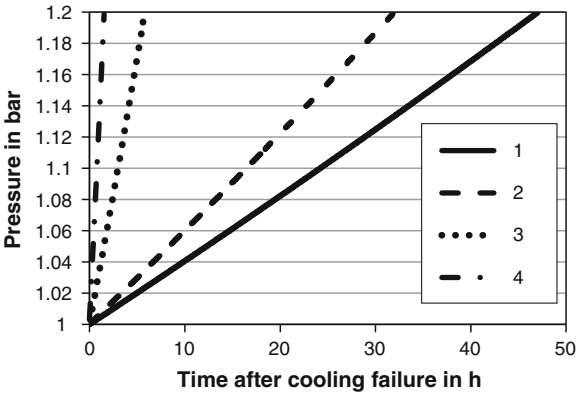


Fig. 3.12 Pressure increase as a function of time after cooling failure (overall heat transfer coefficients: $5.08 \times 10^{-2} \text{ W(m}^2 \text{ K)}^{-1}$ for liquid; $8.40 \times 10^{-3} \text{ W(m}^2 \text{ K)}^{-1}$ for gas: (1) $\varphi = 0.9$, (2) $\varphi = 0.2$) (Overall heat transfer coefficients: $0.38 \text{ W(m}^2 \text{ K)}^{-1}$ for liquid; $0.39 \text{ W(m}^2 \text{ K)}^{-1}$ for gas: (3) $\varphi = 0.9$, (4) $\varphi = 0.2$)

Table 3.3 Final states where there is only liquid in the vessel depending on the degree of filling φ

Degree of filling φ (%)	Final temperature (K)	Final pressure (bar)
95	85.6	2.42
90	93.3	4.71
85	100.2	7.88
80	106.3	11.78
75	111.7	16.15
70	116.2	20.64
65	119.8	24.89
60	122.5	28.51
55	124.5	31.25
50	125.6	32.96

The failure pressure is reached after 47 h ($\varphi = 0.9$), respectively 32 h ($\varphi = 0.2$). With a higher heat transfer rate the corresponding values are 5.7 h ($\varphi = 0.2$) and 1.56 h ($\varphi = 0.2$). It is obvious that the degree of filling at the moment of failure, which is a random quantity, has to be accounted for in safety considerations.

Furthermore, Eq. (3.57) shows that there is a specific volume due to thermal expansion of the (practically incompressible) liquid which leaves no space for the gaseous phase. This must be accounted for when fixing the maximum permissible degree of filling. Table 3.3 shows some values. □

3.6 Endothermic Processes

In general one supposes that the hazard potential of endothermic processes is small compared with that of exothermic ones. However, it must be checked whether one is dealing with a process capable of generating gas. If there is not sufficient relief of the gas a hazardous pressure build-up may result [14].

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What you don't have can't leak.

Trevor Kletz

From the preceding chapters it became clear that hazards can be associated with the handling and conversion of materials in process plants. This is true as well for the erection and the demolition after the end of the industrial activity, hence for the entire life cycle. In what follows, however, the focus is on the design and operation of process plants.

A hazard or a hazard potential is the possibility of suffering harm. The term danger implies that the hazard or hazard potential becomes more concrete and harm has to be expected. Risk is understood to be the combination of the probability (better: expected frequency, vid. Chap. 8) of a damage to occur and of its extent. We speak of safety if a risk has a tolerable level [1].

The supreme principle of plant and process safety is to devise processes and plants such that they do not cause considerable dangers for man, environment and valuable assets [2]. This is to be achieved by a design based on the state of technology, respectively of safety technology, which is represented by numerous statutory regulations, standards, rules and guidelines (cf. [3]). These refer to both the components of technical plants and to the plants themselves [4, 5].

The safe design of components is one of the prerequisites for a safe plant. It is the task of experts of the area in question. For example, explosion proof motors are designed and built by electrical engineers. The great variety of technical components and their safe design, which is component-specific, are not discussed here. The concern rather is the safe design of plants and processes. This refers to the following areas [6]:

- process design,
- plant design,
- operation,
- procedures (safety management).

Safety has to be considered in parallel and interacting with the planning, design, erection and operation of a plant. The procedure is presented below based on [6].

4.1 Procedure for Ensuring Safety in Planning, Building and Operating Plants

4.1.1 Process Design

In the first place the safety technological bases have to be determined. This implies the

- determination and compilation of the safety parameters for materials (vid. Chap. 2) and unit operations,
- selection of appropriate structural materials for apparatuses, pipework, vessels etc.,
- determination of the type and extent of the hazard potential,
- examination of the possibilities for avoiding or reducing hazard potentials (vid. Sect. 4.2),
- determination of the safety technological boundary conditions of the process including the supplies and waste disposal,
- development of the process flow sheet and determination of the basic safety requirements.

Furthermore, the possibilities of reactions have to be clarified by systematic experimental analyses. The ranges of the process parameters (temperature, pressure, material concentrations etc.) have to be identified, within which no undesired reactions can take place. On this basis the permissible ranges for plant operation are fixed and the consequences of leaving them are pointed out.

4.1.2 Planning, Construction and Commissioning of Plants

4.1.2.1 Plant Design

In planning a plant one of the objectives is to design the plant in such a way that

- the occurrence of faults is reduced by using appropriate and reliable technology and by providing for adequate organizational measures (avoidance of faults),
- the plant is fault tolerant, should faults or disturbances occur, which implies, for example, that a single failure alone may not cause impermissible effects (single failure criterion).

In order to achieve this

- the relevant sources of hazards of the envisaged process are identified by comparing the safety characteristics, quantities of materials, process regimes

and process parameters with the characteristics of the proposed equipment and its design parameters and

- the type of and demands on the technological and organizational safety measures for the plant are concretized by systematic safety assessments in line with the respective planning progress.

The aforementioned procedure is carried out iteratively using the safety analysis methods described in Chap. 9. As a result all safety relevant information should be available as required for the licensing procedure and the start of the detailed planning.

4.1.2.2 Safety Examinations in the Context of Procurement and Construction

In the context of procuring components, equipment etc. and constructing the plant the following safety tasks are carried out:

- definitive fixing of the type of demands on the technical safety measures by systematically examining the safety measures on the basis of the final detailed planning documentation,
- formulation of operating instructions, in particular organizational protective measures,
- design of the safety devices,
- documentation of the safety examination representing a holistic safety concept, e.g. in the safety report according to the Major Accident Ordinance.

As a result all safety relevant information and documentation as required for the procurement and construction phase is available.

4.1.2.3 Safety Examination Before and During Plant Commissioning

According to the pertinent regulations the following examinations accompanied by their documentation have to be carried out:

- preliminary examination by independent experts,
- quality examination in the factories of manufacturers of apparatuses and equipment and on the site of the plant,
- supervision of assembly,
- functional test,
- verification for operation by independent experts,
- plant walk-around,
- verification by state authorities,
- check of the operating manual as to completeness and conformity with the safety documentation.

The result is the confirmation that the planned safety devices exist and that their operability is guaranteed. Hence, the approval for commissioning of the plant can be given.

4.1.2.4 Documentation

The results of the safety examination have to be documented. The objective is that the safety concept is available at any time, in particular documents on the following topics:

- safety-relevant material data and their assessment,
- results of the systematic safety examinations and calculations,
- safety-relevant in-plant regulations and operating instructions.

4.1.3 Operation

A prerequisite for safe plant operation is its handling by qualified and reliable operators. The “intrinsic” safety of the plant must be maintained during operation and be improved in the light of new knowledge (“retrofit”). In order to ensure the availability of the technical installations functional tests before the start of the operation are necessary as well as recurrent functional tests, tests motivated by specific causes as well as maintenance and repair. The necessary organizational procedures are ensured by training of the operating and maintenance personnel supported by operating instructions, logbooks, work permits and fixed procedures in case of modifications.

Chemical products are manufactured in continuous or batch processes. A plant may produce a single product or several products one after the other (multi-purpose plant). The corresponding recipes and procedures are described in detail in the operating instructions. This serves to ensure safe processes and the safety of the personnel.

4.1.4 Safety Management

It makes sense to carry out the safety tasks according to an established procedural framework, which together with the corresponding management organization (hierarchy with clear responsibilities) constitutes a safety management system (cf. [7]). The demonstration that such a safety management system has been implemented is required by the Major Accident Ordinance [8].

The central issue of the safety management system is the binding definition of the safety procedures in the company. Among them figure the definition of competences and responsibilities as well as a framework for solving safety problems. Furthermore, the documentation of procedures and results is of importance. Last but not least it must be ensured that the experience gained is used to improve the safety management.

It has proved an advantage that the safety management system encompasses the aspects of process and plant safety, occupational safety and protection of the environment; this is the holistic approach (cf. [7]).

Since plants and processes undergo modifications during their lifetime, a procedure for dealing with modifications has to be established. The modifications and the accompanying safety analyses have to be documented (“management of change”).

Safety activities should be carried out observing the so-called Deming cycle “Plan, Do, Check, Act”.

4.1.5 Quality Assurance

A safe and highly available process plant implies a design of its components and equipment which meets the demands from the process (cf. [4, 5]).

This requires a quality assurance concept which comprises all phases of the life cycle of the plant.

The choice of appropriate structural materials, pre-tests of the materials, and suitable manufacturing methods are of special importance given the multitude of different substances in process plants. The safe containment of the substances must be ensured.

For this purpose a number of tests are carried out:

- Quality assurance during planning, i.e. check of the aptitude of the design of equipment and machinery for the envisaged use.
- Manufacturing surveillance, i.e. individual examination if the design and manufacture of vessels comply with the state of the technology.
- Surveillance of the manufacturing process, i.e. pressure tests to make sure that components exposed to pressure are leak tight under the testing pressure and do not show safety-relevant deformations.
- Final approval tests before commissioning.

In order to ensure compliance with the procedure a comprehensive surveillance is used. It comprises the

- continuous surveillance of the plant and the components by the operator,
- periodic surveillance and tests of the plant and its components at the beginning of operation and in specified time intervals by independent experts,
- surveillance by the state administration first during the licensing procedure and later during operation by unannounced in situ inspections.

4.1.6 Alarm and Hazard Defence Plans, Information of the Public

Alarm and hazard defence plans constitute a precaution which goes beyond the measures just described. They are to limit the damage after the occurrence of an accident. In the context of such plans the activities of the plant personnel in case of

an accident are coordinated with the deployment of the works fire brigade, the public fire brigades, rescue services and other supporting personnel.

Rapid and correct information of the public, if necessary accompanied by warnings, is to ensure the safety of the plant's neighbourhood. It is of use to plan the necessary information paths, to agree on them with the public safety forces and to integrate them into the works alarm and hazard defence plan.

4.2 Principles of Plant Safety and Fundamental Concepts

Starting point for the safe design and operation of a process plant is a safety concept. This is understood to comprise all the organizational and technical measures in a plant and its operation aimed at

- controlling unavoidable hazard potential,
- avoiding malfunctions and
- limiting the consequences of malfunctions.

The underlying objective is, as has been stated above, to design processes and plants in such a way that there is no relevant danger for man, environment and valuable property. This is the protection objective for plant design and operation [2].

In order to achieve this, a strategy to minimize risk is developed, which comprises measures for reducing the frequency of accidents, the associated damage or both.

In this context the safe containment of the materials present in the plant is of special importance, since its loss is, as a rule, the starting point for accident consequences, the source term. Additionally, fires and explosions inside the containment (pipework, vessels, casings etc.) have to be avoided, because its destruction implies a release.

Possible measures may be categorized as follows (cf. [9]); they are ordered in decreasing reliability

- inherent: the hazard potential is eliminated by using materials and process conditions which are not dangerous;
- passive: safety devices are used which work without outside supply of energy and information (e.g. from measuring instruments);
- active: systems are used which intervene in the process following signals received, e.g. an emergency trip system;
- organizational: human interventions; to render them possible signals, e.g. alarms, are required and actions have to be carried out which in part require the use of technical devices.

The above categories are treated below in more detail. In the course of time a barrier concept has been developed. It comprises several levels, as shown in Table 4.1.

This concept is reflected by the corresponding technical devices. It accounts for the fact that technical systems are never totally reliable but fail with a certain probability.

The technical measures at the different levels are staggered so that the measures of a following level must become effective only if those of the preceding level have failed.

The safety concept must remain the basis for all actions during the entire lifetime of the plant. Modifications require a re-assessment.

Figure 4.1 underlines the concept referring to technical devices needed to implement the different levels. Measures of alarm and hazard defence (vid. Sect. 4.1.6) are inscribed in “mitigation”. The terms used in Fig. 4.1 are now explained following [10].

The operational (basic) control system acts during the specified operation of the plant within the range of instrumentation setpoints. Measuring, controlling (open and closed loop) of all relevant process parameters including recording belong to this category. A good quality of the operational equipment is important for safety, since its failure causes demands on devices of the posterior levels, which should be avoided (assigned to level 1 of Table 4.1).

The monitoring system acts during specified operation of the plant beyond the range of operational setpoints but below the tolerable fault limit. It signals permissible faulty states of the plant. There are no safety arguments for not continuing plant operation; however, increased attention is necessary (assigned to level 2 of Table 4.1).

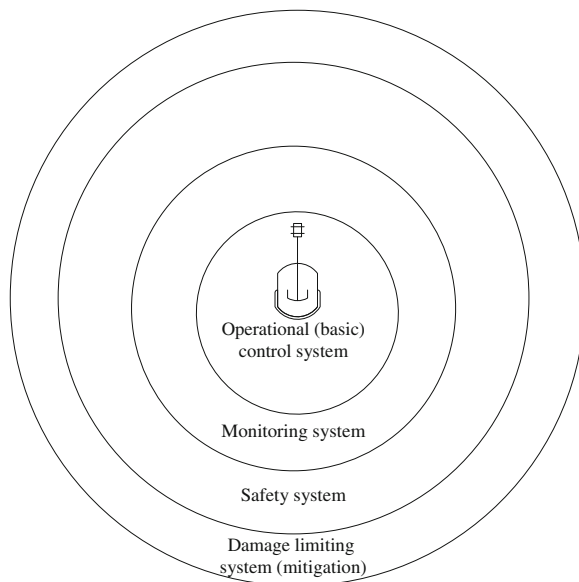
The safety system has the mission to prevent impermissible faulty states of the plant in contrast to the operational and monitoring systems. The safety system has to act before the permissible faulty range is left. In this way it may be discarded with high probability that the process parameters reach the impermissible range before the countermeasure becomes effective (assigned to level 3 in Table 4.1, vid. Example 4.1).

The criterion for assigning equipment to the safety system is that if it did not exist, harm to man, environment or property would have to be expected. It implies as well a “serious hazard” in the sense of the Major Accident Ordinance [8].

Table 4.1 Multi-level safety concept

Level 1	Normal operation with control of parameter setpoints
Level 2	Control of malfunctions with alarms and deactivations of equipment
Level 3	Avoidance of damage by emergency interventions and emergency trips to avoid leaving the region of specified operation
Level 4	Hazard defence using mitigation measures in case of releases of hazardous materials

Fig. 4.1 Concept of safety barriers (layers of protection) of a modern process plant



In the sense of the Major Accident Ordinance the safety system is an accident preventing measure and as such is safety relevant. In order to avoid as far as possible that the safety system is activated, its activation is in many cases preceded by that of a monitoring system.

The *damage limiting system (mitigation)* does not avoid the occurrence of the undesired event (e.g. release of a hazardous material), but serves to limit its impact (e.g. triggering a water curtain to absorb the released gas). In the sense of the Major Accident Ordinance the damage limiting system is safety relevant (assignment to level 4 in Table 4.1).

The variation with time of process parameters e.g. of temperature, pressure, level or several of them together, which can lead to a danger, is illustrated qualitatively in Fig. 4.2.

In line with the multi-level safety concept of Table 4.1 process control equipment (vid. Chap. 6 and [11]) is categorized according to its mission

- operational process control equipment,
- monitoring process control equipment,
- safety process control equipment,
- damage limiting (mitigation) control equipment.

The specific reliability demands on process control equipment are dealt with in Chap. 11. Initially the protection objective for plant design and operation was already mentioned: avoiding major hazards for man, environment and valuable property. In order to achieve this so-called protective tasks have to be carried out. Several of these tasks are needed to reach the objective. In general, alternatives

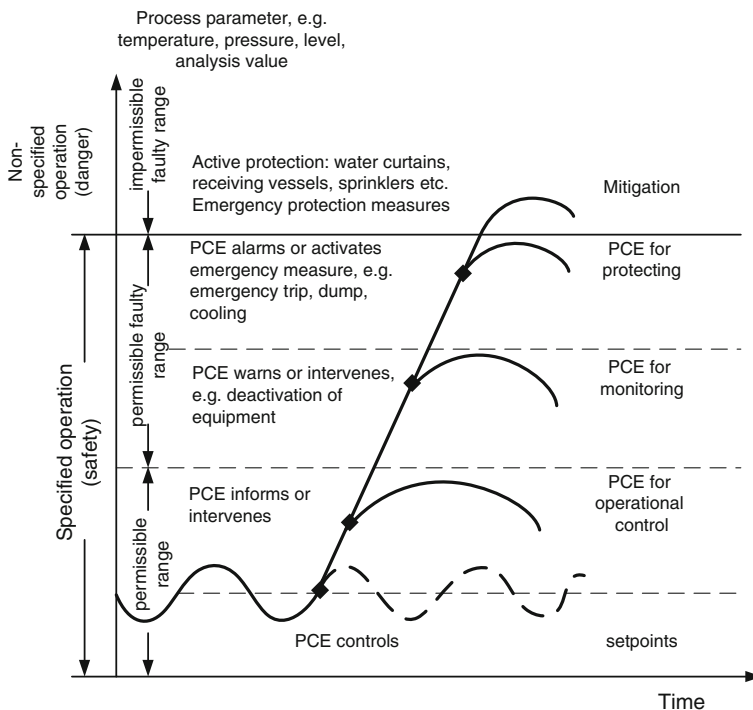


Fig. 4.2 Mode of action of process control engineering (PCE) equipment for plant safety

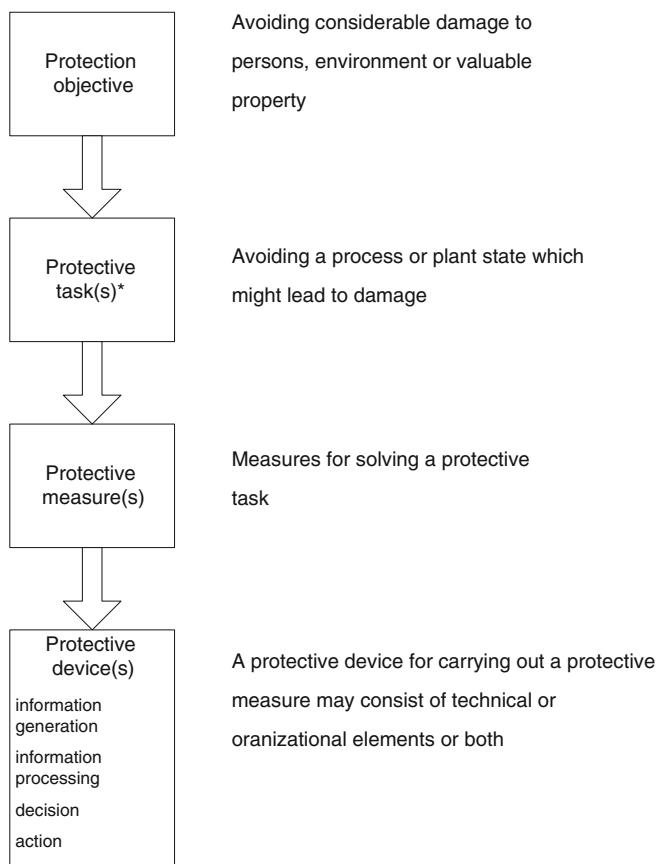
exist, which are technical, organizational or a combination of both. They are called protective measures. The practical implementation of the protective measures is realized by protective devices which consist of the (technical and/or organizational) elements

- information generation,
- information processing,
- decision,
- action.

For the success of the measure all these elements have to exist and perform successfully.

The hierarchical relationship of the above terms is represented in Fig. 4.3.

In order to solve a protective task at least two mutually independent measures have normally to be implemented. Thus, if there is a failure in one of them (including dependent failures) at least one protective measure is still available (single failure criterion, principle of redundancy). It has to be observed that there may be a failure in any element of a protective measure (sensor, amplifier etc.), i.e. the redundancy has to exist all the way through.



*) as a rule the fulfilment of the protection objective requires several protective tasks to be solved

Fig. 4.3 Hierarchy of the terms of protection

If protective measures are implemented through devices with “fail-safe”-behaviour (a failure in the safe direction, e.g. opening of a safety discharge valve on failure of compressed air) or a self-announcing device (including the measures to be taken, when the failure is announced), frequently the redundancy is not implemented.

Often a redundancy is renounced as well, if the protective measure is realized by equipment designed, manufactured and tested according to the state of technology like pressure vessels, safety valves, bursting discs and shut-off and quick opening valves operated with auxiliary power. Equipment satisfying the criteria of the state of technology is normally not supposed to fail.

Table 4.2 Procedure for selecting and determining protective measures

(1) A systematic safety analysis serves to identify events which lead to considerable hazards for the life and health of persons, endanger the environment or valuable property
(2) The protective tasks to be solved are defined for the events under (1) (e.g. avoiding an uncontrolled chemical reaction)
(3) Protective measures are identified which can in principle solve the protection tasks (e.g. limitation of temperatures or concentrations, injection of an inhibitor, pressure relief of the reactor)
(4) At least two protective measures are selected from the measures identified under (3), which represent optimal solutions from a safety point of view (criteria: simplicity, reliability, economy)
(5) The elements of the protective equipment have to be selected from possible alternatives according to the following working principles
• Passively working, i.e. without outside supply of energy or information • Actively working • Organizational

If two (or more) protective measures (redundancy) are employed for solving a protective task, preferably equipment working according to different physical principles is to be used (diverse redundancy). Protective measures totally made up of technical elements are preferred to those involving organizational ones.

Organizational elements must be checked and justified carefully as to required time and feasibility. It must be ensured that they can be performed easily and quickly enough after the occurrence of a malfunction. The organizational elements must be laid down in operating instructions and regularly trained by the personnel (cf. Chap. 5 and Sect. 9.7). Furthermore certain technical equipment must be provided to support manual interventions, e.g. a hand-operated shut-off valve.

The procedure for choosing and determining protective measures is shown in Table 4.2, which explains Fig. 4.3.

An important role for implementing protective measures is played by process control engineering (PCE). Yet the PCE equipment designed for safety is only part of the totality used. The remaining equipment controls the process using either closed loop (with feedback from the process) or open loop controls (without feedback from the process). The part of PCE equipment serving protection and limitation of damage has to satisfy special quality requirements in planning, installation and operation.

The preceding classification applies as well if protective equipment is not only made up of PCE elements but of process and electrical elements. It corresponds to the four levels of the safety concept according to Table 4.1.

4.2.1 Inherent Safety Measures

Although inherent safety measures are reasonable at all levels of the safety concept their important field of application is before the safety concept has been fixed. The following strategies are used:

- keeping the quantity of potentially hazardous substances small (minimization),
- replacing hazardous substances by less hazardous ones (substitution),
- use of less dangerous process conditions, e.g. less dangerous physical states, which would reduce the impact of a potential release (moderation),
- use of simple technology, which makes operator errors less probable; fault forgiving design of the process and the plant (system simplification).

However, it is conceivable that no inherent safety measures exist for a given process. In such a case only engineered safety measures inscribed in the categories of Table 4.2 (passive, active, organizational) can be applied.

Minimization

In the first place alternative processes may be considered, as in Example 4.1. It is important that buffer volumes are kept small by synchronizing the different process steps. Contributions to minimization are to be expected as well from microreactors, which are, however, still in the pilot plant stage [12].

Example 4.1 Reduction of the process inventory in producing nitroglycol

There are two alternative processes for producing nitroglycol ($C_2H_4N_2O_6$), the conventional stirred tank reactor and the reaction in an injector reactor. The latter uses the working principle of an injector (venturi) pump. Glycol is sucked in by a stream of nitric acid flowing through the jet, which reacts there almost instantaneously to form nitroglycol. The hazard potentials are to be compared using the TNT-equivalent (vid. Sect. 10.6.3.1).

Data: Inventory of the stirred tank reactor 100 kg of nitroglycol; inventory of the injector reactor 3 kg of nitroglycol; energies of explosion: nitroglycol 6,743 kJ/kg, TNT 4,650 kJ/kg.

Solution

Total energy of explosion E_{ex}

Stirred tank reactor:

$$E_{ex} = 100 \text{ kg} \cdot 6,743 \frac{\text{kJ}}{\text{kg}} = 674,300 \text{ kJ}$$

$$W_{TNT} = \frac{E_{ex}}{4,650 \frac{\text{kJ}}{\text{kg}}} = \frac{674,300 \text{ kJ}}{4,650 \frac{\text{kJ}}{\text{kg}}} = 145.01 \text{ kg (TNT)}$$

Injector reactor:

$$E_{ex} = 3 \text{ kg} \cdot 6,743 \frac{\text{kJ}}{\text{kg}} = 20,229 \text{ kJ}$$

$$W_{TNT} = \frac{E_{ex}}{4,650 \frac{\text{kJ}}{\text{kg}}} = \frac{20,229 \text{ kJ}}{4,650 \frac{\text{kJ}}{\text{kg}}} = 4.35 \text{ kg}$$

The different consequences of explosions in the two production processes are treated in Example 10.26. $\square$

Substitution

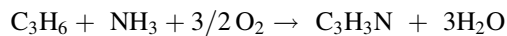
Some substances can be produced using substitutes for feed materials. In [9] examples for alternative processes are given. Example 4.2 is based thereon. Detailed investigations of the environmental impacts of material substitutions can be found, for example, in [13].

Example 4.2 Substitution of hydrogen cyanide in the production of acrylonitrile

According to [9] acrylonitrile (C_3H_3N) is produced by a reaction of acetylene (C_2H_2) with hydrogen cyanide (HCN) according to the following chemical reaction equation:



As an alternative the reaction between propylene (C_3H_6), ammonia (NH_3) and oxygen can be used. Acrylonitrile is then produced according to the following chemical reaction equation:



A release during the production causes a person to be exposed to an airborne concentration of hydrogen cyanide vapour, respectively ammonia vapour of $1,000 \text{ mg/m}^3$ in air during 8 min. The air temperature is 20°C and the atmospheric pressure $100,000 \text{ Pa}$. What is the probability of death in case of

- (a) hydrogen Cyanide ($M_m = 27.03 \text{ g mol}^{-1}$, $Z = 1$),
- (b) ammonia ($M_m = 17.03 \text{ g mol}^{-1}$, $Z = 0.9929$)?

Solution

In order to assess the probabilities of death the probit equations (B3c) for ammonia and (B5) for hydrogen cyanide of Appendix B are used. Since both require arguments in ppm, firstly the concentrations are converted according to Eq. (2.54)

$$C^* = \frac{1,000 \cdot \frac{Z \cdot R_m \cdot T}{p}}{M_n} \cdot C \frac{\text{mg}}{\text{m}^3} = \frac{1,000 \cdot \frac{Z \cdot 8.3145 \frac{\text{J}}{\text{mol K}} \cdot 293.15 \text{ K}}{p}}{M_n} \cdot C \frac{\text{mg}}{\text{m}^3}$$

Accordingly we have $C^*_{\text{hydrogen cyanide}} = 901.7 \text{ ppm}$ and $C^*_{\text{ammonia}} = 1,421.1 \text{ ppm}$ and hence

$$Y = -29.42 + 3.008 \cdot \ln(901.7^{1.43} \cdot 8) = 6.10 \quad \text{for hydrogen cyanide and}$$

$$Y = -35.9 + 1.85 \cdot \ln(1,421.1^2 \cdot 8) = -5.19 \quad \text{for ammonia}$$

The corresponding probabilities of death are calculated according to Sect. 2.6.2 as standard normal distributions with the argument $Y - 5$. Hence we have

$$P_{\text{death,hydrogen cyanide}} = \phi(6.10 - 5) = \phi(1.10) = 0.86$$

$$P_{\text{death,ammonia}} = \phi(-5.19 - 5) = \phi(-10.19) \approx 0$$

This shows the smaller hazard potential of the alternative process. However, a more profound examination would have to account for the differences in dispersion behaviour of the two materials and the possibility of ignition. $\square$

Moderation

Dilution reduces the vapour pressure of a substance. For example, if a material which is a gas at ambient conditions is liquefied under pressure and stored at its vapour pressure, dilution reduces the pressure of storage. In case of a release initial concentrations are lower than for the undiluted material. In [9] the following examples are given:

- solutions of ammonia or methylamine instead of the anhydrous material,
- hydrochloric acid instead of hydrogen chloride,
- diluted nitric or sulphuric acid instead of concentrated fuming nitric acid or oleum (solution of SO_3 in sulphuric acid).

Chemical reactions are occasionally carried out in diluted solutions in order to reduce the rate of reaction and the release of heat. This is shown in Example 4.3 by a reduction of the adiabatic temperature rise.

Example 4.3 Reduction of the mass of reacting material by dilution

The material composition of the contents of the reactor from Example 3.2 is modified. It still contains a mass of 1,650 kg. However, the mass of the material to be converted is reduced from 150 to 90 kg, the difference being replaced by an inert material with a heat capacity of $c_p = 3,800 \text{ J/(kg K)}$. The material to be converted has a heat capacity of $c_p = 2,428 \text{ J/(kg K)}$ and an enthalpy of reaction of $-\Delta H_R = 1,465.4 \text{ kJ/kg}$. The second feed material has a heat capacity of $c_p = 1,717 \text{ J/(kg K)}$. The heat capacity of the reactor amounts to $\bar{C}_w = 10,000 \text{ J/K}$; the temperature of reaction is $T_R = 293.15 \text{ K}$.

Calculate the adiabatic temperature rise and the corresponding final temperature.

Solution

Equation (3.15) is the starting point. The fraction is first expanded by M/M , the molar mass of the reacting material, in order to make the quantities mass-based. We then obtain for the adiabatic temperature rise

$$\Delta T_{\text{ad}} = \frac{90 \text{ kg} \cdot 1,465,400 \frac{\text{J}}{\text{kg}}}{10,000 \frac{\text{J}}{\text{K}} + 110 \text{ kg} \cdot 2,428 \frac{\text{J}}{\text{kg K}} + 40 \text{ kg} \cdot 3,800 \frac{\text{J}}{\text{kg K}} + 1,500 \text{ kg} \cdot 1,717 \frac{\text{J}}{\text{kg K}}} = 42.81 \text{ K}$$

Therefore the final temperature is

$$T = T_R + \Delta T_{\text{ad}} = 293.15 \text{ K} + 42.81 \text{ K} = 335.96 \text{ K} \hat{=} 62.81 \text{ }^{\circ}\text{C}$$

The adiabatic temperature rise has fallen from 74.52 K to a value below 50 K, a limit below which normal operation is considered to be safe [14]. $\square$

System simplification

A simple system structure increases its reliability (vid. Chap. 9). Modifying the statement by Trevor Kletz one might say “not existing components cannot fail”. The possibilities of operating errors are reduced and maintenance becomes easier.

In [9] several examples for the simplification of systems are given. Among them are designs withstanding the maximum explosion pressure (Table 2.17 shows that 10 bar is a good choice in case of deflagrations). This saves the necessity of complicated measuring chains and active systems for explosion pressure suppression, which can fail as well.

If vacuum may occur within an equipment the wall thickness should be chosen such that an implosion cannot take place.

A good example for a simple system structure is the passive trip system presented in the following section.

4.2.2 Passive Safety Measures

Passive safety measures become effective without the supply of outside energy or information (e.g. from measuring instruments). This is true, for example, for the heat removal by natural circulation. In order for it to work only the geometry of the pipework, heat exchanger etc. has to remain unchanged (damage in the course of an accident might restrict its function by leaks or buckling of pipes); a pump is not required.

In what follows the principle of a passive safety measure is explained using the design and functioning of the passive emergency trip system shown in Fig. 4.4 as an example [15].

A pressure build-up is invariably associated with the runaway of an exothermic reaction (e.g., because of the failure of reactor cooling). The causes are the formation of gaseous reaction products, the evaporation of part of the reactor contents or both. This pressure build-up is used to drive the emergency cooling. For this purpose the reactor is equipped with an emergency coolant supply. The corresponding tank is connected to a cooling coil inside the reactor by a pipe. During normal operation bursting disc no. 1 separates the tank from the coil. If the tank is

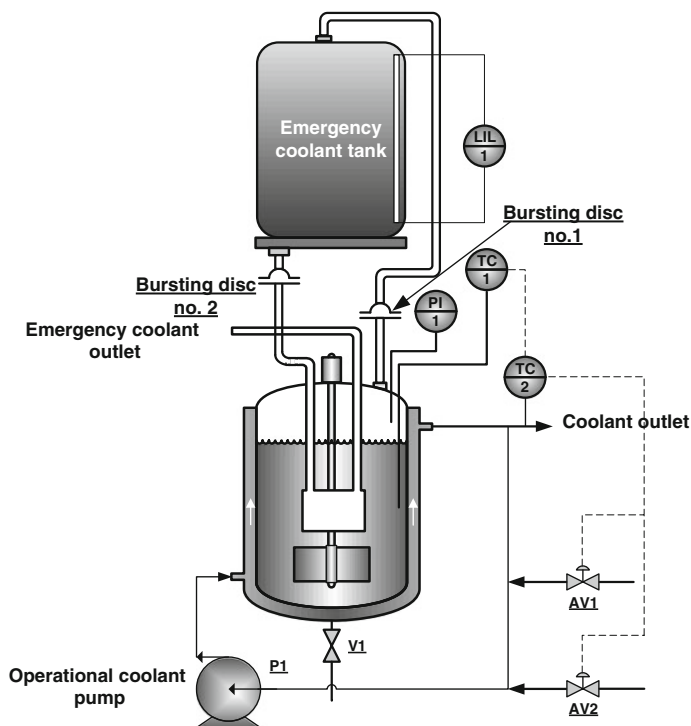


Fig. 4.4 Schematic of the passive emergency trip system

placed above the reactor bursting disc no. 2 closes the outlet of the cooling coil. If it is placed below that bursting disc becomes superfluous.

The outlet discharges into the atmosphere if the reactor content does not cause health or environmental problems. Otherwise it is connected to a receiving tank, scrubber or such like (cf. [10]).

In case of runaway pressure is built up and the bursting disc(s) burst. The pressure energy drives the coolant through the coil thus reducing the temperature of reaction. At the same time the volume available for accommodating the gaseous reaction products and/or the vapour produced by evaporation is increased. Hence, a (partial) pressure relief accompanied by cooling occurs. Advantages of the procedure are:

- largely passive triggering of the safety equipment and realization of the safety measure; hence enhanced reliability, since bursting discs rarely fail,
- the negative effect of the runaway itself serves to control the reaction; the cooling effect generally increases with increasing pressure,
- timely response of the cooling and therefore a cooling effect at a stage when heat release is still close to the quantities produced during normal operation (the Arrhenius function of Eq. (3.3) may still be approximated linearly),

Fig. 4.5 Variations with time of reaction temperature and pressure without cooling and pressure relief—runaway

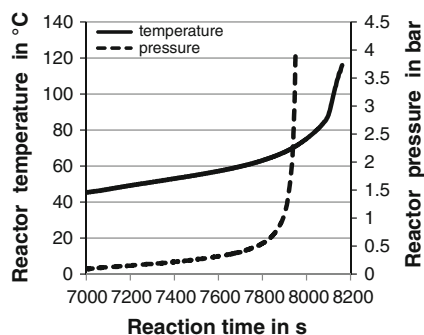
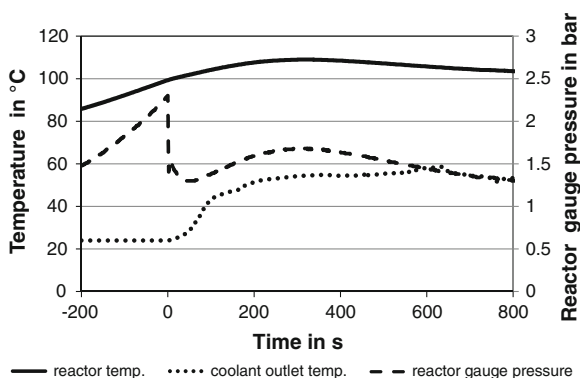


Fig. 4.6 Variations with time of reaction temperature and pressure without cooling, but with pressure relief starting at point in time $t = 0$ s



- no PCE equipment is required to initiate emergency cooling and no pressure pad for driving the emergency cooling is needed,
- emergency coolant tank and heat exchanger serve, at least in part, as pressure abating volume since they are emptied during the cooling process,
- possibility of terminating the reaction without or at least without tangible release from the tank and hence from the reactor.

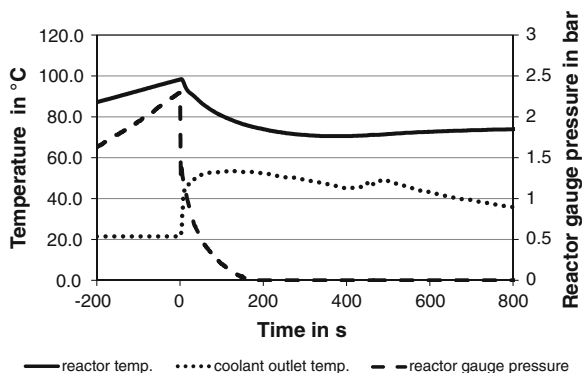
Case study 4.1: Experimental investigation of the passive trip system

In [16] experiments are described which were carried out with the reactor of Fig. 4.4. The laboratory reactor has a volume of 10 l. Amongst others the exothermic esterification of acetic anhydride with methanol according to the following chemical reaction equation was investigated:



The results are shown in Figs. 4.5, 4.6 and 4.7. Figure 4.5 shows the runaway of the reaction without cooling and pressure relief. From Fig. 4.6 it becomes clear that pressure relief leads to a certain stabilization of the reaction. Yet the pressure remains permanently high so that the hazard potential continues to exist. A safe trip only becomes possible if in addition to pressure relief cooling takes place. This is evident from Fig. 4.7.

Fig. 4.7 Variations with time of reaction temperature and pressure with cooling and pressure relief starting at point in time $t = 0$ s



□

4.2.3 Active Safety Measures

The operation of process plants nowadays is monitored and controlled largely by PCE equipment, which is employed at all the levels of Fig. 4.1.

The practical implementation of the protective measures is realized with the following (technical and/or organizational) elements:

- generation of information (sensor and transmitter give a measuring value and/or trigger an alarm);
- processing (reference information (e.g. set point) and measured value lead to a decision on the necessity of an action, either automatically or by the operator);
- action (final control element, manual intervention).

All of these have to be successful in order to realize control or a protective measure.

The filling of a tank, which is shown in Fig. 4.8, serves as an example.

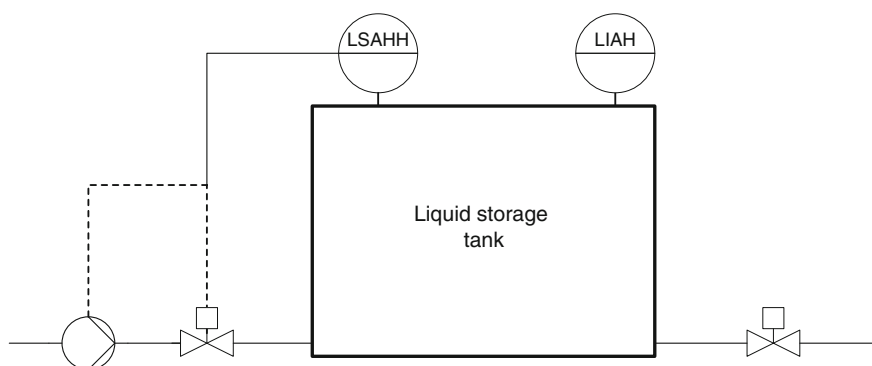


Fig. 4.8 Tank for a liquid with monitored filling

When the nominal liquid level is reached the level indicator (LIAH: Level Indicator and Alarm High) gives an alarm. According to the operating manual the operator should then close the inlet valve and stop the pump. Should he not do this the liquid level would rise further and the instrument Level Switch and Alarm High High (LSAHH) would then close the valve and stop the pump automatically at a higher level.

The operational control is represented here by LIAH, a continuous indication in the control room (indicated by the horizontal line across symbol for the instrument), together with the instruction from the operating manual to observe the rise of the liquid level and to stop the supply on alarm (technical/organizational). Safety is achieved by the automatic stop via LSAHH (technical barrier). In order to avoid confusion two differently sounding signal horns should be provided, one for the operational alarm and the other one for the safety level. A possible deactivation of the level gauge during maintenance should be counteracted by an interlock for valve and pump. In this way the tank cannot be filled when the level gauge LSAHH is not operational. The absence of such an interlock played an important part in the Buncefield accident [17].

Example 4.4 Determination of the time available for an emergency discharge of a reactor

A reactor for producing hexogen (nitrator) is approximately represented by a cylinder. Its diameter is $D = 0.929$ m and its height is $H^* = 1.2$ m. The reactor contains $V = 630$ l of a mixture of nitric acid, hexogen and several side products. The reaction takes place at 12°C . If a temperature of 23°C is reached, the solenoid valve SV is activated. It then opens the discharge valve Y. The reactor content is discharged into the emergency discharge tank where the stirrer M2 starts in order to provide better mixing with its water contents. The reaction is then stopped. Potential freezing of water in winter time should be avoided by temperature alarm low (TAL) in the control room (horizontal line in the symbol indicates a signal in the control room), which is to prompt the operator to take remedial action following instructions from the operating manual.

The outlet pipe from the reactor to the discharge tank has a diameter of $d = 0.2$ m.

Figure 4.9 presents the nitrator with the emergency discharge tank.

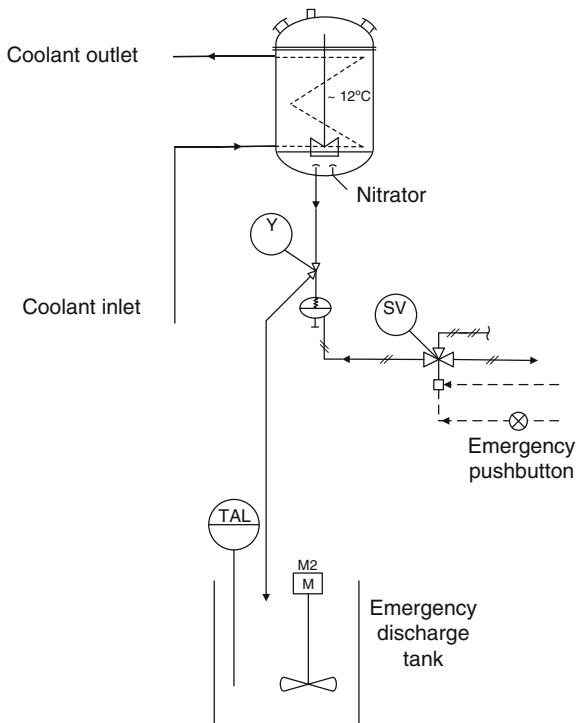
According to [18] a conservative (“pessimistic”) assessment shows that 18 s are available to discharge the reactor contents safely into the emergency discharge tank. Is this enough if a coefficient of discharge of $\mu = 0.82$ (cylindrical connection) is used?

Solution

The potential energy of the liquid column provides the driving force for emptying the reactor. Hence, the initial filling height, H , is needed, i.e.

$$H = \frac{4 \cdot V}{\pi \cdot D^2} = 0.929 \text{ m} \quad (4.2)$$

Fig. 4.9 Emergency trip system for reactor discharge in case of runaway



The mass flow rate discharged through the pipe is obtained from

$$\dot{m}(t) = \mu \cdot \rho \cdot v(t) \cdot \frac{\pi \cdot d^2}{4} = \mu \cdot \rho \cdot v(t) \cdot F_d \quad (4.3)$$

where $\dot{m}(t)$ is the mass flow rate in kg/s, ρ the density of the reactor contents in kg/m³ and $v(t)$ the discharge velocity in m/s.

The time needed for emptying the reactor, t^* , results from

$$\int_0^{t^*} \mu \cdot \rho \cdot F_d \cdot v(t) dt = \int_0^{t^*} \dot{m}(t) dt = m \quad (4.4)$$

In Eq. (4.4) F_d is the cross section of the discharge pipe in m² and m is the mass contained in the reactor in kg.

The discharge velocity is obtained from Bernoulli's equation

$$\frac{\rho}{2} \cdot v(t)^2 = \rho \cdot g \cdot h(t) \quad (4.5)$$

In Eq. (4.5) $h(t)$ is the height of the liquid column which decreases during discharge.

Forming the derivative with respect to time of Eq. (4.5) we obtain

$$v(t) \cdot \dot{v}(t) = g \cdot \frac{dh(t)}{dt} = g \cdot \frac{F_d}{F_r} \cdot \mu \cdot v(t) \quad (4.6)$$

where F_r is the cross sectional area of the reactor in m^2 .

Integrating Eq. (4.6) with the initial condition $v(0) = 0$ we have

$$v(t) = g \cdot \frac{F_d}{F_r} \cdot \mu \cdot t \quad (4.7)$$

Combining Eqs. (4.3), (4.4) and (4.7) and considering that the total mass inside the reactor equals $m = \rho F_r H$ we obtain

$$t^* = \frac{F_r}{F_d \cdot \mu} \cdot \sqrt{\frac{2 \cdot H}{g}} = \frac{\frac{\pi \cdot 0.929^2 m^2}{4}}{\frac{\pi \cdot 0.2^2 m^2}{4} \cdot 0.82} \cdot \sqrt{\frac{2 \cdot 0.93 m}{9.81 \frac{m}{s^2}}} = 26.31 \cdot 0.435 s = 11.4 s \quad (4.8)$$

The 11.4 s required are not too long for discharging the reactor provided that the discharge process (activation by the temperature switch, opening of the solenoid and the discharge valves) needs no more than 6.6 s and thus remains within the conservative time assessment of 18 s. This is technically feasible. $\square$

4.2.4 Organizational Measures

If engineering solutions can only be implemented at incommensurate expense recourse may be had to organizational measures.

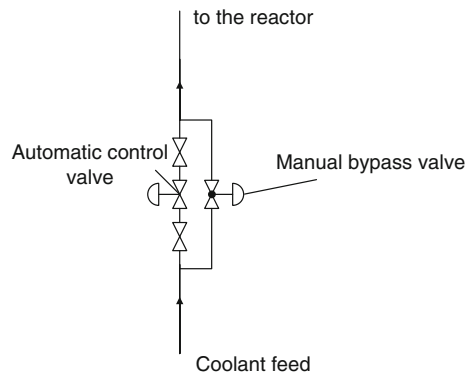
Organizational protection measures are activities carried out by the operators on the basis of instructions in order to avoid transitions of safety-relevant process parameters from a permissible faulty state to an impermissible one.

One has to differentiate between

- safety-relevant activities to be carried out during normal operation or in implementing the chemical process recipe (e.g. control of the type and number of containers of feed materials, checking the position of valves, ensuring the sequence of working steps) and
- acts to be carried out in case of deviations from the permissible range of process parameters in order to avoid their reaching impermissible values.

It is the obligation of the management to provide the corresponding operating instructions, to inform and train the collaborators and to regularly check the

Fig. 4.10 Coolant supply to the reactor with automatic control valve and bypass



effectiveness of the measures. The access of the personnel to the safety-relevant operating instructions must be ensured [10].

As a rule certain engineering provisions must be made in order to make the organizational intervention possible. An example is given in Fig. 4.10. If an alarm sounds because the temperature in a reactor for an exothermic reaction is too high the operating instruction is to fully open the valve of the bypass. If the reason for the increasing temperature is a failure of the temperature control or of the automatic control valve a runaway reaction would be prevented in this way.

4.2.5 Design of Safety Systems

The necessary protective measures have to be implemented by safety equipment, which in turn has to be dimensioned on the basis of the expected technical demands.

In nuclear installations the so-called design basis accidents are used for this purpose [19]. For example, the complete failure of the main coolant pipe of a reactor („2-F“—rupture because the entire cross section is open on both sides) or the failure of the electric supply [19]. The design basis accidents serve to determine the type and dimensions (e.g. capacity, temperatures, cooling power...) of the corresponding safety systems, for example the emergency cooling system for counteracting the breach of the main coolant pipe.

In contrast only general requirements are formulated in the field of process plants. This is explained by fact that we have to deal with a great variety of different plants and equipment, which impedes the formulation of specific requirements. Following these general requirements potential hazards are identified for different equipments by systematic investigations (vid. Chap. 9) and the necessary protective equipments are conceived. The basis is given by the following classification of potential accidents (cf. [20]).

Major accidents against which preventative measures have to be taken („zu verhindernde Störfälle“) result from operational malfunctions in a plant

which can grow into a major accident because a source of hazard is present. Such a development cannot be discarded if the progression of the accident is not stopped or contained by accident preventing measures in such a way that no serious danger arises. Accidents of this type and the accident preventing measures are analyzed and discussed in the safety report.

Major accidents occurring despite preventative measures (“Dennoch Störfälle”) stem from a progression of operational malfunctions which cause a serious danger despite the existence of accident preventing measures. They result from hazard sources which can reasonably be discarded or from the simultaneous impact of several independent sources of hazards. In order to limit the consequences of such accidents plant specific measures and specific measures of hazard defence have to be taken.

Exceptional major accidents (“exzeptionelle Störfälle”) are caused by hazard sources which are beyond any experience and predictability. No specific additional plan-related measures have to be taken against this class of accidents. Among this type of accidents figure, for example, accidents which may arise from war or civil war situations or events.

As an example for the result of systematic safety analyses the following malfunctions in processes with exothermic reactions are to be examined [21]:

- process-related
 - increase of the rate of heat production
 - accumulation of the reaction potential
- plant-related
 - reduction of cooling performance
 - increase of temperature

In particular the following deviations are listed without claiming completeness. These deviations belong to the class of “major accidents to be prevented”, against which protective measures have to be provided:

1. missing components in the reaction mixture
2. excess of a component in the reaction mixture
3. insufficient mixing
4. feeding too fast
5. temperature too low
6. cooling failure
7. obstruction of heat removal
8. unwarranted energy input from outside
9. increase of energy release

In designing columns the following deviations and their consequences should be accounted for:

1. temperature too high/too low
2. pressure too high/too low
3. level too high/too low
4. backflow
5. feeding error (wrong ratios)
6. leak from the column
7. leak from the heat exchangers (reboiler/condenser)
8. wrong substances
9. chemical explosions
10. physical explosions
11. undesired reactions

The impact of some of the deviations mentioned is illustrated in the following case studies, which show model calculations for real plants.

Case study 4.2: Nitration reaction for the production of hexogen [18]

Process Description

The explosive hexogen (RDX) is produced according to the SH process. Hexamine is nitrated with an excess of 8–10 times of concentrated nitric acid (98.5 %). The reaction temperature should not exceed 23 °C in order to avoid runaway. Apart from the reacting substances and the product ammonia, formaldehyde and other materials are present in the reactor. The reaction is exothermic and the mixture is chemically unstable. Hence, the reaction temperature and the excess of nitric acid have to be kept within the permissible range in order to avoid an explosion. The reaction takes place in the nitrator whose P&I diagram is shown in Fig. 4.11. It represents the first part of a cascade of reactors where the reaction is completed and the product is conditioned. The process is continuous and the process stream progresses from reactor to reactor by overflow.

Nitric acid is fed into the reactor at a temperature of 4 °C. Hexamine is supplied to the process via a dosing screw feeder, which is driven by the electric motor M1. The required ratio of the two substances is fixed manually at the start of operation. Since the reaction is exothermic the reactor has to be cooled. This is done by a mixture of water and methanol circulating through half pipes on the reactor jacket (not shown) and through a coil inside of it. The mixture has an inlet temperature of –5 °C. The mass flow of the coolant is controlled by valve TV1 so that the reaction temperature is maintained close to 12 °C. At this temperature the yield of the reaction is sufficient and the temperature is sufficiently far away from its critical value. The position of the control valve is determined by a temperature control loop. The loop consists of the resistance thermometer TE1, the converter TY1, which turns the electric signal from TE1 into a pneumatic one, and the temperature indicator and controller TIC1, which provides the positioning signal for the pneumatic control valve TV1. The reactor is equipped with a stirrer in order to obtain a mixture which is as homogeneous as possible and to avoid local heating.

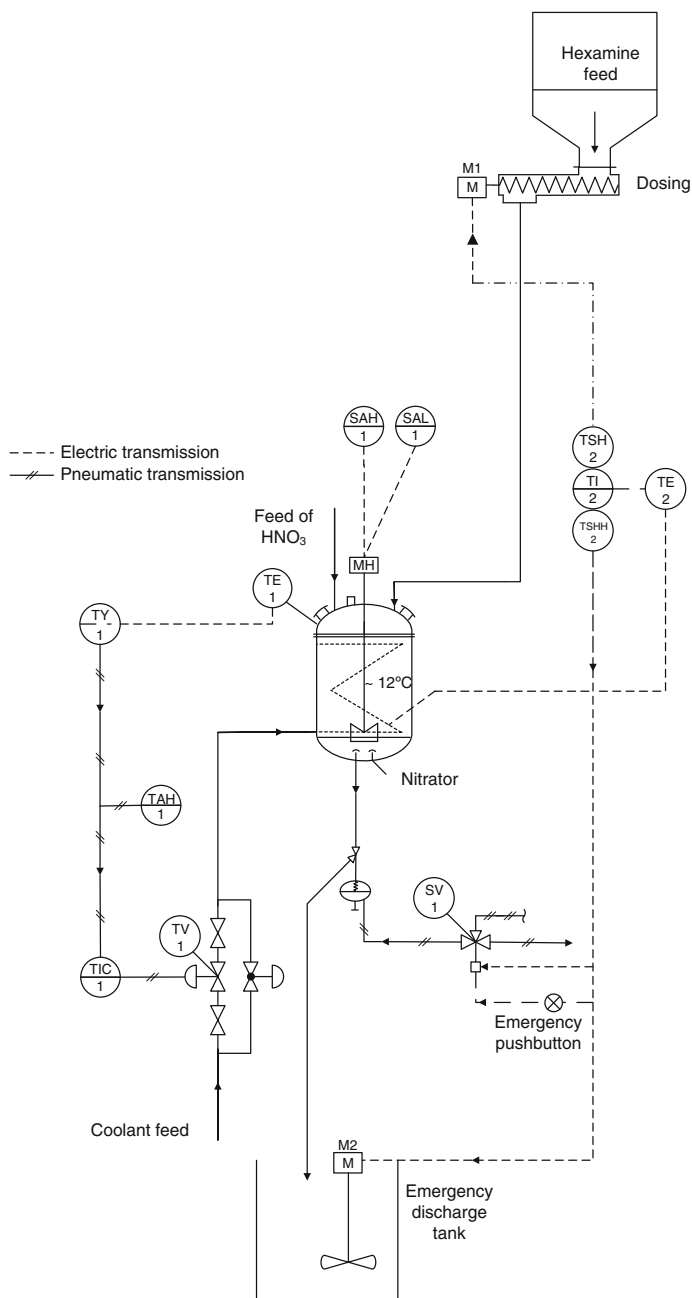


Fig. 4.11 P&I diagram of the nitrator for producing hexogen

Protective Equipment

The process description indicates that the following conditions have to be fulfilled in order to keep the hazard potential of the substances inside the reactor under control:

- the excess of nitric acid has to be ensured;
- the nitration temperature has to be maintained close to 12 °C;
- local heating has to be avoided by stirring.

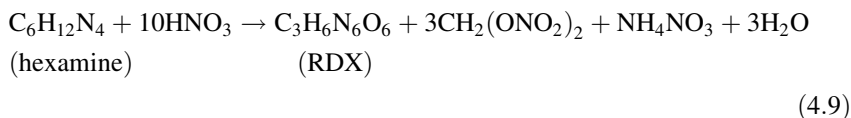
The essential protective equipment for satisfying these requirements is:

- **Reaction temperature**
The temperature control loop is equipped with temperature alarm TA1. Its signal is to prompt the operator to open the bypass of the temperature control, to stop the hexamine supply and to discharge the reactor contents by pushing an emergency button, which in addition activates the stirrer motor M2 of the emergency discharge tank.
- **Stirrer revolutions**
If the number of revolutions falls below its lower limit the instrument SAL1 gives an alarm in the control room. Should the number of revolutions rise above its upper limit, because, for example, the stirrer shaft broke, an alarm is triggered via the instrument SAH1. The operator then has to shut down the reactor by pushing the emergency button.
- **Discharge into the emergency discharge tank**
The discharge into the emergency discharge tank is triggered by an electric measuring chain. This is independent of operational control. It receives its electric supply from batteries, which are permanently charged from the electrical grid so that they would be available even in case of grid failure. The measuring chain consists of the resistance thermometer TE2, the temperature switch TSH2 (setpoint 16 °C), which stops the hexamine feed, if its limiting value is exceeded (level 2 of Table 4.19), and the temperature switch TSHH2 (setpoint 23 °C), which triggers the discharge into the emergency discharge tank (level 3 of Table 4.1). Additionally the instrument TI2 indicates the temperature in the control room. On discharging the solenoid valve SV1 is opened which in turn opens the discharge valve HV1. Concurrently the stirrer M2 is activated in the emergency discharge tank in order to enhance mixing between its water content and the substances from the reactor.

In addition to the automatic discharge just described the reactor may be emptied by pushing emergency pushbuttons, which are installed both in the control room and in the plant and provide an opening signal to SV1 and a starting signal to M2.

Process Model

Several reactions take place concurrently. The complex reaction network may be described by the following simplified equations



for the generation of the product and



for the side reactions. Since there is no knowledge on the kinetics of the latter the following treatment must remain restricted to the main reaction.

The physical properties of the materials involved are presented in Table 4.3.

The reactor is modelled as a continuous stirred tank reactor (CSTR) (cf. [22] and Sect. 3.2.2). The equations on the basis of the reaction Eq. (4.9) are given below; values and explanations of the quantities used are found in Table 4.4. The system of non-linear equations of first order is solved using the Runge-Kutta method.

- Reaction rate

$$r(t, T) = k_R(T) \cdot C_{\text{HNO}_3}(t) \cdot C_{\text{HA}}(t)^n = k_0 \cdot \exp\left(-\frac{E}{R_m \cdot T}\right) \cdot C_{\text{HNO}_3}(t) \cdot C_{\text{HA}}(t)^n \quad (4.11)$$

Table 4.3 Properties of the materials of the nitrating reaction

Material	Property		
<i>Feed</i>			
Hexamine C ₆ H ₁₂ N ₄	Molar mass	M _{HA}	140.19 kg/kmol
	Heat capacity	c _{p,HA}	1.256 kJ/(kg K)
	Temperature	T _{HA,in}	20 °C
Nitric acid HNO ₃	Molar mass	M _{HNO₃}	63.01 kg/kmol
	Heat capacity	c _{p,HNO₃}	1.989 kJ/(kg K)
	Concentration	–	appr. 98.5 %
	Temperature	T _{HNO₃,in}	4 °C
<i>Products and side products</i>			
Hexogen C ₃ H ₆ N ₆ O ₆	Molar mass	M _{RDX}	222.12 kg/kmol
	Heat capacity	c _{p,RDX}	1.19 kJ/(kg K)
Methanediol dinitrate CH ₂ (ONO ₂) ₂	Molar mass	M _C	138.04 kg/kmol
	Heat capacity	c _{p,C}	1.926 kJ/(kg K)
Ammonium nitrate NH ₄ NO ₃	Molar mass	M _D	80.05 kg/kmol
	Heat capacity	c _{p,D}	1.759 kJ/(kg K)
Water H ₂ O	Molar mass	M _{H₂O}	18 kg/kmol
	Heat capacity	c _{p,H₂O}	4.187 kJ/(kg K)
Reaction enthalpy of the nitration reaction		ΔH _r	–274,73 kJ/mol

Table 4.4 Process parameters

General process conditions	Symbol	Value
Volume of the reaction zone	V	630 l
Initial temperature of reaction	T(0)	4.0 °C
Mass of reactor contents	–	970.2 kg
Volumetric flow through the reactor	$\dot{V}$	0.49 l/s
Concentration of hexamine in feed	$C_{\text{HA},\text{in}}$	0.9851 mol/l
Concentration of nitric acid in feed	$C_{\text{HNO}_3,\text{in}}$	20.9087 mol/l
Initial concentration of nitric acid in the reactor	$C_{\text{HNO}_3}(0)$	24.44 mol/l
Heat exchanger surface (jacket and coil)	F	7.0 m ²
Global heat transfer coefficient	U	1.4 kW/(m ² K)
<i>Cooling system and cooling control</i>		
Coolant inlet temperature	$T_{\text{c},\text{in}}$	–5 °C
Specific heat capacity of the coolant (water plus 25 % of methanol)	$C_{\text{p},\text{c}}$	3.6 kJ/(kg K)
Cooler time constant	τ	2,000.0 s
Cooler gain	K	200 kg/(s mV)
Command signal	u_{c}	285.15 mV
Gain of the converter temperature to voltage	$K_{\text{mV/T}}$	1.0 mV/K
Converter gain	K_{I}	1 kg/(s kW)
Integrator coefficient	p_{i}	4,000.0 s

with $k_0 = 47,504,801 \text{ (l/mol)}^{9.958} \text{ s}^{-1}$, $n = 9.958$ and $E = 34390.9 \text{ J/mol}$. $C_{\text{HNO}_3}^0 = C_{\text{HNO}_3}(0)$ denotes the initial concentration of nitric acid. Furthermore we have

- $r(t, T)$ the reaction rate in mol/(l s),
- k_0 the pre-exponential factor (see above),
- E the apparent energy of activation in kJ/mol,
- R_{m} the universal gas constant (8.3145 J/(mol K)),
- $n+1$ the order of reaction (see above),
- T the reaction temperature in K.
- Hexamine (HA)

$$V \cdot \frac{dC_{\text{HA}}}{dt} = \dot{V} \cdot C_{\text{HA},\text{in}} - \dot{V} \cdot C_{\text{HA}} - V \cdot r(t, T) \quad C_{\text{HA}}(0) = 0 \quad \frac{\text{mol}}{\text{l}} \quad (4.12)$$

- Nitric acid (HNO₃)

$$V \cdot \frac{dC_{\text{HNO}_3}}{dt} = \dot{V} \cdot C_{\text{HNO}_3, \text{in}} - \dot{V} \cdot C_{\text{HNO}_3} - 10 \cdot V \cdot r(t, T) \quad C_{\text{HNO}_3}(0) = 24.44 \frac{\text{mol}}{\text{l}} \quad (4.13)$$

- Hexogen (RDX)

$$V \cdot \frac{dC_{\text{RDX}}}{dt} = -\dot{V} \cdot C_{\text{RDX}} + V \cdot r(t, T) \quad C_{\text{RDX}}(0) = 0 \frac{\text{mol}}{\text{l}} \quad (4.14)$$

- Methanediol dinitrate (C)

$$V \cdot \frac{dC_{\text{C}}}{dt} = -\dot{V} \cdot C_{\text{C}} + 3 \cdot V \cdot r(t, T) \quad C_{\text{C}}(0) = 0 \frac{\text{mol}}{\text{l}} \quad (4.15)$$

- Ammonium nitrate (D)

$$V \cdot \frac{dC_{\text{D}}}{dt} = -\dot{V} \cdot C_{\text{D}} + V \cdot r(t, T) \quad C_{\text{D}}(0) = 0 \frac{\text{mol}}{\text{l}} \quad (4.16)$$

- Water (H₂O)

$$V \cdot \frac{dC_{\text{H}_2\text{O}}}{dt} = -\dot{V} \cdot C_{\text{H}_2\text{O}} + 3 \cdot V \cdot r(t, T) \quad C_{\text{H}_2\text{O}}(0) = 0 \frac{\text{mol}}{\text{l}} \quad (4.17)$$

- Energy balance of the process

$$\sum_{i=1}^6 C_i \cdot M_i \cdot c_{p,i} \cdot V \cdot \frac{dT}{dt} = \dot{Q} - \dot{Q}_{\text{cool}} \quad T(0) = 277.16 \quad (4.18)$$

where

$$\dot{Q} = \dot{V} \cdot \left(C_{\text{HA}, \text{in}} \cdot M_{\text{HA}} \cdot c_{p, \text{HA}} \cdot T_{\text{HA}, \text{in}} + C_{\text{HNO}_3, \text{in}} \cdot M_{\text{HNO}_3} \cdot c_{p, \text{HNO}_3} \cdot T_{\text{HNO}_3, \text{in}} - \sum_{i=1}^6 C_i \cdot M_i \cdot c_{p,i} \cdot T \right) + (-\Delta H_r) \cdot r(t, T) \cdot V$$

denotes the heat generated and

$$\dot{Q}_{\text{cool}} = \dot{m} \cdot c_{p,c} \cdot (T - T_{c, \text{in}}) \cdot \left[1 - \exp\left(-\frac{F \cdot U}{\dot{m} \cdot c_{p,c}}\right) \right] \quad (4.19)$$

the heat extracted, with *i* denoting the above mentioned substances (HA, HNO₃, RDX, C, D, H₂O).

Equation (4.19) is the heat exchanger model derived in Example 3.5.

- PI controller for coolant flow

$$\frac{d\dot{m}}{dt} = \frac{K_I}{\tau} \cdot (\dot{Q} - \dot{Q}_{cool}) + \frac{K}{\tau} \cdot s_h \quad \dot{m}(0) = 2.0 \frac{\text{kg}}{\text{s}} \quad (4.20)$$

$$\frac{ds_i}{dt} = \frac{K_{mV/T} \cdot T - u_c}{p_i} \quad s_i(0) = 0 \quad (4.21)$$

$$s_h = u_c - K_{mV/T} \cdot T + s_i \quad s_h(0) = 0 \quad (4.22)$$

Simulation Results

The plant model enables one to calculate in addition to the normal operation several of the operational disturbances mentioned above; they are now briefly commented upon. The corresponding variations of temperature with time are shown in Figs. 4.12, 4.13 and 4.14.

- Normal operation

Table 4.5 shows the mass flow rates of materials and the reaction temperature for stationary normal operation, which is reached about 4.5 h after the start of operation.

- Missing components in the reaction mixture

In order to simulate this malfunction the initial concentration of nitric acid in the reactor was reduced from 24.44 to 0.1 mol/l.

Figure 4.13 shows a sharp increase of the temperature to about 30 °C, which is, however, contained by cooling so that a stationary process at 12 °C would result. This implies that the cooling operates at its maximum. Yet, this scenario would not occur in reality because TSHH2 would trigger an emergency trip shortly after the start of operation.

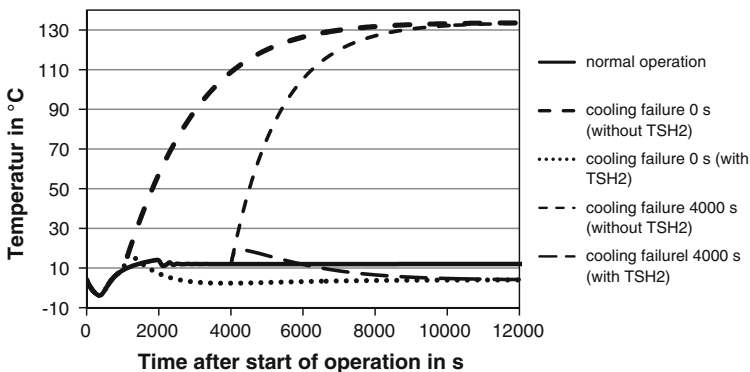


Fig. 4.12 Plots of temperatures over time for normal operation and cooling failure for the nitration of hexamine with and without interruption of the hexamine supply via TSH2

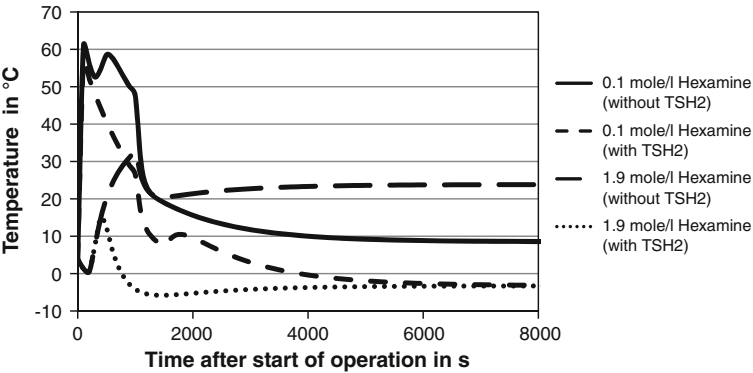


Fig. 4.13 Plots of temperatures over time for 0.1 mol/l of nitric acid in the reactor and 1.9 mol/l of hexamine in the feed stream in the nitration of hexamine with and without interruption of the hexamine supply via TSH2

Fig. 4.14 Plots of temperatures over time with a global coefficient of heat transfer reduced to 70 % with and without interruption of hexamine feed at 15 °C

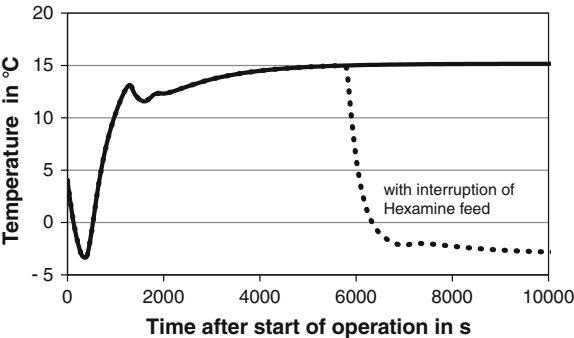


Table 4.5 Characteristic parameter values for stationary normal operation

Parameter	Value
Hexamine feed flow rate	243.60 kg/h
Hexamine outlet flow rate	65.72 kg/h
Nitric acid feed flow rate	2,323.99 kg/h
Nitric acid outlet flow rate	1,407.41 kg/h
Hexogen production	213.10 kg/h
Consumption of hexamine per ton of hexogen	834.74 kg/t
Consumption of nitric acid per ton of hexogen	4,301.08 kg/t
Reaction temperature	12.00 °C

In case the hexamine feed were stopped by TSH2, which would occur approximately 0.33 s after the start of operation, the emergency trip would be activated as well by TSHH2. However, the temperature would be much lower in

the long run than without stopping the hexamine feed. This is because the continuous feed of nitric acid would lower the hexamine concentration in the reactor and thus the reaction rate.

- Excess of components in the reaction mixture

In order to simulate this type of malfunction a calculation with a feed concentration of 1.9 mol/l of hexamine instead of 0.9851 mol/l was performed. The results are shown in Fig. 4.13.

The temperature would reach 25 °C and remain there despite full cooling power, if the reactor contents were not discharged to the emergency discharge tank after about 70 s. If the hexamine feed is stopped by TSH2, the discharge would take place after 419 s. After that the reaction comes to a standstill and the reactor temperature drops to -3.5 °C.

- Insufficient mixing

The consequences of insufficient mixing cannot be assessed with the CSTR model. They require the space dependence of process parameters like concentration and temperature to be accounted for. This may be done by a model on the basis of Computational Fluid Dynamics (CFD).

- Excessively fast feed

Different feed velocities are treated in Case study 4.3.

- Excessively low temperature

Temperatures which are too low are dealt with in Case study 4.3.

- Cooling failure

The failure of cooling at the beginning of reactor operation would lead to extremely high temperatures, as is shown in Fig. 4.12. Two cases are treated, a failure at the start of the operation and a failure 4,000 s later.

If no protection via TSH2 were available, the emergency trip would occur after 1,130 s in the first place, and after 4,049 s in the second, because temperature increases sharply.

However, if the hexamine feed is stopped via TSH2 (Process control engineering (PCE) monitoring equipment; level 2 in Table 4.1), which is activated after 786 s in the first case and after 4,024 s in the second, the variation of temperature with time is milder, since the continuing feed of (cold) nitric acid leads to a reduction of hexamine concentration and hence of the reaction rate.

- Reduction of heat transfer

A reduction of heat transfer is simulated by decreasing the global coefficient of heat transfer to 70 % of its original value. The consequences are shown in Fig. 4.14. The temperature does not reach the setpoint of TSH2, 16 °C.

However, the coolant mass flow rate rises to its maximum, 10 kg/s, whilst it amounts to 5.1 kg/s during normal operation. It has to be borne in mind that the calculated maximum temperature of 15.2 °C is pretty close to the setpoint. Keeping in mind the uncertainties of the calculation one should not assume that 16 °C are not reached. Therefore the variation of temperature with time is calculated as well assuming that the hexamine feed is already stopped at 15 °C. The temperature rise then does not represent any hazard, as can be seen in Fig. 4.14.

Case study 4.3: Production of trichlorophenol in a semi-batch process

The limitation of feeding velocity figures among the engineering measures for implementing inherent safety for a semi-batch reactor. In such a reactor a feed material is fed into the reactor where the other reactant is already present [10]. The restriction may be achieved by using a diaphragm, a small pipe diameter or an adequate pump performance. The effect is now demonstrated taking a process for the production of trichlorophenol as an example. This process was investigated in detail in [22]; the presentation is based on [22, 23].

Process Description

2,4,5-Trichlorophenol is used for manufacturing herbicides, antiseptics or as a fungicide in paper and pulp mills. The process used for its production is carried out in a batch reactor at a pressure of approximately 19 bar using methanol as a solvent.

A total amount of 1,400 kg of the feed, 1,2,4,5-Tetrachlorobenzene (TCB), is suspended in a mashing tub together with 3.8 m³ of methanol (CH₃OH) and 0.05 m³ of sodium hydroxide. The suspension is introduced into the reactor and heated to 141 °C. After that a total quantity of 0.775 m³ of a 50 % aqueous solution of sodium hydroxide (NaOH) is added to the process during a period of time of 60 min. The subsequent time for reaction amounts to 13.5 h. The reaction is exothermic and is held at a temperature of 155 °C by a cooling system once it has been started by heating the mixture with steam of 156 °C.

The initial volume of the reactor contents amounts to 4,825 l reaching 5,600 l after the addition of the sodium hydroxide lye, which is fed into the reactor with a temperature of 25 °C.

It is well known that during the process the highly toxic dioxin (TCDD) is produced, albeit in minute quantities, as long as the nominal range of the reaction parameters is maintained. A deviation of the reaction parameters was the cause of the Seveso accident (cf. [24]), in which an estimated quantity between 0.45 and 3 kg of TCDD was released into the environment.

Reaction Network

The reaction network of the important process steps is shown in Fig. 4.15. The material properties, which are required for the mathematical description of the process, are found in Tables 4.6 and 4.7.

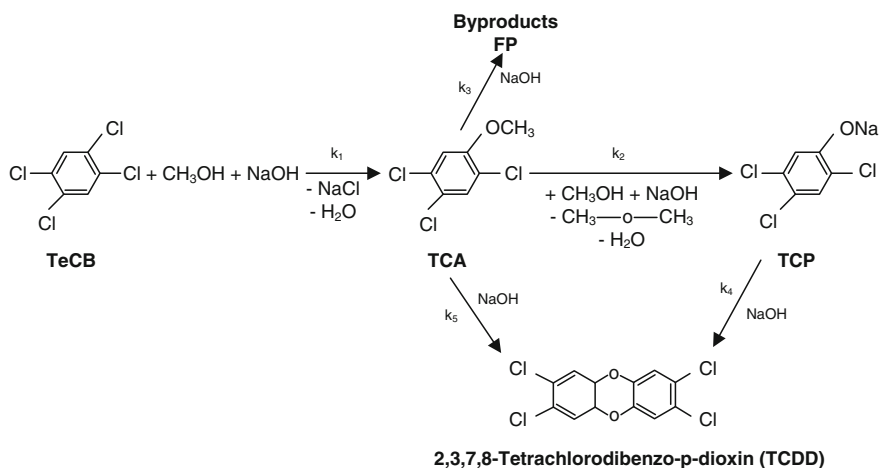


Fig. 4.15 Reaction network for the synthesis of TCP according to the Boehringer process [22]

Table 4.6 Heats of reaction, pre-exponential factors and apparent energies of activation for the reactions of Fig. 4.15

Reaction i	$\Delta H_{R,i}$ in kJ/mol	k_i (428 K) in $\text{m}^3/(\text{mol s})$	$E_{A,i}$ in kJ/mol
1	-112	2.17×10^{-7}	64.8
2	-50.5	7.70×10^{-8}	146.5
3	-50.5	7.92×10^{-9}	194.3
4	not determined	7.90×10^{-14}	240
5	not determined	2.70×10^{-13}	220

Table 4.7 Substances of the process and relevant properties

Number i	Substance	Chemical formula	Molecular mass M_i	Heat capacity c_p in J/(kg K)
1	1,2,4,5 Tetrachlorobenzene (TeCB)	$\text{C}_6\text{H}_2\text{Cl}_4$	215.9	937.9
2	2,4,5 Trichloroanisole (TCA)	$\text{C}_7\text{H}_5\text{Cl}_3\text{O}$	211.4	953.3 ^b
3	2,4,5 Trichlorophenolate (TCP)	$\text{C}_6\text{H}_2\text{Cl}_3\text{ONa}$	219.42	884.8 ^b
4	2,3,7,8 Tetrachlorodibenzo-p-dioxin (TCDD)	$\text{C}_{12}\text{H}_4\text{Cl}_4\text{O}_2$	321.97	889.9 ^b
5	Miscellaneous byproducts	—	200 ^a	700 ^a
6	Aqueous solution of sodium hydroxide (50 %)	$\text{NaOH} + \text{H}_2\text{O}$	40.0 ^c	3,274.0
7	Methanol	CH_3OH	32.04	2,541.0

^aAssumed values; ^bCalculated according to [26], ^cNaOH only

Table 4.8 Process parameters

General process conditions		
U	Global heat transfer coefficient	0.5 kW/(m ² K)
A	Area for heat exchange	12 m ²
T _{in}	Temperature of sodium hydroxide feed	25 °C
ΔH _{mix}	Enthalpy of mixing (NaOH/TeCB)	−30 kJ/mol
V _i	Initial volume	4,825 l
V _f	Final volume	5,600 l
T _d	Feeding period for NaOH	60 min
n _{1,i}	Tetrachlorobenzene (TeCB) (initial quantity)	6,161 mol
n _{4,i}	miscellaneous byproducts (initial quantity)	368 mol
n _{6,i}	Sodium hydroxide (initial quantity)	950 mol
n _{7,i}	Methanol (initial quantity)	93,827 mol
ρ ₆	Density of 50 % aqueous solution of sodium hydroxide	1,521.7 × 10 ^{−3} kg/l
ρ ₇	Density of methanol	773.2 × 10 ^{−3} kg/l
C _R	Heat capacity of the reactor	6,800 kJ/K
Cooling system including control		
Q̇	net rate of heat generation (reaction + mixing − Q̇ _{loss} − feed)	kW
T _{c,in}	Coolant inlet temperature	20 °C
c _{p,w}	Coolant heat capacity (water)	4.179 kJ/(kg K)
a	Coolant/steam mass flow at time t* (when T = 428.15 K is reached)	2 kg/s
τ	Cooling time constant	100.0 s
K	Cooling gain	5.0 kg/(s mV)
u _c	Command signal	428.15 mV
k _c	Proportional gain	10.0
K _{mV/T}	Gain of temperature in mV transducer	1.0 mV/K
K ₀	Gain	10.0
K ₁	Gain	1 kg/(s kW)
p _i	Integrator coefficient	5.0 s

Process Model

The reactor is modelled as a perfect well-stirred semi-batch reactor (cf. [25]). The equations are stated below; values and explanations for the quantities used are found in Table 4.8. The system of non-linear equations of first order is solved by the Runge-Kutta method.

TeCB

$$\frac{dn_1}{dt} = -k_1(428 \text{ K}) \cdot \exp\left[-\frac{E_{A1}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_1 \cdot n_6}{V} \quad (4.23)$$

TCA

$$\begin{aligned}
 \frac{dn_2}{dt} = & k_1(428 \text{ K}) \cdot \exp\left[-\frac{E_{A1}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_1 \cdot n_6}{V} - k_2(428 \text{ K}) \\
 & \cdot \exp\left[-\frac{E_{A2}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V} - k_3(428 \text{ K}) \cdot \exp\left[-\frac{E_{A3}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \\
 & \cdot \frac{n_2 \cdot n_6}{V} - k_5(428 \text{ K}) \cdot \exp\left[-\frac{E_{A3}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V}
 \end{aligned} \quad (4.24)$$

TCP

$$\begin{aligned}
 \frac{dn_3}{dt} = & k_2(428 \text{ K}) \cdot \exp\left[-\frac{E_{A2}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V} \\
 & - k_4(428 \text{ K}) \cdot \exp\left[-\frac{E_{A4}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_3 \cdot n_6}{V}
 \end{aligned} \quad (4.25)$$

TCDD

$$\begin{aligned}
 \frac{dn_4}{dt} = & k_5(428 \text{ K}) \cdot \exp\left[-\frac{E_{A5}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V} \\
 & + k_4(428 \text{ K}) \cdot \exp\left[-\frac{E_{A4}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_3 \cdot n_6}{V}
 \end{aligned} \quad (4.26)$$

Byproducts

$$\frac{dn_5}{dt} = k_3(428 \text{ K}) \cdot \exp\left[-\frac{E_{A3}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V} \quad (4.27)$$

NaOH

$$\begin{aligned}
 \frac{dn_6}{dt} = & -k_1(428 \text{ K}) \cdot \exp\left[-\frac{E_{A1}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_1 \cdot n_6}{V} - k_2(428 \text{ K}) \\
 & \cdot \exp\left[-\frac{E_{A2}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V} - k_3(428 \text{ K}) \cdot \exp\left[-\frac{E_{A3}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \\
 & \cdot \frac{n_2 \cdot n_6}{V} - k_5(428 \text{ K}) \cdot \exp\left[-\frac{E_{A5}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V} - k_4(428 \text{ K}) \\
 & \cdot \exp\left[-\frac{E_{A4}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_3 \cdot n_6}{V} + \frac{\rho_6 \cdot \dot{V}_{in}}{2 \cdot M_6}
 \end{aligned} \quad (4.28)$$

CH₃OH

$$\begin{aligned} \frac{dn_7}{dt} = & -k_1(428 \text{ K}) \cdot \exp\left[-\frac{E_{A1}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_1 \cdot n_7}{V} \\ & - k_2(428 \text{ K}) \cdot \exp\left[-\frac{E_{A2}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_7}{V} \end{aligned} \quad (4.29)$$

Energy balance for the process

$$\begin{aligned} \left(C_R + \sum_{i=1}^5 M_i \cdot c_{pi} \cdot n_i + 2 \cdot c_{p6} \cdot M_6 \cdot n_6 + c_{p7} \cdot M_7 \cdot n_7 + C_P \right) \cdot \frac{dT}{dt} = & k_1(428 \text{ K}) \\ & \cdot \exp\left[-\frac{E_{A1}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_1 \cdot n_6}{V} \cdot |\Delta H_1| + k_2(428 \text{ K}) \cdot \exp\left[-\frac{E_{A2}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \\ & \cdot \frac{n_2 \cdot n_6}{V} \cdot |\Delta H_2| + k_3(428 \text{ K}) \cdot \exp\left[-\frac{E_{A3}}{R_m} \cdot \left(\frac{1}{T} - \frac{1}{428}\right)\right] \cdot \frac{n_2 \cdot n_6}{V} \cdot |\Delta H_3| - \rho_6 \cdot c_{p6} \cdot \dot{V}_{in} \cdot (T - T_{in}) \\ & + \frac{\rho_6}{2 \cdot M_6} \cdot \dot{V}_{in} \cdot |\Delta H_{mix}| - \dot{Q}_{cool} - \dot{Q}_{loss} \end{aligned} \quad (4.30)$$

- NaOH feed

$$\dot{V}_{in} = \frac{V_f - V_i}{T_d}$$

- Heat capacity C_P (accounts for the heat capacity of residual products, which produces an increase of the total heat capacity from 15,600 to 20,100 kJ/kg after feed)

$$C_P = 116.82 \cdot (n_{7,i} - n_7)$$

- Heat loss rate from the reactor (which varies with reaction temperature and amounts to 21 kW at 155 °C)

$$\dot{Q}_{loss} = 0.15556 \cdot (T - 293.15)$$

Energy balance for the coolant and the PI controller

$$\dot{Q}_{cool} = \dot{m} \cdot c_{p,w} \cdot (T - T_{c,in}) \cdot \left[1 - \exp\left(-\frac{A \cdot U}{\dot{m} \cdot c_{p,w}}\right) \right] \quad (4.31)$$

$$\frac{d\dot{m}}{dt} = \frac{K_1}{\tau} \cdot (\dot{Q} - \dot{Q}_{cool}) + \frac{K}{\tau} \cdot s_h \quad \dot{m}(t^*) = a \quad (4.32)$$

$$\frac{ds_i}{dt} = \frac{K_0}{p_i} \cdot (u_c - K_{mV/T} \cdot T) \quad s_i(0) = 0 \quad (4.33)$$

$$s_h = k_c \cdot (u_c - K_{mV/T} \cdot T) + s_i \quad s_h(0) = 0 \quad (4.34)$$

Simulation results

Table 4.9 contains important process parameters with and without cooling failure and for different durations of NaOH feed; the quantity fed is the same in all cases.

It is obvious that little dioxin is produced during normal process operation. However, cooling failure leads to a more than hundredfold increase. The critical parameter is process temperature. Slower feed has virtually no influence if cooling is normal. Neither the quantity of product nor that of dioxin differ substantially from those with faster feed. Yet, in case of cooling failure much less dioxin is to be expected for slow feeding (just four times the quantity of normal operation). This is a safety advantage, which is underlined once again in Fig. 4.16, where the strong decrease of TCDD contents with increasing feed time is shown.

It is obvious from Fig. 4.17 that only a cooling failure during the first 2 h of operation leads to high quantities of TCDD in case of feeding the NaOH within 1 h. If the feeding is spread over 10 h cooling failure during the first 7 h leads to larger quantities of TCDD than with cooling in operation. Yet, these are smaller than for the “1 h case”. Hence, the better strategy can only be identified if frequencies of coolant failure are accounted for. These are higher for the “10 h case”

Table 4.9 Substances produced and process parameters with cooling and cooling failure at the beginning of operation

Operating regime	NaOH feed during 1 h		NaOH feed during 10 h	
	Cooling	No cooling	Cooling	No cooling
Maximum quantity of TCDD in mol/in kg	0.0201	2.275	0.0209	0.0750
	0.0065	0.732	0.0093	0.0241
Maximum quantity of TCP in mol/in kg	4,708	4,791	4,687	5,304
	1,033	1,051	1,028	1,164
Maximum temperature in K	428.15	478.2	428.15	444.5
Final temperature in K	394.2	420.4	414.8	426.5
Time of start of cooling in min	25.0	–	190.0	–
Heat removed by coolant in kJ	768,968	–	288,583	–

Fig. 4.16 Plot of TCDD content after cooling failure at start of operation over duration of NaOH feed (with the total quantity of NaOH unchanged)

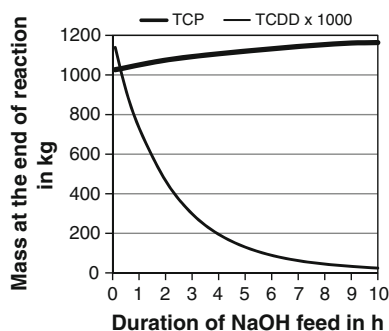
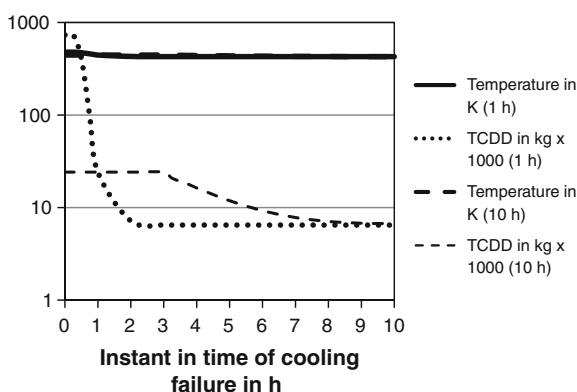


Fig. 4.17 Plot of temperatures and quantity of TCDD produced over the instant in time of cooling failure after the start of operation



than for the “1 h case”, whilst consequences are smaller for the “10 h case” than for the “1 h case” (vid. Chaps. 8–10).

In what follows the consequences of stopping the NaOH feed after cooling failure (with a delay time of 5 s) is investigated. This corresponds to level 2 of Table 4.1. i.e. the use of a monitoring system, which in the present case may, for example, be implemented by a temperature switch stopping the feed pump.

Figures 4.18 and 4.19 show that the temperature rise is efficiently limited by interrupting the NaOH feed. In addition, the data of Table 4.10 show that only very small quantities of TCDD are produced.

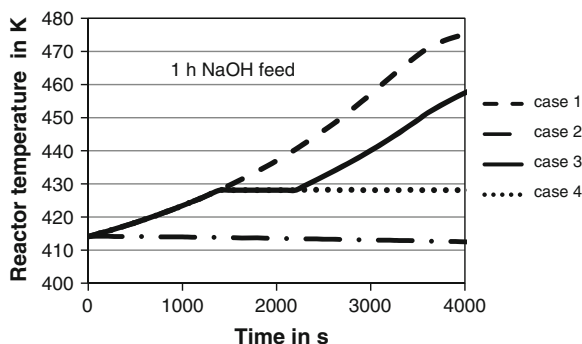


Fig. 4.18 Plot of reaction temperatures over the instant of cooling failure without and with stop of NaOH feed for the complete feeding within 1 h (*case 1* cooling failure immediately after start of operation; *case 2* cooling failure immediately after start of operation with stop of NaOH feed; *case 3* cooling failure 2,000 s after start of operation; *case 4* cooling failure 2,000 s after start of operation with stop of NaOH feed)

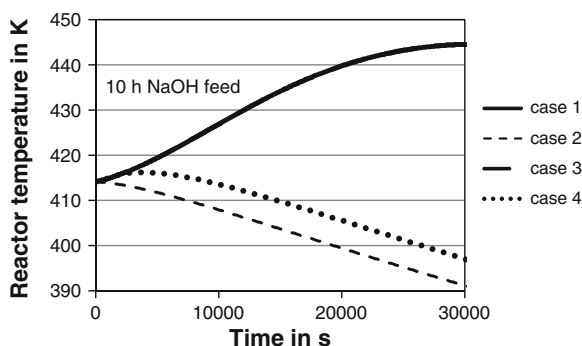


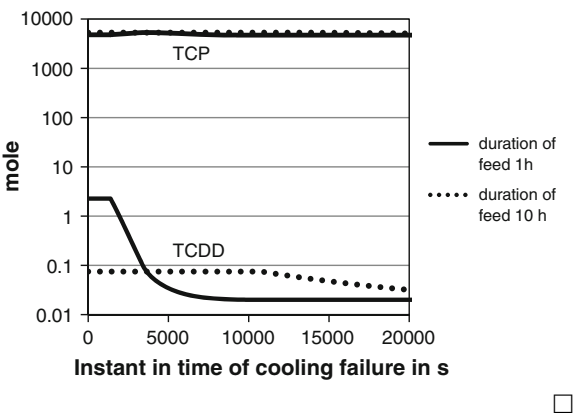
Fig. 4.19 Plot of reaction temperatures over the instant of cooling failure without and with stop of NaOH feed for the complete feeding within 10 h (*case 1* cooling failure immediately after start of operation; *case 2* cooling failure immediately after start of operation with stop of NaOH feed; *case 3* cooling failure 2,000 s after start of operation; *case 4* cooling failure 2,000 s after start of operation with stop of NaOH feed; *cases 1* and *3* are practically coincident)

Figure 4.20 underlines the importance of the instant in time of cooling failure for the production of different materials. Whilst the impact on TCP production is virtually negligible, TCDD production shows marked differences. It is interesting to note that slower feeding of NaOH does not always lead to less TCDD being produced than faster feeding. The quantities produced depend on the (unforeseeable) stochastic point in time of coolant failure. Details are found in [23].

Table 4.10 Temperatures and quantities of TCDD as functions of the instant in time of cooling failure with and without interruption of NaOH feed

Instant in time of cooling failure	Without stop of NaOH feed		With stop of NaOH feed	
	Final quantity of TCDD in kg	Maximum temperature in K	Final quantity of TCDD in kg	Maximum temperature in K
<i>NaOH feed within 1 h</i>				
0	0.732	478.2	3.79×10^{-6}	414.2
2,200	0.217	467.3	3.35×10^{-3}	428.2
<i>NaOH feed within 10 h</i>				
0	2.41×10^{-2}	444.6	3.60×10^{-6}	414.2
2,200	2.42×10^{-2}	444.6	2.45×10^{-5}	416.2

Fig. 4.20 Production of TCP and TCDD over the instant of time of cooling failure



4.3 External Events

According to [8] the operator of a plant does not only have to make provisions against plant internal hazard sources but also against external ones (literally in Germany: environmentally caused hazard sources). This concerns impacts from outside the establishment¹ (and hence on the plant) which may jeopardize the function of safety-relevant parts of the plant [27]. Such impacts may originate from:

¹ “establishment” means the whole area under the control of an operator where dangerous substances are present in one or more installations, including common or related infrastructures or activities; establishments are either lower-tier establishments or upper-tier establishments; “lower-tier establishment” means an establishment where dangerous substances are present in quantities equal to or in excess of the quantities listed in Column 2 of Part 1 or in Column 2 of Part 2 of Annex I, but less than the quantities listed in Column 3 of Part 1 or in Column 3 of Part 2 of Annex I, where applicable using the summation rule laid down in note 4 to Annex I; “upper-tier establishment” means an establishment where dangerous substances are present in quantities equal to or in excess of the quantities listed in Column 3 of Part 1 or in Column 3 of Part 2 of Annex I, where applicable using the summation rule laid down in note 4 to Annex I [8].

- neighbouring establishments or plants,
- neighbouring transport installations and
- natural hazards,

if they imply an increased risk for safe operation.

Impacts from neighbouring establishments may result from fires and explosions (vid. Sect. 10.6), missile generation (vid. Sect. 10.9), ground motion or releases of toxic materials (vid. Sect. 10.5).

Neighbouring transport installations (roads, rails, waterways) are to be regarded as external hazards, if the increased risk is caused by the traffic conditions in the vicinity of the establishment (e.g. traffic density, traffic routing, type of transports, weather conditions). Under certain circumstances civil and military air traffic is included.

Natural hazards are, for example:

- flood or flood waves,
- weather influences (e.g. extreme temperatures, storms and thunderstorms),
- forest fires,
- landslides, land subsidence or rock bursts,
- earthquakes, as far as the establishment is located in an area, which is considered as prone to earthquakes in [28].

It is obvious that a more profound investigation of some of the phenomena mentioned requires methods from areas of knowledge outside the scope of this book. On the other hand, some of the assessments needed may be performed with methods of plant safety, which are discussed in the sections mentioned above.

In what follows earthquakes are briefly treated.

4.3.1 Earthquakes

The design of plants against earthquakes requires, as a rule, the determination of response spectra of the object under consideration (building, vessel etc.) to the excitation caused by the movements from the earthquake. A detailed treatment is beyond the present scope. Instead a simple assessment of the loads on the support columns of a spherical tank is presented based on [24]. However, it goes beyond the treatment given there by explicitly accounting for stochastic parameters.

Earthquakes are generally characterized by indicating acceleration, velocity and ground displacement. Comprehensive methods for assessing earthquake effects account for all three parameters. In what follows only the horizontal acceleration is addressed.

According to [29] the annual number of earthquakes of magnitude greater M on the Richter scale can be described by

$$h_M = e^\alpha \cdot \frac{\exp(-\beta \cdot M) - \exp(-\beta \cdot M_{\max})}{1 - \exp(-\beta \cdot M_{\max})} \quad (4.35)$$

For the lower Rhine basin, one of Germany's seismically most active zones [28], $\alpha = 4.6$, $\beta = 1.8$ and $M_{\max} = 6.9$ are to be used. $M_{\max}$ represents the maximum expected earthquake magnitude. As can be seen from Eq. (4.35) the expected frequency of earthquakes of any magnitude ($M = 0$) in the lower Rhine basin is given by

$$h_0 = \exp(4.6) = 99.5 \text{ a}^{-1}$$

The probability for an earthquake to occur which has a magnitude less than or equal to M is obtained from Eq. (4.35) as follows

$$P\{m \leq M\} = 1 - \frac{\exp(-\beta \cdot M) - \exp(-\beta \cdot M_{\max})}{1 - \exp(-\beta \cdot M_{\max})} \quad (4.36)$$

The complementary probability distribution, i.e. the probability for an earthquake with a magnitude larger than M , is

$$P\{m > M\} = \frac{\exp(-\beta \cdot M) - \exp(-\beta \cdot M_{\max})}{1 - \exp(-\beta \cdot M_{\max})} \quad (4.37)$$

For calculating the effects of an earthquake the acceleration b_e at the site of the plant under examination is required. This may be assessed by relations of the following type (cf. [30])

$$b_e = b_1 \cdot e^{b_2 \cdot M} \cdot R^{-b_3} \quad (4.38)$$

In Eq. (4.38) b_1 , b_2 and b_3 are constants which are specific for the location; b_e results in cm s^{-2} . R is the so-called focal distance in km. It is obtained from

$$R = \sqrt{h^2 + r^2} \quad (4.39)$$

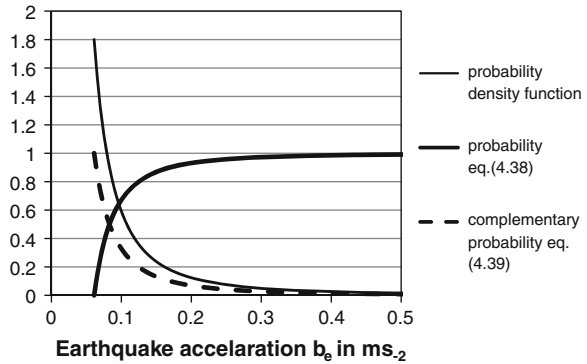
In Eq. (4.39) r is the distance between the location of the epicentre on the surface of the earth and the location of the plant in km and h is the so-called focal depth in km. The latter is the vertical distance between the earth's surface and the focus of the earthquake in the earth's crust. It is considered as constant here although in reality it is a stochastic quantity.

Since [29] makes no indication of the values of these parameters, the values from [30] are used here for the sake of example, i.e. $b_1 = 2,000$, $b_2 = 0.8$ and $b_3 = 2$.

Figure 4.21 shows the probability density function (pdf) (derivative of Eq. (4.36) with respect to m), the probability and the complementary probability for the acceleration b_e . The latter is connected via Eq. (4.38) with the magnitude M , where the parameters for the lower Rhine basin are used in Eqs. (4.37) and (4.38).

The load from the earthquake is considered as acceleration in three orthogonal directions, two horizontal and one vertical.

Fig. 4.21 Probability density function, probability distribution and complementary probability distribution for the earthquake acceleration b_e for an earthquake with a focal depth of $h = 18$ km and a site at a distance of $r = 2$ km from its epicentre



The vertical excitation is assessed to be $2/3$ of the horizontal. The overall structural response is given by

$$W_0 = \left[\sum_{i=1}^3 W_i^2 \right]^{1/2} \quad (4.40)$$

where W_i denotes the load in direction i and W_0 the overall load.

For the horizontal load incorporating the two orthogonal accelerations and a dynamic correction factor of 2 we have

$$W_h = \sqrt{2} \cdot 2 \cdot m \cdot b_e \quad (4.41)$$

In Eq. (4.41) m is the total mass of the object under consideration in kg and b_e the acceleration of the earthquake in m/s^2 .

In what follows the above considerations are applied to the failure of the supports of a tank. The overturning couple caused by the earthquake tries to overturn the tank. It gives the force exerted on the pedestal bolts

$$K = \frac{W_h \cdot l}{n \cdot a} \quad (4.42)$$

In Eq. (4.42) l is the height of the supporting columns of the tank, n the number of bolts and a the spacing plus the inset of the bolts on the support column base plate (m). The following tensile stress results in the bolts from the force K

$$\sigma = \frac{K}{A} \quad (4.43)$$

In Eq. (4.43) K is the force according to Eq. (4.42) and A the cross sectional area of a single bolt. If σ exceeds the permissible tensile stress for the bolt material it is assumed that the tank is overturned.

Example 4.5 Overturning probability for a spherical storage tank due to an earthquake

A spherical tank has a mass of $m = 171,000$ kg including its supports. Its content amounts to 1,200,000 kg. It is fastened with $n = 24$ bolts to a support column base plate with $a = 0.68$ m. The cross sectional area of each bolt is $A = 8 \times 10^{-4}$ m². The active length of the support columns is $l = 7.94$ m and the permissible stress of the bolt material is $\sigma_{\text{per}} = 0.6 \times 10^9$ Pa. The earthquake acceleration is $b_e = 1.4$ m/s².

What is the tensile stress in the bolts and does the tank overturn?

Solution

- Deterministic approach

From Eq. (4.41) we have

$$W_h = 1.4142 \cdot 2 \cdot 1,371,000 \text{ kg} \cdot 1.4 \text{ ms}^{-2} = 5,428,830.96 \text{ N}$$

The force exerted on each bolt is calculated from Eq. (4.42) to give

$$K = \frac{5,428,830.96 \text{ N} \cdot 7.94 \text{ m}}{24 \cdot 0.68 \text{ m}} = 2,641,232.71 \text{ N}$$

The tensile stress in any bolt is obtained according to Eq. (4.43)

$$\sigma = \frac{2,641,232.71 \text{ N}}{8 \times 10^{-4} \text{ m}^2} = 3.3 \times 10^9 \text{ Pa} > \sigma_{\text{per}}$$

This stress is larger than the permissible stress. Hence, the bolts fail and the tank overturns.

By combining Eqs. (4.41)–(4.43) one obtains the acceleration which can just be tolerated if failure is to be avoided, $b_{e,\text{per}}$,

$$\begin{aligned} b_{e,\text{per}} &= \frac{\sigma \cdot A \cdot n \cdot a}{\sqrt{2} \cdot 2 \cdot m \cdot l} = \frac{0.6 \times 10^9 \text{ Pa} \cdot 8 \times 10^{-4} \text{ m}^2 \cdot 24 \cdot 0.68 \text{ m}}{1.4142 \cdot 2 \cdot 1,371,000 \text{ kg} \cdot 7.94 \text{ m}} \\ &= 0.2544 \text{ ms}^{-2} \hat{=} 25.44 \text{ cm s}^{-2} \end{aligned}$$

Rearranging Eq. (4.38) $b_{e,\text{per}}$ enables one to calculate the tolerable magnitude, M_{per} . In doing this it is assumed that the focal depth of the earthquake is $h = 18$ km and that the site of the tank lies $r = 30$ km away from its epicentre. The parameters for the lower Rhine basin given above are used.

$$M_{\text{per}} = \frac{1}{b_2} \cdot \ln\left(\frac{b_{e,\text{per}} \cdot R^{b_3}}{b_1}\right) = \frac{1}{0.8} \cdot \ln\left(\frac{25.44 \cdot 34.99^2}{2,000}\right) = 3.43$$

Inserting M_{per} in Eq. (4.35) one obtains

$$h_M = e^\alpha \cdot \frac{e^{-\beta \cdot M} - e^{-\beta \cdot M_{\text{max}}}}{1 - e^{-\beta \cdot M_{\text{max}}}} = e^{4.6} \cdot \frac{e^{-1.8 \cdot 3.43} - e^{-1.8 \cdot 6.9}}{1 - e^{-1.8 \cdot 6.9}} = 0.2068 \text{ a}^{-1}$$

Hence, such an earthquake is expected to occur 0.2068 per year, i.e. on the average once every 4.84 years.

- Probabilistic approach

A number of input parameters used in the calculation are stochastic. Therefore they are described by random variables and their corresponding probability distributions.

Equation (4.36) already showed this for the earthquake magnitude. Other random variables are the degree of filling of the tank and the focal depth. For the sake of the example the following assumptions are made:

- Degree of filling: rectangular distribution between $a = 0.1$ and $b = 0.9$
- Focal depth: rectangular distribution between $a = 10$ and $b = 18$ km
- Permissible stress for bolts: rectangular distribution between $a = 0.6 \times 10^9$ and $b = 0.7 \times 10^9$ Pa

These values are inserted in the pdf of the rectangular distribution (Eq. (C33) of Appendix C).

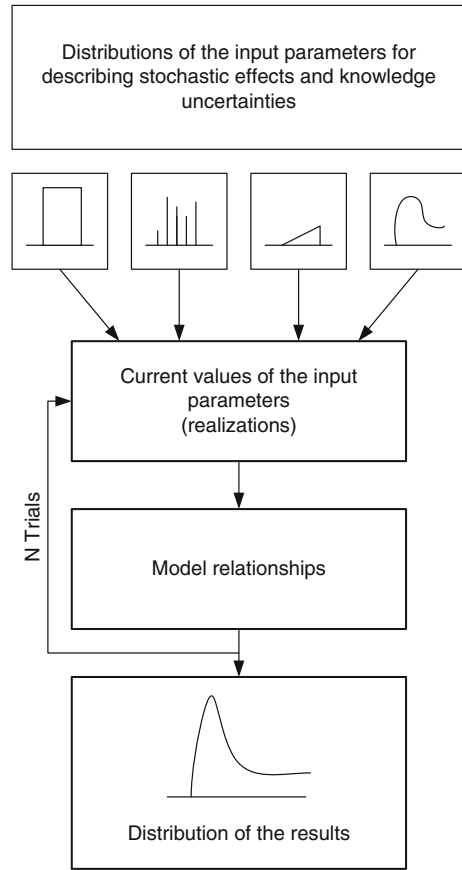
The solution is obtained with the Monte Carlo method (cf. [31]). Using random numbers concrete values (realizations) of the random input parameters are generated. With this input the calculation is performed just as with the deterministic approach. This may lead to combinations of input parameters which result in the permissible stress for the bolts being exceeded and combinations where this does not occur. The calculation is repeated many times. The failure probability (support column failure) is assessed by dividing the number of failure cases by the total number of repetitions of the calculations. The latter are called trials. Figure 4.22 shows a schematic of the procedure.

Basis for the realizations (current concrete values) from the different distributions are random numbers, z , which are uniformly distributed on $[0, 1]$. They are transformed into the distribution in question as follows:

- Magnitude of the earthquake by setting the probability (left hand side) in Eq. (4.37) equal to z and isolating m

$$m = - \frac{\ln(z \cdot (1 - e^{-\beta \cdot M_{\text{max}}}) + e^{-\beta \cdot M_{\text{max}}})}{\beta}$$

Fig. 4.22 Schematic of a Monte Carlo calculation for taking into account uncertainties of input variables due to stochastic effects and insufficient knowledge



- rectangularly distributed quantities

$$X = a + (b - a) \cdot z$$

where X represents the degree of filling, the focal depth or the permissible strength of the bolts, respectively.

The failure probability under the condition that an earthquake occurred is $7.39 \times 10^{-4} \pm 0.17 \times 10^{-4}$.

If the expected frequency of the occurrence of an earthquake is incorporated, one obtains the expected frequency of tank overturning as $h_0 \cdot 8.72 \times 10^{-4} = 99.5 \text{ a}^{-1} \cdot 7.39 \times 10^{-4} = 7.35 \times 10^{-2} \text{ a}^{-1}$, i.e. on the average once every 13.6 years.

Since this frequency is considered to be too high, the cross section of the bolts is increased to $7.85 \times 10^{-3} \text{ m}^2$. This leads to an expected frequency of tank overturning of $1.293 \times 10^{-4} \text{ a}^{-1}$, i.e. on the average once every 7,734 years. This

Table 4.11 Characteristic parameters of the distributions of the results (calculations with $N = 10,000,000$ trials)

Bolt cross section in m^2	5th percentile	Expected value	95th percentile
8.00×10^{-4}	7.21×10^{-4}	7.39×10^{-4}	7.55×10^{-4}
7.85×10^{-3}	5.93×10^{-7}	1.30×10^{-6}	2.01×10^{-6}

Table 4.12 Conditional probabilities $w_{i/10}$ and expected frequencies $h_{i/10}$ for the destruction of several tanks out of a group of 10 tanks

Number of affected tanks i	$p = 7.39 \times 10^{-4}$		$p = 1.30 \times 10^{-6}$	
	$w_{i/10}$	$h_{i/10}$ in a^{-1}	$w_{i/10}$	$h_{i/10}$ in a^{-1}
0	0.9926	98.76	0.99998	99.50
1	7.34×10^{-3}	0.73	1.30×10^{-5}	1.29×10^{-3}
2	2.44×10^{-5}	2.43×10^{-3}	7.60×10^{-11}	7.56×10^{-9}
3	4.81×10^{-8}	4.79×10^{-6}	2.64×10^{-16}	2.63×10^{-14}
4	6.22×10^{-11}	6.19×10^{-9}	6.00×10^{-22}	5.97×10^{-20}

is deemed acceptable. Table 4.11 shows the characteristic parameters of the distributions of the results for both cases.

Let us assume that there are $k = 10$ identical storage tanks at the site. Then we may ask for the probability of the overturning of several tanks. This is answered by using the binomial distribution

$$w_{i/k} = \binom{k}{i} \cdot p^i \cdot (1 - p)^{k-i}$$

The corresponding frequencies are obtained by multiplying this equation with $h_0 = 99.5 \text{ a}^{-1}$, i.e.

$$h_{i/k} = h_0 \cdot w_{i/k}$$

Table 4.12 states results up to four affected tanks; the probabilities of more than four tanks being destroyed are even smaller. $\square$

4.4 Plant Layout and Spacing

The arrangement of machinery and equipment is part of a detailed plant layout. Appropriate segregation is important for plant safety. The following presentation draws upon [24, 32].

It makes sense to position the equipment in a process plant following the P&I diagram. This minimizes the transport of materials, which is desirable from both the point of view of economy as well as that of safety.

Fires, explosions and toxic releases may have impacts inside the plant. For example, they may affect installations adjacent to their place of origin and thus lead to the so-called Domino effect. Since their intensity diminishes with distance (e.g. inversely proportional or inversely proportional to the square), distances between equipments make sense from the safety standpoint. On the other hand, they produce costs because of increased space requirements and higher energy consumption for the transport of materials.

Methods for assessing the effects of fires, explosions and toxic releases are dealt with in Chap. 10. The results obtained with the methods described there can be the basis for a rational planning of the distances between process units.

In some cases experience-based recommendations for distances exist [32] and, in particular, for the storage of flammable materials in [33].

In [24] the following contributions to plant safety from adequate distances between process units are listed:

- segregation of different risks;
- minimization of vulnerable pipework;
- containment of accidents;
- limitation of exposure;
- efficient and safe construction;
- efficient and safe operation;
- efficient and safe maintenance;
- safe control room design;
- emergency control facilities;
- fire fighting facilities;
- access for emergency services;
- security.

A flowchart of the iterative process for determining adequate distances between process units is shown in Fig. 4.23.

4.5 Fire and Explosion Protection

There are many reasons for fires and explosions in a process plant. They result from a chemical reaction where a combustible material reacts with oxygen and heat is released. Fire and explosion properties of materials were already dealt with in Chap. 2.

A fire occurs if a heat source enters into contact with a combustible material. If a combustible solid or liquid material is heated vapours evolve first. If their concentration is sufficiently large, a flammable mixture with the oxygen of the air is formed. If this mixture is heated further to its ignition point, combustion starts. The same applies to mixtures of combustible gases or vapours, if mixed with oxygen and heated. Hence, there are three conditions, which are essential for a fire,

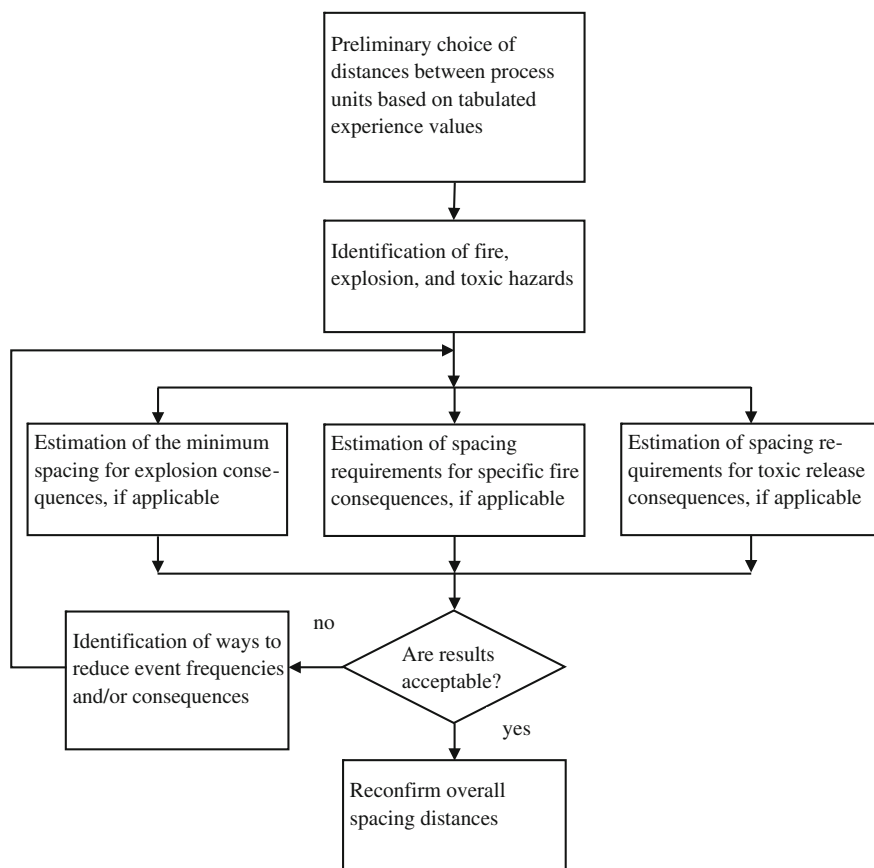


Fig. 4.23 Site layout flowchart (after [32])

namely fuel, oxidant, and energy. They are represented by the so-called fire triangle of Fig. 2.1.

The fire triangle shows how to combat a fire. In the first place, the fuel supply can be interrupted. This is especially important for fires due to leaks in process plants. Secondly, heat can be removed. This is frequently done by extinguishing a fire with water. The third approach is to cut off the oxygen supply. This can be done in several ways, for example by covering the fire with foam or an inert gas.

A fire is maintained only, if its heat generation is equal or larger than its heat losses. The heat stems from the combustion of the material involved. If that is solid or liquid it has to be evaporated in the first place, which implies a heat loss. If liquids or solids burn there usually is a positive feedback. The heat produced by combustion leads to evaporation of the material and thus to a further spread of the fire.

A fire needs a source of ignition as long as it is not self-sustaining. The duration of exposure to the ignition source may then be more important than its maximum temperature. In safety analyses for process plants it should be conservatively assumed that a source of ignition is always present [24].

Different heat balances may apply to different areas of a fire. Thus a fire with a strongly positive heat balance in its inner zone may have but a slightly positive balance in its outer region. If it is extinguished from its outer edge, this represents an attack from the weakest part and hence is particularly effective.

Flammable mixtures of gas and air burn if their composition lies within the explosion limits and an ignition source is present. Ignition of a flammable mixture can occur if

1. the bulk temperature is high enough or
2. local ignition occurs.

The mixture is combusted if its bulk is heated to its self-ignition temperature or an ignition source of sufficient energy impacts part of the mixture.

Fires in process plants are essentially, but not exclusively, consequences of leaks. Amongst others the following types of fire can be expected:

- gland or seal fires in pumps;
- fires at flanges or joints of pipes;
- lagging fires, for example with pipes and vessels (e.g. for being soaked with oil);
- cable fires;
- storage tank fires.

Hence, leaks have to be avoided and sources of ignition to be eliminated.

4.5.1 Sources of Ignition

Potential sources of ignition include amongst others [24]:

1. flames, direct heating and hot surfaces;
2. hot work;
3. friction and impact;
4. chemical energy;
5. vehicles;
6. arson and sabotage;
7. self-heating;
8. static electricity;
9. electrical equipment;
10. radio frequency (RF) emissions.

Many of the potential ignition sources result from operational activities in the plant. These should therefore be handled safely by an adequate work order system.

Areas of the plant where the hazard of fire exists should be fenced off. Cigarettes and lighters should be handed over at the entrance. All equipment to be used in such an area should be sufficiently protected.

From the list of ignition sources self-heating and electricity are treated in more detail below by way of example.

4.5.1.1 Self-heating

Self-heating of a solid is a process of slow combustion. The material undergoing this process may act as an ignition source or cause a fire or an explosion.

Self-heating may result for example from the following situations:

- oil rags left on steam pipes;
- dirty cotton waste left in the pocket of a boiler suit;
- damp clothing stowed away in a locker;
- oil-soaked lagging material;
- dust layers on hot surfaces;
- insulation of electric cables (e.g. following heating due to overload).

Self-ignition occurs if the heat removal from the material is smaller than the energy released by self-heating, which increases with rising temperature according to law of Arrhenius. The temperature where heat release equals heat removal is the self-ignition temperature. Situations of self-ignition can be avoided by adequate design and safety culture.

Some of the materials used, stored or transported in a process plant are capable of self-heating. A well-known example is the spontaneous combustion of a heap of coal. If the materials to be stored are too hot, for example after passing through a dryer, the hazard of self-ignition is increased.

In what follows some theoretical considerations on self-heating are presented. The basic equation for analyzing self-heating is

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \rho \dot{q} \quad (4.44)$$

In order to enable one to solve the differential Eq. (4.44) analytically the heat source is described by zero-order combustion kinetics. The temperature dependence of the reaction rate is, as usual, modelled by the equation of Arrhenius

$$\dot{q} = \Delta H_v \cdot k_0 \cdot \exp\left(-\frac{E}{R_m \cdot T}\right) \quad (4.45)$$

This makes of Eq. (4.45) a non-linear differential equation. The quantities in Eqs. (4.44) and (4.45) have the following meaning:

$\dot{q}$	heat release rate in W/kg
ΔH_v	combustion enthalpy in J/kg
ρ	density in kg/m ³
c_p	heat capacity in J/(kgK)
k_0	pre-exponential factor in s ⁻¹
E	apparent energy of activation in J/mol
λ	thermal conductivity in W/(km)
R_m	universal gas constant J/(mol K)
T	temperature in K
t	time in s

For one-dimensional geometries Eq. (4.44) becomes

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \cdot \left(\frac{\partial^2 T}{\partial x^2} + \frac{j}{r} \frac{\partial T}{\partial x} \right) + \rho \dot{q} \quad (4.46)$$

In Eq. (4.46) $j = 0$ is used for a slab with infinite length in two directions, $j = 1$ for an infinitely long cylinder and $j = 2$ for a symmetric sphere.

In what follows the solutions of Eq. (4.46) for slab geometry ($j = 0$) and an infinitely long hollow cylinder ($j = 1$) are given; they refer to the stationary case, i.e.

$$\frac{\partial T}{\partial t} = 0 \quad (4.47)$$

The slab is assumed to have a thickness of $2a$. It is cooled by air on both sides. This results in a symmetric temperature profile with its maximum in the middle of the slab.

In order to write Eq. (4.46) in a more compact form the following abbreviations are used

$$z = \frac{x}{a} \quad (4.48)$$

$$\theta = \frac{E}{R_m T_a^2} \cdot (T - T_a) \quad (4.49)$$

$$\delta = \frac{\dot{q} \rho k_0}{\lambda} a^2 \frac{E}{R_m T_a^2} \exp\left(-\frac{E}{R_m T_a}\right) \quad (4.50)$$

In Eqs. (4.48)–(4.50) we have

- a half thickness of the slab in m
- x distance from the origin in m (the slab extends from $-a$ to a)

z the normalized distance from the origin $z \in [-1, 1]$

θ dimensionless temperature

and the index „a“ denotes the surface of the slab.

If Eqs. (4.48) through (4.50) are used and the following approximation is introduced

$$-\frac{E}{R_m \cdot T} \approx -\frac{E}{R_m \cdot T_a} + \theta \quad (4.51)$$

we have

$$\frac{d^2\theta}{dz^2} = -\delta \exp(\theta) \quad (4.52)$$

The boundary conditions for solving Eq. (4.52) are

- in the middle of the slab ($z = 0$)

$$\theta = \theta_0 \quad (4.53)$$

and

$$\frac{d\theta}{dz} = 0 \quad (4.54)$$

- on the surface of the slab ($z = 1$)

$$\theta = \theta_a = 0 \quad (4.55)$$

The general solution of Eq. (4.52) is (vid. [24])

$$\theta = \ln B - 2 \ln \left[\cosh \left(z \sqrt{\frac{\delta B}{2}} + C \right) \right] \quad (4.56)$$

where B and C are the constants of solution to be determined from the boundary conditions.

From Eq. (4.54) we obtain $C = 0$ and from Eq. (4.55)

$$B = \cosh^2 \left(\sqrt{\frac{\delta B}{2}} \right) \quad (4.57)$$

The boundary condition of Eq. (4.53) gives

$$\ln B = \theta_0 \quad (4.58)$$

Equations (4.57) and (4.58) enable one to determine the maximum or critical value δ_c ; it amounts to

$$\delta_c = 0.878 \quad (4.59)$$

The corresponding critical value of θ is

$$\theta_c = 1.187 \quad (4.60)$$

If one looks at the definitions of δ in Eq. (4.50) and θ in Eq. (4.49) it becomes evident that a certain geometry has to coincide with certain material properties in order for the generated heat to be removed. For example, widening the slab and retaining the material properties would then lead to less than the generated heat being removed. Self-ignition would result.

In what follows the solution for the hollow cylinder is given. It might serve to model thermal or electrical insulation. The inner radius is denoted by r_i , the outer radius by r_a . The analogue of Eq. (4.52) for one dimensional cylindrical geometry is

$$\frac{d^2\theta}{dz^2} + \frac{1}{z} \frac{d\theta}{dz} = -\delta \exp(\theta) \quad (4.61)$$

In Eq. (4.61) apart from Eq. (4.51) the following abbreviations were used

$$z = \frac{x}{r_i} \quad (4.62)$$

$$\theta = \frac{E}{R_m T_i^2} \cdot (T - T_i) \quad (4.63)$$

$$\delta = \frac{\dot{q} \rho k_0}{\lambda} r_i^2 \frac{E}{R_m T_i^2} \exp\left(-\frac{E}{R_m T_i}\right) \quad (4.64)$$

The boundary conditions are

- inner surface ($z = 1$; subscript “i”), fixed temperature, heat flux equal to 0

$$\theta_i = 0 \quad (4.65)$$

$$\frac{d\theta}{dz} = 0 \quad (4.66)$$

Hence, the heat flux from the pipe into the lagging is set equal to zero, so that the pipe is introduced into the calculation for the lagging only via θ_i .

- outer surface ($z_a = r_a/r_i$) with a fixed temperature

$$\theta = \theta_a \quad (4.67)$$

The general solution of Eq. (4.61) is

$$\theta = \ln \left(\frac{2F^2 G z^{F-2}}{\delta (1 + G z^F)^2} \right) \quad (4.68)$$

In Eq. (4.68) F and G are the constants of solution to be determined from the boundary conditions. From Eq. (4.66) we have

$$F = \frac{2 \cdot (1 + G)}{1 - G} \quad (4.69)$$

and from Eq. (4.65)

$$F = \sqrt{\frac{\delta \cdot (1 + G)^2}{2G}} \quad (4.70)$$

Inserting the boundary condition of Eq. (4.67) in Eq. (4.68) we obtain

$$\theta_a = \ln \left(\frac{2F^2 G z_a^{F-2}}{\delta_c (1 + G z_a^F)^2} \right) \quad (4.71)$$

The three unknowns F , G and δ_c can then be determined from Eqs. (4.69) to (4.71).

The heat flux per meter is obtained by differentiating Eq. (4.68) and multiplying the result by the perimeter $2\pi z$, where z is the dimensionless radius defined above.

$$q'(z) = -\lambda \cdot \frac{d\theta}{dz} \cdot \frac{dT}{d\theta} = -\lambda \cdot \left(\frac{F-2}{z} - \frac{2GFz^{F-1}}{1 + Gz^F} \right) \cdot \frac{2\pi z R T_i^2}{E} \quad (4.72)$$

However, the previous calculation does not show whether the heat fluxes on the surface of the lagging, which result from Eq. (4.72) for $z = z_a$, can in fact be removed. This depends on the convective heat transfer coefficient.

More flexibility of the treatment is achieved by converting the non-linear Eq. (4.61) into a linear one. This is done by approximating the exponential term by a linear one, viz.

$$\delta \cdot \exp(\theta) \approx -2 \cdot \beta \cdot \theta \quad (4.73)$$

Since the approximate equality stipulated by Eq. (4.73) will only rarely be obtained, the linear equation resulting from inserting Eq. (4.73) in Eq. (4.61)

$$\left(\frac{d^2\theta}{dz^2} + \frac{1}{z} \frac{d\theta}{dz} \right) - 2 \cdot \beta \cdot \theta = 0 \quad (4.74)$$

is solved iteratively. The abbreviations of Eqs. (4.63) and (4.64) were used as well to formulate Eq. (4.74).

The boundary conditions result from convective heat transfer on the inner and outer boundary, i.e.

$$q''(r_i) = -\lambda \cdot \frac{dT}{dr} \Big|_i = \alpha_i \cdot (T_i - T) \quad (4.75)$$

$$q''(r_a) = -\lambda \cdot \frac{dT}{dr} \Big|_a = \alpha_a \cdot (T - T_u) \quad (4.76)$$

where T_u is the temperature of the surroundings in K. Using the above abbreviations the boundary condition of Eq. (4.75) becomes

$$\frac{d\theta}{dz} \Big|_i = -\text{Bi}^{(i)} \cdot (\theta_i - \theta) = \text{Bi}^{(i)} \cdot \theta \quad (4.77)$$

and that of Eq. (4.76)

$$\frac{d\theta}{dz} \Big|_a = -\text{Bi}^{(a)} \cdot (\theta - \theta_u) \quad (4.78)$$

In Eqs. (4.77) and (4.78) λ is the thermal conductivity of the material of the hollow cylinder, α the coefficient for convective heat transfer, and Bi Biot's number on the inner (i) and outer (a) surfaces of the hollow cylinder, respectively, with

$$\text{Bi} = \frac{\alpha \cdot r}{\lambda} \quad (4.79)$$

The general solution of the linear differential Eq. (4.74) is

$$\theta(z) = C \cdot I_0(\sqrt{2 \cdot \beta \cdot z}) + D \cdot K_0(\sqrt{2 \cdot \beta \cdot z}) \quad (4.80)$$

In Eq. (4.80) I_0 and K_0 are the modified Bessel functions of order 0 (vid. [34]).

Application of the boundary conditions of Eqs. (4.77) and (4.78) gives the following system of algebraic equations

$$\begin{aligned}
& C \cdot I_1 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) \cdot \sqrt{2 \cdot \beta} - D \cdot K_1 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) \cdot \sqrt{2 \cdot \beta} \\
& = -Bi^{(a)} \cdot \left[C \cdot I_0 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) + D \cdot K_0 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) - \theta_u \right] \\
& C \cdot I_1 \left(\sqrt{2 \cdot \beta} \right) \cdot \sqrt{2 \cdot \beta} - D \cdot K_1 \left(\sqrt{2 \cdot \beta} \right) \cdot \sqrt{2 \cdot \beta} \\
& = Bi^{(i)} \cdot \left[C \cdot I_0 \left(\sqrt{2 \cdot \beta} \right) + D \cdot K_0 \left(\sqrt{2 \cdot \beta} \right) \right]
\end{aligned} \tag{4.81}$$

The constants of solution C and D of Eq. (4.81) may be obtained, for example, using Kramer's rule (vid. [34]). In Eq. (4.81) the relations

$$\begin{aligned}
I_0'(\lambda \cdot x) &= \lambda \cdot I_1(\lambda \cdot x) \text{ and} \\
K_0'(\lambda \cdot x) &= -\lambda \cdot K_1(\lambda \cdot x)
\end{aligned}$$

were used, where I_1 and K_1 are the modified Bessel functions of order 1.

The iteration consists in solving Eqs. (4.80) and (4.81) with a starting value of β . Subsequently the following expressions are determined which enable one to compare the exact result (left hand side of Eq. (4.73), denoted by A) and the approximate result (right hand side of Eq. (4.73), denoted by B). J is the choice of the number of mesh points between the inner and outer radius, e.g. 350.

$$A = 2\pi\delta \cdot \sum_{j=1}^{J-1} \exp(\theta_j) \cdot (z_{j+1} - z_j)^2 \quad \text{and} \quad B = -2\pi\beta \cdot \sum_{j=1}^{J-1} \theta_j \cdot (z_{j+1} - z_j)^2 \tag{4.82}$$

Subsequently β is modified as follows

$$\begin{aligned}
\beta &\leftarrow \beta + \Delta\beta \quad \text{if} \quad A > B \\
\beta &\leftarrow \beta - \Delta\beta \quad \text{if} \quad A < B
\end{aligned}$$

with $\Delta\beta$ being a quantity $<\beta$ which is reduced by a factor <1 at every change from $A > B$ to $A < B$.

The iteration ends when

$$\left| \frac{A - B}{A} \right| < \varepsilon$$

where ε is a fixed small number, e.g. 10^{-6} .

In case of the boundary conditions according to Eqs. (4.65) and (4.67) (fixed temperature on the outer surface) the system of equations for determining the constants of solution is

$$\begin{aligned}
& C \cdot I_1 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) \cdot \sqrt{2 \cdot \beta} - D \cdot K_1 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) \cdot \sqrt{2 \cdot \beta} \\
& = -Bi^{(a)} \cdot \left[C \cdot I_0 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) + D \cdot K_0 \left(\sqrt{2 \cdot \beta} \cdot \frac{r_a}{r_i} \right) - \theta_u \right] \quad (4.83) \\
& C \cdot I_0 \left(\sqrt{2 \cdot \beta} \right) + D \cdot K_0 \left(\sqrt{2 \cdot \beta} \right) = 0
\end{aligned}$$

The remainder of the calculation proceeds as described above.

By varying input parameters it is found that the critical thickness of the lagging decreases with increasing temperature of the pipe, i.e. the lagging must be thinner in order to avoid self-ignition. This is a requirement counteracting the quality of heat insulation.

Example 4.6 Calculation of the critical radius of a hollow cylinder

The critical radius of a hollow cylinder according to Eq. (4.61) and the corresponding temperature profile are to be calculated. Such a hollow cylinder is used here to model pipework lagging.

Data: $\dot{q} = 8,371 \text{ kW/kg}$; $\rho = 30 \text{ kg/m}^3$; $k_0 = 0.04 \text{ s}^{-1}$; $\lambda = 4.19 \times 10^{-5} \text{ kW/(m K)}$; $E/R_m = 3,019.63 \text{ K}$; $T_a = 313 \text{ K}$; $T_i = 573 \text{ K}$; $r_i = 0.0508 \text{ m}$; $r_a = 0.078 \text{ m}$; $T_u = 293.15 \text{ K}$

Solution

From Eqs. (4.69) to (4.71) the following values are obtained:

$F = 7.9084$ and $G = 0.5963$; $\delta_c = 29.2715$ and $\theta_a = -2.38912$

The heat flux per meter on the lagging surface according amounts to Eq. (4.72) to ($T_a = 299.05 \text{ K}$)

$$\begin{aligned}
q'(r_a) &= q'(z_a) = -\lambda \cdot \left(\frac{F-2}{z_a} - \frac{2GFz_a^{F-1}}{1+Gz_a^F} \right) \cdot \frac{2\pi z_a R T_i^2}{E} \\
&= -4.193 \cdot 10^{-2} \frac{\text{W}}{\text{mK}} \cdot (-5.9026) \cdot 1048.9778 \text{ K} = 259.62 \frac{\text{W}}{\text{m}}
\end{aligned}$$

The corresponding heat flux is

$$q''(r_a) = \frac{q'(r_a)}{2\pi r_a} = \frac{259.62 \frac{\text{W}}{\text{m}}}{2 \cdot 3.1416 \cdot 0.078 \text{ m}} = 529.74 \frac{\text{W}}{\text{m}^2}$$

If Eq. (4.76) is applied to the above result one obtains

$$\alpha_a = \frac{q''(r_a)}{T_a - T_u} = \frac{529.74 \frac{\text{W}}{\text{m}^2}}{313 \text{ K} - 293.15 \text{ K}} = 26.69 \frac{\text{W}}{\text{m}^2 \text{ K}}$$

Obviously the coefficient of convective heat transfer at the outer surface would have to amount to $\alpha_a = 26.69 \text{ W/(m}^2 \text{ K)}$ in order to fulfil the boundary conditions

of the problem. However, the usual movement of air (especially inside rooms) just allows values of α_a between 2 and 10 W/(m² K) to be reached.

Results of a comparative calculation are shown in Fig. 4.24. It is based on Eq. (4.80) using the boundary condition of Eq. (4.81) with $\alpha_a = 6.9$ W/(m² K) and shows that the surface temperature becomes much higher, viz. 138.3 °C, if the heat is to be removed with realistic coefficients of convective heat transfer. This is problematic with respect to the protection of employees and efficient use of energy.

A calculation with the boundary condition of Eq. (4.83) and $\alpha_i = 400.0$ W/(m² K) shows that the heat transfer from the pipe to the lagging (heat losses from the pipe) amounts to

$$q''(r_i) = 67.7 \frac{\text{W}}{\text{m}^2}$$

The heat losses from the surface (different boundary condition) in this case amount to

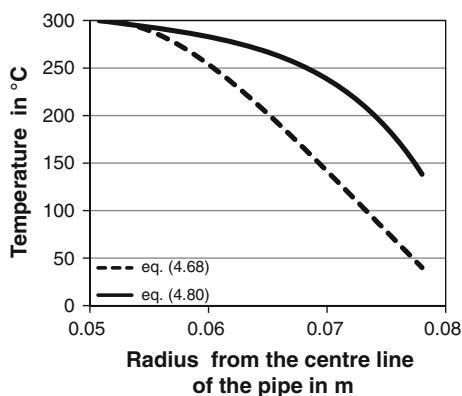
$$q''(r_a) = 814.3 \frac{\text{W}}{\text{m}^2}$$

The difference between heat supply to and removal from the pipe gives the heat generation within the lagging. □

Example 4.7 Self-ignition of a pipe lagging

A pipe DN 80 (88.9 mm outer diameter) is equipped with a lagging of thickness of 4.1 mm. Normally steam at 150 °C passes through it. An operator mistakenly exposes the pipe to steam of 175 °C by placing a multi-port valve into a wrong position. An interlock, which would have prevented this, is not installed. The ambient temperature is 20 °C. Is self-ignition (at 181 °C) to be expected?

Fig. 4.24 Temperature profile inside the lagging of a pipe with different coefficients of convective heat transfer at the surface—Eq. (4.68) and $\alpha_a = 26.69$ W/(m² K) and Eq. (4.80) with $\alpha_a = 6.9$ W/(m² K)



Data: $\dot{q} = 20 \text{ MW/kg}$; $\rho = 26.5 \text{ kg/m}^3$; $\kappa_0 = 0.136 \text{ s}^{-1}$; $\lambda = 2.5 \times 10^{-2} \text{ W/(m K)}$; $E = 22.0 \text{ kJ mol}^{-1}$; $T_B = 423.15 \text{ K}$ resp. 523.15 K ; $T_u = 293.15 \text{ K}$; $r_i = 0.088 \text{ m}$; $r_a = 0.095 \text{ m}$.

Coefficients for convective heat transfer: $\alpha_i = 400.0 \text{ W/(m}^2 \text{ K)}$ and $\alpha_a = 6.9 \text{ W/(m}^2 \text{ K)}$

The results are shown in Fig. 4.25.

At 150°C the calculation according to Eq. (4.68) requires a coefficient of convective heat transfer of $\alpha_a = 13.0 \text{ W/(m}^2 \text{ K)}$, at 175°C even one of $\alpha_a = 29.0 \text{ W/(m}^2 \text{ K)}$. Both are difficult to achieve in practice. The calculation according to Eq. (4.80) was carried out with $\alpha_a = 6.9 \text{ W/(m}^2 \text{ K)}$. A high surface temperature is required to remove the heat.

With a steam temperature of 175°C and $\alpha_a = 6.9 \text{ W/(m}^2 \text{ K)}$ the calculation does not converge and thus shows that self-ignition would occur.

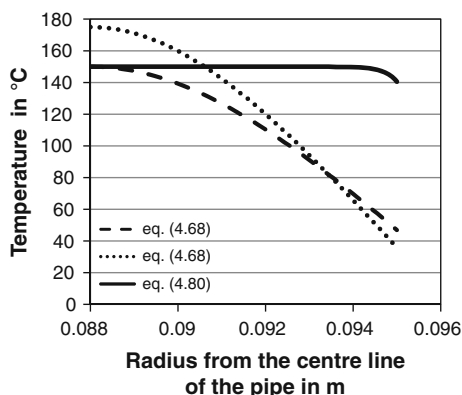
This demonstrates the dependence of the results on the values of the coefficient for convective heat transfer. Yet, no arbitrary choice is possible. The value depends on the conditions in the surroundings with α_a between 2 and $10 \text{ W/(m}^2 \text{ K)}$ representing well the situation in closed rooms, as already mentioned. Hence, it is assumed that self-ignition takes place, if the valve is opened in the wrong position.

The heat transfer from the pipe to the lagging is practically equal to zero. The heat flux per meter hence almost totally results from reactions inside the lagging; it amounts to

$$q'(r_a) = 557.6 \frac{\text{W}}{\text{m}}$$

The results are strongly influenced by the boundary conditions. Which values of the heat transfer coefficients are appropriate depends on the movement of the air surrounding the pipe, which is a stochastic quantity. It is recommended to use more realistic boundary conditions (convective heat transfer) and to provide for a safety factor. Additionally one has to be aware of the fact that the boundary conditions and values of coefficients may be modified by random events such as

Fig. 4.25 Temperature profiles in a pipe lagging according to different methods of calculation



- reduction of the heat removal due to dust layers,
- reduction of the heat removal due to objects placed on the lagging, e.g. boiler suit,
- increase of the reactivity of the insulation material by exposure to substances such as oil.

All of this has to be taken into account when fixing safety factors. □

4.5.1.2 Static Electricity

Static electricity is an important source of ignition, which has to be accounted for in process plants. It is a surface effect related to the contact and separation of bodies. One of the bodies retains a positive charge after separation, the other one a negative one. If the body consists of an electric conductor and is connected to the earth charges move freely and the body returns to the uncharged state. If there is no connection with the earth, the charge is retained showing differences of potential between 1 and 70 kV.

In the process industry there are numerous procedures by which badly conducting materials enter into mutual contact. Processes in which gas-solid mixtures or dusts are used or pneumatic transport should be mentioned in this context. Hence, the following areas where static electricity is to be expected are identified:

- transport of fluids or gases through pipes;
- filling of tank wagons or rail tankers;
- stirring;
- grinding, sieving and pneumatic conveying;
- formation of spray and mist (e.g. with vapour leaks);
- conveyor belts and nutsche filters;
- human body (e.g. because of walking).

Static charging basically leads to high voltages accompanied by low currents. It causes spark discharge or the less dangerous brush discharge. The hazard potential of static charges is assessed by comparison with the lowest energy of ignition of the flammable material in question. In doing this account has to be made of whether the material is a gas, part of a mixture or suspended dust.

Static charges only present a danger if the accumulated charges produce an electric field strong enough to cause a discharge in a flammable atmosphere. That normally means that the electric field strength at some point reaches the limiting breakdown field strength in air ($E_D = 3 \times 10^6 \text{ V/m}$).

The following practically relevant types of electrostatic discharges are distinguished [35]

- spark discharge,
- corona discharge,
- brush discharge,
- propagating brush discharge,
- bulking brush discharge,
- lightning-like discharge.

They are characterized below [35]

Spark discharges take place between electrodes, for example between an isolated charged piece of metal and a grounded piece of metal. The charge may be generated by direct contact, for example with charged bulk material or by induction, i.e. charge separation in an electric field. Practical examples for this are an isolated support cage in a bag filter housing, a sieve or a perforated plate with a non-conducting gasket.

Spark discharges can ignite mixtures of gas, solvent vapour or dust with air and hence hybrid mixtures as well. Ignition can be avoided if all conducting objects which can be charged are grounded electrostatically (resistance to ground $\leq 10^6 \Omega$).

The energy of a spark discharge is usually taken to be equal to that stored in a capacitor [36]

$$W = \frac{CU^2}{2} \quad (4.84)$$

In Eq. (4.84) C is the capacitance of the capacitor in F (Farad), i.e. the capability to store electric charges, and U the applied voltage. The equation is used for other configurations as well; values for the capacitance for selected objects are given in Table 4.13.

Corona discharges are typical single electrode discharges, which occur in a strongly inhomogeneous electric field, typically at sharp conducting and grounded points or edges. This is in contrast with spark discharges. A corona discharge may

Table 4.13 Capacitance of conducting objects—potential: voltage difference to the ground [37]

Charged object	Capacitance in pF (1 picofarad = 10^{-12} F)	Potential in kV
Flange	10	10
Small metal item (scoop, hose nozzle)	10–20	10
Bucket	10	10
Small container (50 l drum)	50–100	8
Medium metal container (200–500 l)	50–300	20
Person	100–200	12
Big plant equipment surrounded by a grounded structure	100–1,000	15

occur if the radius of curvature of a grounded electrode is very small (<1 mm). The electric field in the vicinity of the tip of the electrode is strongly distorted. This leads to a very weak gas discharge which is restricted to the immediate vicinity of the tip. Contrary to a spark discharge it is not triggered abruptly and does not lead to electrical discharge channels which are visible with the naked eye. Experience shows that corona discharges are only mildly incendive. A corona discharge can neither ignite mixtures of dust and air nor mixtures of solvent vapours with air with a minimum energy of ignition above 0.2 mJ.

Brush discharges can occur, if an electrode with a large radius of curvature approaches accumulations of charges, for example on a non-conducting object. A partial discharge then occurs on its surface and luminous brush type discharge channels are observed in the vicinity of the electrode. Such discharges are caused by a number of working processes such as grinding, sieving, stirring, mixing, separating as well as pneumatic transport. The potential for brush discharges to occur at a charged spherical electrode are calculated as follows [36]. On the surface of a sphere with potential U , which is distant from the ground compared with its radius of curvature, there exists the electrical field

$$E = \frac{U}{r} \quad (4.85)$$

In Eq. (4.85) r denotes the radius of the sphere.

Brush discharges at apparatuses, vessels and packaging materials can be avoided by using conducting materials or limiting the size of chargeable surfaces.

Propagating brush discharges arise from intense friction of non-conducting films covering conducting supports, e.g. from metals. This type of discharge is observed inside air jet mills, cyclones and transport pipes with non-conducting inner liners. The energy released amounts to approximately 1 J and can ignite, in principle, fuel-air mixtures (cf. Table 2.8). Propagating brush discharges can be avoided by using conducting materials.

Bulking brush discharges can occur when conveying highly chargeable coarse-grained powders at high velocity in vessels and silos. The discharge spreads over the surface of the highly charged powder in the direction of conducting surfaces of plant equipment. If additionally fine-grained dust is present, a hazard of dust explosion may exist.

Lightning-like discharges can occur between a charged cloud of dust and a grounded object. According to [35] it is unlikely that such discharges occur in technical plants.

The electrical field strength is described by

$$E = -\frac{dU}{dx} \quad (4.86)$$

Only the absolute value of E is of interest. This is why the minus sign is often omitted.

In case of a homogeneous field we have

$$E = -\frac{U}{x} \quad (4.87)$$

The force exerted in the x-direction by a charge of Q is

$$K_x = Q \cdot E \quad (4.88)$$

In Eq. (4.88) Q is the charge in As and E the field strength in V/m. The unit As V/m corresponds to J/m = N.

In order to assess the breakdown voltage of electrodes the empirical law of Paschen is used

$$U_D = 2.44 \times 10^6 \cdot d + 6.53 \times 10^4 \cdot \sqrt{d} \quad (4.89)$$

In Eq. (4.89) the distance between electrodes d is in m; the breakdown voltage U_D then results in V.

Example 4.8 Determination of breakdown voltage and permissible voltage

A voltage of $U = 4,000$ V is applied to two conducting slabs with a distance of $x = 1$ mm between them. Does a discharge occur? Which are the voltages causing discharge if the distances between the plates are $x = 5, 10, 50$ mm?

Solution

According to Eq. (4.87) we have a field strength of

$$|E| = \frac{4,000 \text{ V}}{0.001 \text{ m}} = 4 \times 10^6 \frac{\text{V}}{\text{m}}$$

Since $|E| > E_D = 3 \times 10^6$ V/m (breakdown field strength) discharge is to be expected. The results for other distances between the slabs are given in Table 4.14. $\square$

Example 4.9 Energy released by an electrical discharge

The energies released by discharges from the objects listed in Table 4.13 are to be calculated.

Table 4.14 Voltages leading to discharges for different distances between slabs

x in mm	U in V
5	15,000
10	30,000
50	150,000

Table 4.15 Energies released by discharges from different objects

Charged object	Energy in mJ
Flange	0.5
Small metal item (scoop, hose nozzle)	0.5–1
Bucket	0.5
Small container (50 l drum)	2–3
Medium metal container (200–500 l)	10–60
Person	7.2–14.4
Big plant equipment surrounded by a grounded structure	11.3–112.5

Solution

The calculations are based on Eq. (4.84). The results are given in Table 4.15. A comparison with the minimum energies for ignition of Table 2.8 shows that any of the materials listed there can be ignited even by discharges from a flange or a bucket. □

Example 4.10 Ignition of spilled petrol

While filling a car a person wearing insulating shoes spills petrol on his clothing. A discharge occurs, when the car is opened with its key. Does ignition occur?

Data: Minimum energy of ignition for petrol 0.8 mJ, capacitance of the person 100 pF, potential difference 12,000 V.

Solution

According to Eq. (4.84) the following amount of energy is released

$$W = \frac{100 \times 10^{-12} \frac{\text{As}}{\text{V}} \cdot 12,000^2 \text{V}^2}{2} = 0.0072 \text{ VAs} \hat{=} 7.2 \text{ mJ}$$

Since $7.2 > 0.8$ mJ ignition has to be expected. □

4.5.1.3 Electrostatic Charging

A prerequisite for the accumulation of electrostatic charges is a process which generates charges whilst the charge decay is slower.

The best known form of electrostatic charging is frictional electricity. It occurs if at least two materials are in contact with each other and separated afterwards. On separation one of the surfaces loses electrons and hence becomes positively charged, whilst the other gains electrons resulting in a negative charge. If the surfaces belong to insulators or ungrounded conductors, the separation of charges is maintained. Solids, liquids and aerosols in gases (mainly impurities) can be charged by friction. Voltages and polarity of the charges depend on the properties of the materials involved. Additionally, there are factors of influence such as

- surface roughness, surface properties

The roughness of a surface determines the number of contact points and thus influences the charging. Contact pressure plays a role. The smoother the surface or the higher the contact pressure the higher is the charge. Depending on the substance covering a surface higher or lower charges may result than in the case of a clean surface.

- separation velocity

The faster the two surfaces are separated from each other the smaller is the recombination of positive and negative charges, i.e. high velocity favours the accumulation of charges.

Another important mechanism is induction. If a body is moved in an electrostatic field a charge is induced on its surface. If the body is a grounded electrical conductor the charge flows to the ground. If the body is an insulator, the charge is retained.

If a voltage is applied to an object, a current flows. If charges are dissipated at the same time, an equilibrium state results, which is described by Ohm's law

$$U = R \cdot I \quad (4.90)$$

In Eq. (4.90) U is the voltage in V, I the current in A and R the resistance in Ω .

Now the charging and discharging processes are described taking a capacitor as a simple example. The treatment is applicable to more complex configurations as well.

The maximum charge of a capacitor to which the voltage U_0 is applied is

$$Q_0 = C \cdot U_0 \quad (4.91)$$

Its time-dependent charging process is described by

$$\frac{dQ}{dt} = I_0 - I \quad (4.92)$$

since the current applied from outside I_0 is counteracted by the current I resulting from the charging process.

Inserting Eqs. (4.90) and (4.91) in Eq. (4.92) we have

$$R \cdot C \cdot \frac{dQ}{dt} = Q_0 - Q \quad (4.93)$$

where $R \cdot C = \tau$ is the relaxation time with unit $V/A \cdot A/V \cdot s = s$. It is the time during which the charge changes by a factor of e .

Integration of Eq. (4.93) with the initial condition of an empty capacitor, $Q(0) = 0$, yields

$$Q(t) = Q_0 \cdot \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] = I_0 \cdot \tau \cdot \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (4.94)$$

where the term behind the second equality sign results from a comparison of Eq. (4.92) with Eq. (4.93).

The above equations show that U and I are related by a constant factor of proportionality with Q . Hence, analogously to Eq. (4.94) the following relationships apply for the time-dependence of current and voltage

$$I(t) = I_0 \cdot \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (4.95)$$

and

$$U(t) = U_0 \cdot \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (4.96)$$

If a capacitor with its maximum possible charge is discharged and the initial condition $Q(0) = Q_0$ is used (for simplicity's sake time is newly counted from $t = 0$), the discharge process is described by

$$Q(t) = Q_0 \cdot \exp\left(-\frac{t}{\tau}\right) \quad (4.97)$$

Analogous relationships apply to the time dependence of voltage and current.

In what follows several operations of the process industry are presented where the above relations apply. Further details are found in [24, 37].

Flow through pipes and filters

Electrostatic charges can occur by the flow of liquids through pipes and into vessels, cleaning of big vessels with high pressure water jet cleaners, during stirring or flows through filters.

The streaming currents generated by the flow of liquids through pipes are generally described by empirical formulas [24] such as

$$I \propto u^m \cdot d^n \quad (4.98)$$

In Eq. (4.98) u is the flow velocity and d the inner pipe diameter; m and n are constants derived from an adaptation of the formula to experimental results. A detailed discussion of different adapted equations is found in [24]. Several of them are listed below

- from investigations of toluene

$$I_s = 2.24 \times 10^{-11} d^{1.8} u^{1.45+0.01d} \cdot \exp(0.4 \cdot \log_{10} d \cdot \log_{10} u) \quad (4.99)$$

Table 4.16 Conductivities and relaxation times of selected materials [39]

Liquid	Electrical conductivity κ in S/m	Relaxation time τ in s
<i>Low conductivity</i>		
Highly pure paraffins	10^{-14}	2000
Lubricants	10^{-14} – 10^{-9}	0.02–2,000
Purified aromatic compounds, e.g. Toluene, Xylene	10^{-13} – 10^{-11}	2–200
Petrol (depending on sulphur content) ^a	10^{-13} – 10^{-10}	0.2–200
Ether	10^{-13} – 10^{-10}	0.2–200
Natural gas condensate without corrosion inhibitor	10^{-11} – 10^{-10}	0.2–2
<i>Medium conductivity</i>		
Fuels ^a and oils with conducting additives	5×10^{-11} – 10^{-9}	0.02–0.04
Heavy (black) fuel oils	5×10^{-11} – 10^{-7}	2×10^{-4} –0.4
Ester	10^{-10} – 10^{-6}	2×10^{-5} –0.2
<i>High conductivity</i>		
Crude oil	$\geq 10^{-9}$	≤ 0.02
Alcohols	10^{-6} – 10^{-4}	2×10^{-7} – 2×10^{-5}
Water, not demineralized	$\geq 10^{-4}$	$\leq 2 \times 10^{-7}$
Water, demineralized	5×10^{-6}	10^{-6}

^aParticularly high charges are encountered when using low-sulphur fuels as e.g. with conductivities <50 pS/m and sulphur content <50 ppm

Note On freezing the conductivity of liquids may vary by orders of magnitude with a corresponding impact on the charging process

- for the flow of petrol in steel pipes

$$I_{\infty} = 3.75 \times 10^{-14} \cdot u^2 \cdot d^2 \quad (4.100)$$

- and more conservatively

$$I_{\infty} = 2.5 \times 10^{-13} \cdot u^2 \cdot d^2 \quad (4.101)$$

In Eqs. (4.99)–(4.101) we use

- d pipe diameter in cm
u flow velocity in cm/s

The charge generated in a liquid by separation of charges can be compensated by relaxation or recombination.

Relations for calculating the charge in case of settling of droplets of immiscible liquids or solid particles are found in [24].

Filling of containers

Electrostatic problems relating to containers are treated in detail in [24, 38, 39]. One has to distinguish

- (1) containers made of conducting material and grounded;
- (2) containers made of conducting material and insulated from the ground;
- (3) containers made of insulating material.

Containers in the process industry generally belong to category (1). Nevertheless larger charges can be accumulated in liquids contained in such containers. They are then discharged to the ground via the container wall. This is true particularly if the liquid is a bad conductor (electrical conductivity <100 pS/m, (vid. Table 4.16). The ignition hazard then depends on the surface potential of the liquid, which is directly proportional to the charge density inside the container. The relaxation time of the liquid τ then is the determining parameter. The accumulated charge results from Eq. (4.94). In order to calculate the current recourse is had to one of the Eqs. (4.99)–(4.101). This implies the assumption of a constant charge density and thus a mixing time that is small compared with the relaxation time. Liquids with very small conductivities have very large relaxation times (cf. Table 4.16).

If a container of category (2) is filled the accumulated charge is given by

$$Q(t) = I_0 \cdot R_E \cdot C \cdot \left[1 - \exp\left(-\frac{t}{R_E \cdot C}\right) \right] \quad (4.102)$$

Since the container behaves like Faraday's pail the relaxation time of the liquid does not influence the result. Rather it is influenced by R_E , the resistance between container and ground, which according to [39] has to be $<10^6 \Omega$, and C the capacitance of the container (cf. Table 4.13).

In containers of category (3) a charge can accumulate in the liquid. It is discharged as soon as a connection with the ground is established. By contact with conducting objects, e.g. a metal level gauge, a discharge can occur. An amount of energy according to Eq. (4.84) is then released.

Example 4.11 Calculation of the time-dependence of the electrical charge in a container filled with toluene

A cylindrical container with a height of $H = 6$ m and a cross sectional area of $F = 19.63$ m² is filled with $V = 100$ m³ of toluene through an inlet pipe with a nominal diameter of DN 50 (inner diameter $d = 53$ mm). The filling process lasts for $t_F = 60$ min and leads to a level of $h = 5.09$ m.

How much charge is accumulated at the end of the filling process if

1. a grounded container made of conducting material
2. an ungrounded container made of conducting material

are used?

At what point in time t^* after the end of filling has the charge dropped to 0.1 % of its original value?

Data: $R_E = 10^{11} \Omega$; $C = 1,000 \text{ pF}$; $\tau = 20 \text{ s}$; $\kappa = 8 \times 10^{-14} \text{ S/m}$; $\text{MEZ} = 0.24 \text{ mJ}$

Solution

Calculation of the velocity of flow u

$$u = \frac{4 \cdot V}{t_F \cdot \pi \cdot d^2} = \frac{4 \cdot 100 \text{ m}^3}{60 \text{ min} \cdot \pi \cdot 0.053^2 \text{ m}^2} = 755.45 \frac{\text{m}}{\text{min}} \triangleq 1259.09 \frac{\text{cm}}{\text{s}}$$

The streaming current generated by the flowing liquid is calculated according to Eq. (4.99)

$$\begin{aligned} I_s &= 2.24 \times 10^{-11} 5.3^{1.8} 1,259.59^{1.45+0.01 \cdot 5.3} \cdot \exp(0.4 \cdot \log_{10} 5.3 \cdot \log_{10} 1259.59) \\ &= 5.05 \times 10^{-5} \text{ A} \end{aligned}$$

In case of the grounded container the accumulated charge is obtained from Eq. (4.94)

$$\begin{aligned} Q(t = 3,600 \text{ s}) &= I_0 \cdot \tau \cdot \left[1 - \exp\left(-\frac{t_F}{\tau}\right) \right] \\ &= 5.05 \times 10^{-5} \text{ A} \cdot 20 \text{ s} \cdot \left[1 - \exp\left(-\frac{3,600 \text{ s}}{20 \text{ s}}\right) \right] = 0.001 \text{ As} \end{aligned}$$

For the ungrounded container the charge results from Eq. (4.102), which gives

$$\begin{aligned} Q(t = 3,600 \text{ s}) &= I_0 \cdot R_E \cdot C \cdot \left[1 - \exp\left(-\frac{t_F}{R_E \cdot C}\right) \right] \\ &= 5.05 \times 10^{-5} \text{ A} \cdot 10^{11} \frac{\text{V}}{\text{A}} \cdot 1,000 \times 10^{-12} \frac{\text{As}}{\text{V}} \\ &\quad \cdot \left[1 - \exp\left(-\frac{3,600 \text{ s}}{10^{11} \frac{\text{V}}{\text{A}} \cdot 1,000 \times 10^{-12} \frac{\text{As}}{\text{V}}}\right) \right] = 0.005 \text{ As} \end{aligned}$$

The stored energies are calculated from Eqs. (4.84) and (4.91); they give

$$W = \frac{C \cdot U^2}{2} = \frac{Q^2}{2 \cdot C} = \frac{(0.001 \text{ As})^2}{2 \cdot 1,000 \times 10^{-12} \frac{\text{As}}{\text{V}}} = 500 \text{ J}$$

for the grounded container.

For the ungrounded container we have

$$R = \frac{h}{\kappa \cdot F} = \frac{5.09 \text{ m}}{8 \times 10^{-14} \frac{\text{S}}{\text{m}} \cdot 19.63 \text{ m}^2} = 3.24 \times 10^{12} \Omega$$

$$C = \frac{\tau}{R} = \frac{20 \text{ s}}{3.24 \times 10^{12} \Omega} = 6.17 \times 10^{-12} \frac{\text{As}}{\text{V}}$$

and thus for the stored energy

$$W = \frac{C \cdot U^2}{2} = \frac{Q^2}{2 \cdot C} = \frac{(0.005 \text{ As})^2}{2 \cdot 6.17 \times 10^{-12} \frac{\text{As}}{\text{V}}} = 2,025,931.9 \text{ J}$$

If a conducting object is approached to the liquid surface of the ungrounded container a brush discharge and ignition of the toluene are to be expected. This is true as well for the grounded container.

In order to calculate the time required until the charge accumulated at the end of filling drops to 0.1 % of its original value Eq. (4.97) is used. After rearrangement it is

$$-\tau \cdot \ln \frac{Q(t^*)}{Q_0} = t^*$$

for the grounded container and

$$-R_E \cdot C \cdot \ln \frac{Q(t^*)}{Q_0} = t^*$$

for the ungrounded container.

With $Q(t^*)/Q_0 = 0.001$ we have $t^* = 138.2 \text{ s}$ for the grounded container and a stored energy of 0.5 mJ. For the ungrounded container we have $t^* = 921.0 \text{ s}$ and a stored energy of 2.03 J. In both cases the charge may still be incensive.

Example 4.12 Reduction of the ignition hazard by reducing the filling velocity

In order to reduce the ignition hazard with the grounded container of Example 4.11 the inlet pipe is replaced by one with a nominal diameter of DN 100 and an inner diameter of $d = 105.3 \text{ mm}$. The duration of the filling process is prolonged to 2 h.

Datum: Minimum ignition energy of toluene: 0.24 mJ

The filling velocity now is $u = 159.5 \text{ cm/s}$

Using Eq. (4.99) we obtain

$$I = 1.02 \times 10^{-5} \text{ A}$$

The accumulated charge then is

$$Q(t = 7,200 \text{ s}) = 1.02 \times 10^{-5} \text{ A} \cdot 20 \text{ s} \cdot \left[1 - \exp\left(-\frac{7,200 \text{ s}}{20 \text{ s}}\right) \right] = 0.000204 \text{ As}$$

The stored energy according to Eqs. (4.84) and (4.91) amounts to

$$W = \frac{C \cdot U^2}{2} = \frac{Q^2}{2 \cdot C} = \frac{(0.000204 \text{ As})^2}{2 \cdot 1,000 \times 10^{-12} \frac{\text{As}}{\text{V}}} = 20.8 \text{ J}$$

Hence, even in this case ignition must be expected, since $20.8 > 0.24 \text{ mJ}$. Nevertheless approximately 113.7 s after the end of filling the stored energy would be less than the minimum ignition energy. $\square$

With respect to the transport of liquids in plastic pipes reference is made for example to [40].

Dusts

Dusts can be charged electrostatically following contact and separation of particles or contact and separation of particles from packaging materials or pipe surfaces.

Most chemical dusts are bad conductors. Hence, they generate static electricity. Table 4.17 gives an overview.

The charge per particle increases less than proportionally with its diameter, i.e. the charge per unit of mass decreases with increasing diameter. The decrease of charge with time is described just as with liquids by relaxation times. The discharge often takes the form of a brush discharge. The biggest problem is presented by storage in a container made of conducting material which is insulated from the ground. Details can be found e.g. in [24].

Example 4.13 Filling of a barrel with a bulk material [41]

An ungrounded metal barrel is filled with a bulk material. The charging current I amounts to 10^{-7} A . The resistance to the ground R_E of the barrel is $10^{11} \Omega$ and its capacitance 50 pF . What is the maximum energy of a discharge spark?

Solution

The maximum potential of the barrel is

$$U_{\max} = I \cdot R_E = 10^{-7} \text{ A} \cdot 10^{11} \Omega = 10^4 \text{ V}$$

Table 4.17 Charge of bulk materials with medium and high specific resistances [41]

Process	Specific charge in $\mu\text{C/kg}$
Sieving	10^{-5} – 10^{-3}
Pouring	10^{-3} – 10^{-1}
Scroll feeder transport	10^{-2} – 1
Grinding	10^{-1} – 1
Micronizing	10^{-1} – 10^2
Pneumatic transport	10^{-1} – 10^3

This is accompanied by a stored charge of

$$Q_{\max} = C \cdot U_{\max} = 50 \times 10^{-12} \text{ F} \cdot 10^4 \text{ V} = 50 \times 10^{-8} \text{ As}$$

and a maximum spark energy of

$$W_{\max} = \frac{C \cdot U^2}{2} = \frac{50 \times 10^{-12} \text{ F} \cdot (10^4 \text{ V})^2}{2} = 2.5 \text{ mJ}$$

This value must be compared with the minimum ignition energy of the bulk material (cf. Table 2.26). $\square$

Sprays and mists

Static electricity is also produced if a gas containing particles in liquid or solid form is discharged from an opening. This applies, for example, to flash releases. The charge is accumulated in the droplets.

Moving machinery

Static electricity is generated as well by the relative movement of surfaces in machine parts. This can occur, in particular, with conveyer belts or equipment on rolls.

The voltages produced by a conveyer belt can lie in the range of 10^6 V , since the system practically acts as a Van-de-Graaf generator.

The human body

The human body can be charged electrostatically. This mostly occurs by contact with charged objects or friction with clothing. Potentials of several 10,000 V may then result. Since the capacitance of the human body amounts to about 200 pF, the energy of the discharge may reach 10 mJ according to Eq. (4.84), (cf. Example 4.9).

4.5.2 Protective Measures Against Fires and Explosions

A detailed description of measures for avoiding ignition hazards caused by ignitions in locations with an explosion hazard or when handling explosive materials is found in [37]. These measures may be applied analogously to avoiding ignition hazards under conditions other than atmospheric, for example, higher pressures and temperatures, other oxidants than air or other reactive systems like chemically unstable materials such as peroxides or ethylene oxide.

In general we distinguish measures,

- which avoid or restrict the formation of a hazardous explosive atmosphere (primary explosion protection),
- which prevent the ignition of a hazardous explosive atmosphere (secondary explosion protection),
- which limit the consequences of an explosion to a harmless level (tertiary explosion protection).

Primary measures are to be preferred to secondary measures, which in turn are to be preferred to tertiary ones.

Table 4.18 provides an overview of protective measures against ignition sources.

Fundamental for the protection measures is the classification of plants according to zones, which is done on the basis of a hazard analysis (cf. [42]), for which the qualitative methods of safety analysis of Chap. 9 are used.

The areas with a hazard of explosion are divided into zones according to frequency and duration of the occurrence of an explosible atmosphere [5, 37]. They determine the extent of the measures to be taken and are defined as follows:

Zone 0 is an area in which a hazardous explosive mixture of air with flammable gases, vapours or mist is present permanently, frequently or for long periods.

Zone 1 is an area in which during normal operation a hazardous explosive mixture of air with flammable gases, vapours or mist is formed occasionally.

Zone 2 is an area in which during normal operation a hazardous explosive mixture of air with flammable gases, vapours or mist does not occur or, if it occurs, only exists for a short time.

Zone 20 is an area in which a hazardous explosive atmosphere in the form of a cloud of flammable dust contained in air is present permanently, frequently or for long periods.

Zone 21 is an area in which during normal operation a hazardous explosive atmosphere in the form of a cloud of flammable dust contained in air can occasionally be formed.

Zone 22 is an area in which during normal operation a hazardous explosive atmosphere in the form of a cloud of flammable dust contained in air does not normally occur or, if it occurs, only exists for a short time.

The definitions contain undetermined terms such as “frequently”, “over long periods of time”, “occasionally” etc. Concrete numbers, which would make sense, are avoided. An orientation can be provided by the numbers indicated in Table 4.19, which can be applied analogously to zones 20–22.

Zone 0 usually only comprises the interior of containers or apparatuses (evaporators, reaction vessels etc.) if the conditions for Zone 0 are fulfilled.

Zone 1 can comprise amongst others the

- closer surroundings of zone 0,
- closer surroundings of feeding inlets,
- closer surroundings of filling and emptying devices,
- area immediately surrounding highly fragile apparatuses or pipes made of glass, ceramics or such like,
- area immediately surrounding an insufficiently tight gland, e.g. with pumps or valves,
- interior of apparatuses such as evaporators or reaction vessels.

Table 4.18 Types of ignition sources according to EN 1127-1 (after [45])

Type of ignition source	Ignition process	Protective measures
Hot surfaces	If an explosible atmosphere has contact with heated surfaces (hot pipework, boilers, hot spots in stored material), ignition can occur. The temperature at which ignition takes place depends on the size and geometry of the heated object, on the concentration gradient near the wall and to some extent on the wall material.	Monitoring of surface temperatures
	Rotating parts of bearings, shaft penetrations, gland seals etc. may become sources of ignition if not lubricated sufficiently.	Appropriate design features Adequate choice of structural materials
Flames and hot gases	Flames are exothermic chemical reactions at temperatures of about 1,000 °C and more, which proceed quickly and are often accompanied by luminescence	Limitation of temperature, separation of flammable particles, avoiding backflow of gases and flashback
	Reaction products are hot gases and with flames of dusts or sooty flames glowing solid particles. The flames themselves just as the hot reaction products can ignite an explosible atmosphere. Flames, even of very small dimensions, belong to the most efficient sources of ignition.	
Mechanical sparks	By friction, impact or grinding particles can be separated from solid materials. Their temperature can be high due to the energy absorbed in the separation process. If the particles consist of	Limitation of the relative velocity to <1 m/s
		Replacement of inadequate materials or material combinations
(continued)		

Table 4.18 (continued)

Type of ignition source	Ignition process	Protective measures
	oxidizable materials like iron or steel they can reach temperatures well above 1,000 °C; the particles become sparks. Sparks with large surfaces occur while welding and cutting; they belong to the most efficient sources of ignition. Ignition is caused by an aluminothermic reaction (iron oxide/aluminium) due to impact. The quantity of aluminium or magnesium involved does not have to be more than 10⁻³ g. Impacts with energy of 200 J and more of hard steel on other hard metals as well as the use of cutting discs produce sparks with high energies of ignition. Sparks of high incendiarity can be caused by light impact (around 1 J) of an arbitrary material on rusty steel, if there are traces of aluminium or magnesium at the place of impact. Even the use of tools made of spark proof materials (copper, monel, beryllium bronze) can lead to such sparks.	With machinery, e.g. fans the gap width between rotating and fixed parts has to be monitored. Furthermore deposits of dusts and condensate as well as the ingress of particles have to be avoided. Adequate combinations of materials (vid. VDMA 24169)
Electrical equipment	With electrical equipment, e.g. PCE equipment or motors, even low voltages may produce electric sparks (e.g. when opening or shutting electrical circuits). Leakage currents and hot surfaces may be sources of ignition, too.	Provide for efficient protective measure by following pertinent technical standards

(continued)

Table 4.18 (continued)

Type of ignition source	Ignition process	Protective measures
Electrical leakage currents, cathodic corrosion protection	In electrically conductive equipment stray or leakage currents can flow • as reverse currents to electric generators (in particular in the area of electric trains and major welding equipment), if, for example, conductors like rails, pipes and cable liners laid on or in the earth reduce the resistance of the reverse path, • due to earth contact in faulty electrical equipment, • due to induction (e.g. in the vicinity of electrical equipment with high currents or high frequencies), • due to lightning. If such equipment is separated, connected or bridged electrical sparks may result even at low potential differences. These are capable of igniting an explosible atmosphere. Furthermore ignition is possible due to heating of the current paths mentioned above. When applying cathodic corrosion protection with an external power supply the ignition hazard mentioned is also to be expected. When using	Potential equalization, respectively additional electrical override required Cathodic corrosion protection to be implemented according to the pertinent rules and regulations
		(continued)

Table 4.18 (continued)

Type of ignition source	Ignition process	Protective measures
Static electricity	consumable anodes ignition hazards from electrical sparks are normally not to be expected.	
	As a consequence of separation of surfaces with at least one electrically chargeable material involved incendive discharges of static electricity may occur under certain conditions.	Use of conductive materials/charge dissipating materials <i>Charge dissipating</i> is a material with a specific resistance of more than $10^4 \Omega\text{m}$ and less than $10^9 \Omega\text{m}$ or an object with a surface resistance between 10^4 and $10^9 \Omega$ measured at 23 °C and 50 % relative humidity of air or with a surface resistance between 10^4 and $10^{11} \Omega$ measured at 23 °C and 30 % relative humidity of the air.
		Provision of adequate protective measures according to BGR 132 Dangerous discharges from insulator surfaces can be avoided by increasing the surface conductivity and/or the relative humidity of the air to at least 65 %.
	The discharge of a charged insulated conductor may very easily lead to incendive sparks. With charged non-conducting objects, mostly but not only plastics, brush discharges and in case of quick separation (e.g. foils through rollers, transmission belts) also propagating brush	

(continued)

Table 4.18 (continued)

Type of ignition source	Ignition process	Protective measures
Lightning	discharges may occur. Brush discharges can normally only ignite explosible mixtures of gases and vapours, spark and propagating brush discharges additionally explosible dust/air and spray/air mixtures.	
	If lightning strikes an explosible atmosphere, ignition always takes place. Additionally there is a possibility of ignition due to strong heating of the current path of the lightning. A lightning strike causes strong currents which can produce incendive sparks in all directions even at larger distances from the location of the strike.	Overcurrent protection should be installed in adequate places.
	Electromagnetic fields are generated by any equipment producing or using high-frequency electrical energy (high-frequency equipment). Transmitters (e.g. mobile phones) or medical, scientific or industrial high frequency generators for heating, drying or tempering and for cutting and welding belong to this class.	Potential equalization required Provision of adequate lightning protection systems
Electromagnetic fields in the frequency range from 9 kHz to 300 GHz	All conductors within the radiation field act as receiving aerials; they are capable of igniting an explosible atmosphere if the field is strong enough and the conducting object big enough.	Provision of a safety distance between transmitter and receiving objects within the explosion hazard zone
		With transmitter aerials emitting in preferential directions the safety distance may be direction-dependent. Use of approved and appropriate high-frequency equipment only

(continued)

Table 4.18 (continued)

Type of ignition source	Ignition process	Protective measures
Electromagnetic radiation in the frequency range from 3×10^{11} to 3×10^{15} Hz, respectively wave lengths between 1,000 and 0.1 μm (visible spectrum)	Radiation in the visible spectrum can become a source of ignition by absorption in an explosible atmosphere or on solid surfaces, especially if focussed. For example, sunlight may cause ignition, if objects focus the radiation (e.g. filled spray bottle, concave mirror etc.). In case of laser radiation (e.g. transmission of messages, rangefinder, surveying, visual range measuring device) the power density even of the unfocussed radiation may be high enough as to cause ignition.	Limitation of radiation intensity Use of approved and appropriate equipment only
Ionizing radiation	Ionizing radiation, for example generated by an UV radiator, cathode ray tubes, laser, radioactive substances, accelerators or nuclear reactors can ignite explosible atmospheres, in particular those with dust particles.	The energy of a radiation pulse or the energy flux (power) of a permanent radiation should be kept so low that it is not sufficient to ignite the explosible atmosphere. Or the radiation must be encapsulated safely, so that any escape of radiation which might ignite the explosible atmosphere is prevented; additionally the heating of surfaces by radiation must be prevented so that ignition of the surrounding explosible atmosphere is not possible and that the explosible atmosphere cannot penetrate into the encapsulation or that an explosion occurring inside the encapsulation cannot affect the surrounding explosible atmosphere.
	Furthermore a radioactive source may heat up by self-absorption so that the ignition temperature of the surrounding explosible atmosphere is exceeded. By impact with ionizing radiation explosible substances and mixtures, especially if highly reactive radicals are formed, may be produced. The causes are radiolysis and chemical decomposition which thus create further explosion hazards.	

(continued)

Table 4.18 (continued)

Type of ignition source	Ignition process	Protective measures
Ultrasound	If ultrasound is used large portions of the energy released by the sound generator are absorbed by solid or liquid materials. Due to inner friction an exposed object is heated up so that it may reach, in an extreme case, a temperature above the ignition temperature of surrounding explosible materials.	Ultrasound should only be applied if the generated sound energy does not create an ignition hazard.
Adiabatic compression, shock waves, flowing gases	Shock waves and adiabatic compression can produce such high temperatures that an explosible atmosphere (including deposited dust) can be ignited. The temperature rise depends primarily on the pressure ratio and not on the pressure difference. Shock waves may, for example, arise when compressed gases in pipes are decompressed. They then penetrate regions of lower pressure at supersonic velocity.	Dangerous shock waves and compressions can normally be avoided if valves between equipment with large pressure differences can only be opened slowly.
	When shock waves are deflected or reflected by pipe elbows, restrictions, pipe end flanges, closed shut-off valves or such like particularly high temperatures are produced. In outlet pipes of air compressors and in connected vessels lubricant mists can be ignited by compression and explode.	

(continued)

Table 4.18 (continued)

Type of ignition source	Ignition process	Protective measures
Chemical reactions	Exothermic chemical reactions can heat up substances and thus become sources of ignition. Reactions underlying self-heating can already occur at ambient temperature. However, they then are normally so slow that the energy released is quickly transmitted to the surroundings so that the system temperature remains constant. Obstruction of heat transfer or storage at elevated temperature may cause an increase of the reaction rate to such an extent that the conditions for ignition are reached.	Materials with a tendency towards self-heating should be avoided.

Table 4.19 Quantitative proposal for zoning [46]

Degree of hazard	Annual frequency of the occurrence of the mixture	Frequency of the occurrence of the mixtures (detail)	Duration of the existence of the mixtures
Zone 0	Higher than in zone 1, e.g. more than 1000 times	Higher than in zone 1, e.g. more than 3 times/day	Longer than in zone 1
Zone 1	≥ 10 times <1000 times	$\geq$ once/month <3 times/day	Longer than 0.5 to 10 h
Zone 2	≥ 1 times <10 times	$\geq$ once/year <once/month	Shorter than 0.5 h

Zone 2 can comprise amongst others the

- areas surrounding Zones 0 or 1, or
- areas surrounding flanges with flat gaskets of conventional design with pipes in closed rooms.

Areas in which flammable materials are transported only in pipes with welded or brazed joints are not considered as having an explosion hazard.

Zone 20 as a rule only comprises the interior of apparatuses (mills, dryers, mixers, transport pipes, silos etc.), if dust can form explosive mixtures in dangerous quantities frequently or for prolonged periods of time.

Zone 21 may comprise amongst others areas surrounding apparatuses containing dust, if the dust can leak into the surroundings and settle there in endangering quantities (e.g. in milling locations, where the dust may leak from the mill and settle).

Zone 22 may comprise, for example, the storage of containers which are permeable for dust.

The classification comprises, of necessity, subjective elements. The following systematic approach is recommended:

- identification of the hazard potential,
- assessment of the hazard potential,
- delimitation of zones.

The classification should comprise the entire plant. The result of the classification should be laid down in written retrievably and consulted in case of modifications of use in order to enable one to modify the classification, if necessary.

General protection measures and measures to be used in specific cases are distinguished [43, 44]. The extent of the necessary protective measures is determined by the zone in question. The engineering implementation is the task of the designers of the corresponding apparatuses.

Tables 4.20, 4.21 and 4.22 provide an overview of the different types of ignition protection. For identification the corresponding designation is attached to the label Ex, for example Ex d in case of a flameproof enclosure.

Table 4.20 Types of ignition protection for electrical equipment exposed to hazards by gases and vapours (after [47])

Type of ignition protection	Designation	Standard	Basic principle	Main application
Flameproof enclosure	d (note 1)	EN 60079-1	Equipment parts which can ignite an explosible atmosphere are enclosed in a casing. This casing is designed to withstand the pressure caused by an explosion of an explosible mixture in its interior. Thus propagation to its surrounding atmosphere is prevented.	Switch devices and switchgear, commanding and signalling devices, controls, motors, transformers, heaters, lamps, potentiometers
Increased safety	e (note 1)	EN 60079-7	Additional technical measures are implemented in order to prevent with high reliability the possibility of impermissibly high temperatures, sparks and electric arcs inside or outside of an equipment, which do not occur during normal operation.	Terminal and junction boxes, control boxes for accommodating Ex devices (which are protected according to a different types of ignition protection), squirrel cage motors, lamps, installation materials, inductive ballasts, transformers
Pressurization	p	EN 60079-2	The occurrence of an explosible atmosphere inside a casing is prevented by maintaining a protective gas overpressure with respect to the surrounding atmosphere. If necessary the interior of the casing is permanently supplied with a protective gas so that the flammable mixture is diluted.	Switchgear and control cabinets, analysis equipment, big motors, slip ring and collector motors
Intrinsic safety	ia, ib, ic (note 2)	EN 60079-11	The equipment used in the explosion hazard zone only contains intrinsically safe circuits. A circuit is intrinsically safe if neither a spark nor a thermal effect can cause the ignition of a standard explosible atmosphere. The corresponding tests are carried out under standardized conditions, which comprise both normal operation and certain faulty states.	Measurement and control devices, communication devices, sensors, actors

(continued)

Table 4.20 (continued)

Type of ignition protection	Designation	Standard	Basic principle	Main application
Oil immersion	o	EN 60079-6	Electric equipment or parts thereof, starting resistors of the equipment are immersed in a protective liquid (e.g. oil) in such a way that an explosible atmosphere above the surface or outside the capsule cannot be ignited.	Transformers, starting resistors
Powder filling	q	EN 60079-5	By filling the casing of an electric equipment with a fine-grained grouting compound it is achieved that an electric arc formed during intended use inside its casing does not ignite a surrounding explosible atmosphere. Neither ignition by flames nor by increased temperatures may occur on the surface of the casing.	Transformers, capacitors, heating cable installation boxes
Encapsulation	ma, mb, mc (note 3)	EN 60079-18	Parts which may ignite an explosible atmosphere are embedded in a grouting compound so that the explosible atmosphere cannot be ignited.	Switch gear for low power, commanding and signalling devices, indicators, sensors

(continued)

Table 4.20 (continued)

Type of ignition protection	Designation	Standard	Basic principle	Main application
Type of protection	n	EN 60079-15	Electric equipment is not capable of igniting a surrounding explosible atmosphere (during normal operation and well-defined abnormal operating conditions). Electric equipment using this type of protection can only be used in category 3 (zone 2).	C: enclosed switch gear, non-incendive equipment, hermetically tight equipment, sealed equipment, encapsulated equipment P: simplified pressurized encapsulation A: non-sparking equipment L: energy limited electric circuit R: vapour proof

Note 1

Types of ignition protection „d/e“
The most important type of ignition protection for switch gear is “flameproof enclosure” mostly accompanied by the protection type “increased safety”. The ignition protection type “increased safety” implies that measures are taken to avoid sources of ignition with a high degree of reliability. However, switch gear creates sources of ignition by its operation itself. Therefore switch gear cannot be explosion protected by this protection type alone. Yet, together with the protection type “flameproof enclosure” “increased safety” plays an important role for switchgear and control cabinets. Also with modern explosion protected lamps a combination of several ignition protection types is applied in order to achieve an optimum as to safety, functionality and economy

Note 2

Intrinsically safe electric equipment and intrinsically safe parts of equipment are assigned to the ignition protection types ia, ib and ic. Equipment of the ignition protection type „ia” is appropriate for use in zone 0 (category 1), that of ignition protection type „ib” for use in zone 1 (category 2) and that of ignition protection type „ic” for use in zone 2 (category 3)

Note 3

Intrinsically safe electric equipment and intrinsically safe parts of equipment are assigned to the ignition protection types „ma”, „mb” und „mc”. Devices of the ignition protection type „ma” are appropriate for use in zone 0 (category 1), those of ignition protection type „mb” for use in zone 1 (category 2) and those of ignition protection type „mc” for use in zone 2 (category 3)

Table 4.21 Types of ignition protection for electrical equipment exposed to hazards by dusts (after [47])

Type of ignition protection	Designation	Standard	Basic principle	Main application
Pressurization	p	EN 61241-4	The occurrence of an explosible atmosphere inside a casing is prevented by maintaining a protective gas overpressure with respect to the surrounding atmosphere. If necessary the interior of the casing is permanently supplied with a protective gas so that the flammable mixture is diluted.	Switchgear and control cabinets May only be used in zones 21 and 22
Intrinsic safety	ia, ib, ic (note 4)	EN 60079-11 (EN 61241-11 only until August 4th 2014 harmonized)	The electronic circuits must satisfy the requirements of group II B of IEC 60079-11. Protection level IP 6X or encapsulation required. Limitation of the temperatures of all outer surfaces	Measurement and control devices, communication devices, sensors, actors
Encapsulation	ma, mb, mc (note 5)	EN 60079-18 (EN 61241-18 since August 1st 2012 no longer harmonized)	Parts which may ignite an explosible atmosphere are embedded in a grouting compound so that the explosible atmosphere cannot be ignited.	Switch gear for low power, commanding and signalling devices, indicators, sensors
Protection by casing	tD	EN 61241-1 (since July 7th 2010 no longer harmonized)	Based on the limitation of the maximum surface temperature of the casing and on the restriction of dust ingress by using a dust proof (IP 6X) and dust protected (IP 5X) casing	Controls and control cabinets

Note 4

Intrinsically safe equipment is assigned to ignition protection types ia, ib and ic

Devices of the ignition protection type „ia” are appropriate for use in zone 20 (category 1), those of ignition protection type „ib” for use in zone 21 (category 2) and those of ignition protection type „ic” for use in zone 22 (category 3)

Note 5

Electric equipment is assigned to the ignition protection types „ma”, „mb” und „mc”. Devices of the ignition protection type „ma” are appropriate for use in zone 0 (category 1), those of ignition protection type „mb” for use in zone 1 (category 2) and those of ignition protection type „mc” for use in zone 2 (category 3)

Table 4.22 Types of ignition protection for non-electrical equipment (after [47])

Type of ignition protection	Designation	Standard	Basic principle	Main application
Flow restricting enclosure	fr	EN 13463-2	–	Only for zone 2 or zone 22
Flame—proof enclosure	d	EN 13463-3	A type of ignition protection where equipment parts which may ignite an explosible atmosphere are enclosed in a casing. This casing is designed to withstand the pressure caused by an explosion of an explosible mixture in its interior. Thus propagation to its surrounding atmosphere is prevented.	Direct current motors
Constructional safety	c (hc)	EN 13463-5 (in the future: EN ISO 80079-37)	A type of ignition protection where constructive measures are applied which guarantee the protection against possible ignition by moving parts, heated surfaces, sparks and adiabatic compression.	Agitators, worm conveyers, clutches, brakes, gear boxes, hydrostatic equipment, pneumatic equipment, belt drives, fans
Control of ignition sources	b (hb)	EN 13463-6 (in the future: EN ISO 80079-37)	By monitoring sources of ignition which may arise although not present during normal operation such as heated parts or mechanical sparks a reaction in critical situations becomes possible. The basic idea of the ignition protection type “control of ignition sources” is to monitor potential sources of ignition in such a way that they can be eliminated before they become effective. Parameters such as temperature, level, revolutions, vibrations are monitored. It is essential for this type of protection and hence for this category that the monitoring equipment is highly reliable.	Gear boxes, face seals

(continued)

Table 4.22 (continued)

Type of ignition protection	Designation	Standard	Basic principle	Main application
Liquid immersion	k (hk)	EN 13463-8 (in the future: EN ISO 80079-37)	Protection type with which potential sources of ignition cannot become active or are totally segregated from the flammable atmosphere. This is achieved by immersing the ignition source totally in a protective liquid or by immersing its active surfaces and moistening them continuously. The explosible atmosphere above the liquid surface or outside the equipment casing can thus not be ignited.	

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The employees of industrial firms are exposed to hazards during work. These constitute a danger if they manifest themselves by disease, injury or death.

Hazards resulting from the use of work equipment, from the process and the handling of hazardous substances as well as those resulting from an accident have to be distinguished. Protection from the former is regulated primarily in the labour protection act [1] and the occupational safety [2] and hazardous substance [3] ordinances; protection from the consequences of major accidents is regulated in [4].

In [5] hazards from using work equipment, their assessment and possible countermeasures are described. Furthermore features of the work environment are treated which may have an influence on accidents. Many of the statements do not only apply to the process industry alone, but are independent of the industrial branch considered. In particular the following topics are dealt with:

- mechanical hazards:
 - unprotected moving machinery parts,
 - parts with a dangerous surface,
 - transport and moving work equipment,
 - uncontrolled moving parts,
 - hazard of falls,
 - hazard of plunges.
- electricity hazards
- hazardous substances
- biological exposure
- fire and explosion hazards
- cold and hot media
- climate
- lightning
- noise
- vibration
- radiation

- assimilation of information, handling of actuators
- physical stress
- psychical stress

With respect to the process industry a number of aspects are treated below based on [6].

The safety of workplaces in industry, and in particular, in the process industry results from the integration of the following three areas:

- **Technology**

Safety and personal safety must be considered from the very beginning of the planning of a plant. They concern the design of the plant, the layout of the workplaces as well as their environment and the working conditions of the personnel. After initiation of production the plant and the work equipment must be maintained in order to ensure permanent safety.

- **Organization**

An organizational framework or a safety management system is required to avoid accidents or incidents. It comprises procedures for monitoring the production process and the work environment such that hazards are understood and controlled. To this end hazard analyses for work places are carried out (cf. [5, 7, 8]) and events are evaluated in order to identify and implement measures apt to avoid their recurrence or to make them at least less probable. This has to be a continuous process.

- **Humans**

Safety requires the involvement of all employees. The collaborators are very familiar with the production process and the operational procedures. Hence, they must be involved in the development of the safety organization and procedures.

Knowledgeable and attentive collaborators are an essential for safety. They must be qualified and trained regularly. The necessary knowledge on the production process and operating procedures must be imparted to them in order to enable them to work safely. The training should also refer to specific health risks, safe behaviour and the correct behaviour in emergency situations.

5.1 Safe Design and the Procurement of Safe Apparatuses and Work Equipment

The design or modification of a plant should be carried out in such a way that a safe and trouble free operation at acceptable cost is possible. In order to achieve this amongst others the following should be observed [8]:

- The concept of inherent safety (cf. Sect. 4.2.1).
- Assurance of the mechanical integrity and reliability of apparatuses.

- Observation of proven design and safety rules and standards.
- Realization of systematic safety reviews at the different stages of planning and procurement including HAZOP analyses (cf. Sect. 9.1.2.3).
- Examination of all relevant operating procedures, operating and workplace conditions of plant and personnel (including the occurrence of malfunctions and equipment failures) in order to prevent unnecessary occupational hazards.

This includes that all relevant legal requirements and guidelines for the design and erection of plants and the manufacturing of apparatuses are observed (cf. [9, 10]).

Identification and understanding of the hazards of a process implies that the employees dispose of the necessary information, such as:

- process documentation, flow charts, P&I diagrams and process descriptions,
- design documentations for apparatuses and their operating instructions,
- documentation on the chemical and physical properties as well as on the hazards of the substances to be handled.

The corresponding documents have to be updated regularly.

5.2 Apparatuses, Machinery and Tools

The equipment required for working in a process plant comprises a wide spectrum: process apparatuses and machinery, machine tools, lifting equipment, hand tools, ladders, control room equipment, office machines etc.

Basic requirements are that the employees are equipped with work equipment suited for their work and the conditions of their workplace and that this equipment fulfils the legal provisions on design, construction and placing on the market. Safety and health must be guaranteed during intended use. If a hazard is unavoidable all the same appropriate additional measures have to be adopted in order to minimize the hazard.

Additionally, collaborators have to be trained. This requires

- pertinent information on hazards which may arise from the use of work equipment (even if not in operation),
- instructions with details on conditions of use, conceivable deviations and user experience,
- clearly understandable information and instructions (if necessary, in foreign languages).

If the use or maintenance of work equipment entails specific hazards it may only be used by personnel specifically trained for its use.

If safety depends on how work equipment is mounted or installed a test prior to its first use or start-up is required. In process plants tests and approvals are carried out before operation starts. Their purpose is to ensure that all equipment of the plant is installed correctly, operational and can be operated safely.

Work equipment has to be safe during its entire life cycle. Therefore it has to be maintained and repaired if necessary. Regular recurrent inspections are to guarantee safe functioning and an early detection of possible flaws. In fixing inspection intervals the following aspects should be taken into account:

- legal requirements for the work equipment or the installation,
- hazards associated with the use of the work equipment,
- operating and work place conditions,
- intended use and ranges of the operating parameters,
- instructions of the manufacturer or supplier,
- production quality of the work or plant equipment,
- operating experience and results from previous inspections.

Additional inspections should be carried out for specific reasons, for example after

- accidents or damage,
- modifications of work equipment,
- longer interruptions of production or standstills,
- environmental impacts.

The inspections must be carried out by designated bodies or specifically prepared personnel in compliance with the pertinent legal requirements.

Recently there are efforts to fix the times between inspections of functionality and integrity on the basis of probabilistic considerations (cf. Chap. 9). This is known as risk-based inspection or risk-based maintenance.

5.3 Hazard Assessment

In order to identify possible workplace hazards and to take remedial action a hazard assessment is carried out. It comprises the following six steps:

1. Systematic identification of working areas and workplaces to be assessed.
2. Collection of information about the workplaces, tasks to be performed, work equipment and processes, materials and chemical substances involved, assigned personnel.
3. Identification of the hazards at the workplaces with regard to the tasks to be performed.
4. Assessment of the potential hazards in order to eliminate or mitigate them.
5. Definition and planning of measures for eliminating or reducing the hazards for employees not deemed to be tolerable.

6. Documentation of the assessment results.

For this purpose often checklists are used, which normally include the following aspects:

- Unsafe work spaces—slippery surfaces, disorderliness, falling objects and tools, narrow work places and transport paths.
- Adverse ergonomic conditions of work—lifting or carrying heavy loads, heavy physical work, forced or poor postures, unfavourable ambient conditions (hot, cold, outdoors), poor lighting.
- Falls from height—high workplaces, climbing points, unsecured openings.
- Mechanical hazards—moving vehicles and machines, moving parts of machinery, uncontrolled moving objects, objects and parts with sharp edges or rough surfaces.
- Electricity—electric shock, electric arc, unwarranted voltage on casings, contact with active conductors, work near conductors under high voltage, use of electrical hand tools.
- Chemical substances—exposure to gases, vapours, aerosols, dusts of harmful chemicals to be handled or present in the breathing air, incorporation of liquid or solid harmful substances or exposure via skin or digestive tract, exposure to unpleasant smells.
- Explosion—possible presence of an explosible atmosphere at or near workplaces, possibility of a confined explosion inside equipment or apparatuses, thermal explosion (runaway reaction), decomposition of unstable substances, physical explosion (contact of water with hot melts or other hot liquid media).
- Fire—presence of flammable solids, liquids or gases at or near workplaces.
- Physical impacts—noise, vibration, ultrasound, ultraviolet or infrared radiation, laser, microwave or ionizing radiation, electromagnetic fields, electrostatic discharge.
- Hot/cold surfaces with a potential for injury.
- Overpressure, vacuum—release of media under pressure, leakage, opening of closed systems under pressure or vacuum.
- Biological hazards—from bacteria, viruses, parasites, mould as well as from biological agents used at work, inadvertently present or contained as contaminants in materials handled or present in the work environment.
- Stress, violence, harassment (mobbing) and other psychological factors.

The hazard assessment should actively involve the collaborators. Gender, age and health status of the collaborator whose workplace is assessed should be taken into account.

Based on the hazard assessment preventative and protective measures of different levels have to be identified and implemented:

1. Elimination of the hazard.
2. Reduction of the hazard by technical measures.

3. Reduction of the hazard by organizational measures.
4. Reduction of the hazard by personal protective equipment.

Measures inscribed in the first two levels are more effective and hence to be preferred. Organizational measures require the participation of the employees. Therefore they should not be relied upon exclusively, although they form part of any safety management strategy. If the hazards cannot be controlled sufficiently at the first three levels recourse must be had to personal protective equipment.

Example 5.1 Fall from a scaffold

A worker falls from a scaffold of a height of 7 m during maintenance work. Which consequences are to be expected, if he hits the ground

- (a) with his feet
- (b) with his head?

Solution

The potential energy E_{pot} of a body with a mass of m kg at a height of h m above ground is

$$E_{\text{pot}} = m \cdot g \cdot h \quad (5.1)$$

In a fall it is transformed into kinetic energy. If air resistance is conservatively neglected, the kinetic energy of the impact, E_{kin} , is

$$E_{\text{kin}} = \frac{m}{2} \cdot v_0^2 = m \cdot g \cdot h \quad (5.2)$$

The velocity on impact v_0 in m/s follows from Eq. (5.2) as

$$v_0 = \sqrt{2 \cdot h \cdot g} \quad (5.3)$$

The (negative) acceleration or deceleration on braking, b , is obtained from

$$d = \int_0^{t^*} (v_0 - b \cdot t) dt = v_0 \cdot t^* - \frac{b}{2} \cdot t^{*2} \quad (5.4)$$

and

$$v_0 - b \cdot t^* = 0 \quad (5.5)$$

In Eq. (5.4) d is the available braking distance in m. From Eqs. (5.4) and (5.5) we obtain the braking deceleration

$$b = \frac{v_0^2}{2 \cdot d} \quad (5.6)$$

The falling person arrives at the ground during the accident considered here after

$$t^* = \sqrt{\frac{2 \cdot h}{g}} = \sqrt{\frac{2 \cdot 7 \text{ m}}{9.81 \frac{\text{m}}{\text{s}^2}}} = 1.19 \text{ s} \quad (5.7)$$

According to Eq. (5.3) the speed of the impact amounts to $v_0 = 11.72 \text{ m/s}$.

- (a) Owing to the possibility of absorbing part of the kinetic energy with the legs a braking distance of $d = 0.2 \text{ m}$ is assumed for applying Eq. (5.6). Hence we have a deceleration of $343.4 \text{ m/s}^2 \hat{=} 35 \text{ g}$ according to Eq. (5.6).
- (b) If the impact occurs on the head, a braking distance of $d = 0.005 \text{ m}$ is assumed, since the skull bone lies immediately below the scalp. Consequently Eq. (5.6) results in a deceleration of $13,735.8 \text{ m/s}^2 \hat{=} 1,400.2 \text{ g}$.

According to [11] accelerations (or decelerations) of a falling body of more than 40 g are expected to be fatal. Hence, death is expected in case (b), whilst the fall of case (a) may be survived. $\square$

Example 5.2 Injury from electrical shock

Owing to an electrical defect the casing of an apparatus presents a voltage of $U = 230 \text{ V}$. During maintenance a worker touches the casing with his bare hand. The path of the electric current is as follows: casing-hand-body-shoe-ground. The workman wears conducting shoes in order to avoid electrostatic charging, which might be an undesired source of ignition (vid. Sects. 4.5.1.2 and 4.5.1.3). What consequences are to be expected?

How does the situation change if the workman wears the prescribed insulating shoes (ground resistance $R_E = 2,000 \Omega$)?

Data Contact resistance (casing-hand) $R_U = 300 \Omega$; impedance of the body: $R_K = 1,300 \Omega$; Assumption: contact resistance (body-ground) $R_B = 0 \Omega$, since shoes are made of conducting material.

Remark Conservatively the calculation is based on the maximum voltage.

Solution

The solution is obtained using Eq. (4.91). Accounting for the fact that the resistances are connected in series we obtain

$$I = \frac{U}{R_U + R_K + R_B} = \frac{230 \text{ V}}{1,300 \Omega + 300 \Omega} = 143.8 \text{ mA}$$

Since ventricular fibrillation occurs at 80 mA even after a short period of exposure and apnea may result [12], this accident is probably fatal. However, if the employee wears the prescribed shoes we have

$$I = \frac{U}{R_{\text{Ü}} + R_K + R_B} = \frac{230 \text{ V}}{1,300 \, \Omega + 300 \, \Omega + 2,000 \, \Omega} = 63.9 \text{ mA}$$

Between 50 and 80 mA there is only a hazard of apnea so that the shoes are probably life-saving. Yet it has to be borne in mind that the resistance values of the human body vary substantially. For example, they are reduced by sweating. On the other hand higher values apply in case of horny skin. Hence, the results are uncertain. This circumstance should be accounted for if the calculations are used as a basis of decision.

Example 5.3 Fall on a staircase

A collaborator with a height of $l = 1.8 \text{ m}$ hastens up a flight of stairs, stumbles and falls backwards with his head on a stair, since he does not manage to regain control of his body. The slope of the staircase is 45° . What consequences are to be expected?

Solution

The fall of a person is treated according to the theory of the falling rod (the resistance of the air is negligible). The angular velocity ω then is (cf. [13])

$$\omega^2 = 3 \cdot \frac{g}{l} \cdot (\cos \varphi_0 - \cos \varphi) \quad (5.8)$$

In Eq. (5.8) $\omega = \frac{d\varphi}{dt}$; φ is the angle with respect to the vertical line and φ_0 a small angle at the beginning of the fall caused by the stumble, l is the height of the person and g the acceleration of gravity. The non-linear differential Eq. (5.8) is solved by the Runge-Kutta procedure (cf. [14]).

The acceleration ω is used to calculate an impact velocity $v = \omega \cdot x$. The starting point in this is the foot which is assumed fixed; x is the distance from the foot, which lies between 0 and l , the height of the person.

From Eq. (5.8) we obtain with $\varphi_{\text{max}} = 90^\circ + 45^\circ = 135^\circ$ an angular velocity of $\omega = 5.33 \text{ s}^{-1}$.

Injuries are to be expected predominantly from impacts in the head region where the kinetic energy is highest.

The velocity results from $v_0 = \omega \cdot x$ for the skull (centre of gravity at $x = 1.75 \text{ m}$) as 13.52 m/s .

According to Eq. (5.6) we have the following deceleration with a braking distance of $d = 0.005 \text{ m}$:

Skull ($x = 1.75 \text{ m}$): $18,279.04 \text{ m/s}^2 \hat{=} 1,863.3 g$

Death of the person is to be expected (vid. Example 5.1). □

5.4 Personal Protective Equipment

Personal protective equipment (PPE) should only be used

- as an interim (short-time) measure before other measures can be implemented,
- if there is no engineering solution for avoiding contact between humans and media,
- if the engineering solutions for avoiding contact between humans and media are insufficient,
- during activities such as maintenance, cleaning and repair,
- in emergency situations.

Persons who use personal protective equipment should know why they have to wear it and how to employ it, how to maintain and how to repair it as well as when it must be replaced.

Which personal protective equipment must be used depends on the type of hazard and on which part of the body is to be protected. Table 5.1 gives an overview.

5.5 Safe Handling of Chemical Substances

Whenever hazardous materials are present at the workplace or its environment, safety measures have to be taken in order to minimize the hazard for collaborators and other persons. This is done by

- eliminating or minimizing the inhalation of chemical substances by controlling their concentrations in the air (keeping them as far as possible below existing threshold limit values) and the application of measures for reducing exposure,
- avoiding or reducing skin contact,
- avoiding the incorporation of solid or liquid materials.

The safe enclosure of materials must be ensured in process plants. Yet, the contact of employees with hazardous substances may not be totally avoided. The “normal operation” of such a plant entails a number of standard procedures such as filling, pouring in, decanting, draining, emptying, sampling, changing filter elements or cleaning. These may cause direct contact with substances. Additionally, maintenance work may require closed systems to be opened, thus leading to exposure.

Table 5.1 Hazards and corresponding personal protective equipment [6]

Organ/body part to be protected	Hazards	Personal protective equipment
Eyes	Chemical or metal splashes, dust, projectiles, gas and vapour, strong light, laser radiation	Safety spectacles, goggles, face shields, hand shields, visors
Head	Swinging, falling or flying objects, head bumping, hair entanglement	Industrial safety helmets, hair nets
Respiratory tract	Dust, vapour, gas, aerosols, oxygen-deficient atmospheres	Disposable filtering face piece or respirator, filtering half or full-face respirators, air-fed helmets, breathing apparatus (independent from ambient air)
Whole body	Temperature extremes, adverse weather, chemical or metal splashes, spray or jets from pressure leaks or spray guns, impact or penetration, contaminated dust, excessive wear or entanglement of own clothing	Conventional or disposable overalls, boiler suits, specialized protective clothing, chemical protective clothing, chain-mail or acid-proof aprons, high-visibility clothing
Hands and arms	Abrasion, temperature extremes, cuts and punctures, impact, chemicals, electric shock, skin infection, biological contamination	Gloves, gauntlets, mitts, wrist cuffs, armlets
Feet and legs	Wetness, electrostatic build-up, slipping, cuts and punctures, falling/rolling objects, bumping, squeezing, metal and chemical splashes, abrasions, heat/cold	Safety boots and shoes with protective toe caps and, if necessary, penetration-resistant soles, gaiters, leggings, spats
Hearing	Noise	Ear plugs—universal or custom fit, semi-insert ear plugs, ear muffs

5.5.1 Filling, Draining and Conveying of Hazardous Materials

In order to protect the personnel from contact with hazardous materials these should be handled as seldom as possible, i.e.:

- if filling and draining operations must frequently be performed manually and mostly with the same product, the best solution is to do this in a closed system (e.g. fixed piping from storage or receiver tank to mixing vessel or reactor, dosing of solids in powder form via receiver hopper and screw feeder);
- the use of gas return pipes or closed venting systems when conveying liquids avoids the breathing of vessels with varying liquid levels into work environments;

- the use of fixed drain systems or transfer lines allows one to handle residual liquid quantities without open contact and minimizes spills;
- limiting the use of hoses contributes to the reduction of liquid spills;
- proven spill-reducing, drainable connections are recommended if the use of flexible piping or hoses is required;
- mechanical integrity and reliability of systems containing hazardous materials must be ensured;
- hazardous dusts, vapours and gases in the air at workplaces have to be withdrawn by suction at their point of release;
- adequate ventilation of workplaces has to be provided.

5.5.2 Sampling

Samples have often to be taken in process plants in order to

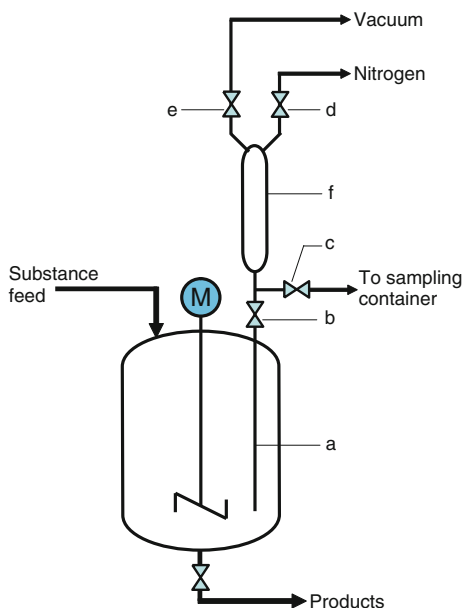
- control the type and quality of stored or supplied feed materials,
- monitor or control chemical reactions and other process steps,
- determine the quality and properties of intermediate products, products, and utility streams (vapour, water, air etc.).

Samples should be taken in such a way that the personnel does not enter into contact with hazardous materials. Should this not be possible, personal protective equipment has to be used.

Sample taking from vessels or tanks through the manhole should be avoided, especially if flammable materials are present. The discharge of flammable materials entails the possibility of a build-up of electrostatic charges (vid. Sects. 4.5.1.2 and 4.5.1.3). Hence, they should not flow into open sample containers. A closed sample taking system should rather be used, for example a nitrogen purged sample container, as shown in Fig. 5.1. It serves to take a sample from a vessel with vacuum without requiring a flushing stream prior to sample taking. When the sampling container is connected the following work steps are taken:

1. open product valve (b),
2. open nitrogen valve (d) and blow the immersion tube (a) empty with nitrogen,
3. open vacuum valve (e) and draw the product to fill the gauge vessel (f),
4. close product valve (b) and vacuum valve (e),
5. open sample valve (c) and nitrogen valve (d) to transfer the liquid sample from the gauge vessel (f) to the connected sampling container with nitrogen pressure,
6. open product valve (b),
7. close sample valve (c) and nitrogen valve (d).

Fig. 5.1 Sampling with vacuum in a closed system.
a Immersion tube. **b** Product valve.
c Sample valve. **d** Nitrogen valve.
e Vacuum valve. **f** Gauge vessel



5.5.3 Cleaning of Vessels and Other Equipment

Occasional cleaning of equipment of a process plant is unavoidable in order to remove fouling products (scale) and dirt. This serves to maintain the functioning of the plant and the product quality. Cleaning mostly requires work in narrow spaces especially if vessels are concerned. Specific hazards for the personnel may then derive from residual harmful substances still present. Therefore systems are preferred which automatically carry out the necessary cleaning procedures such as:

- rinsing,
- cleaning with water or other cleaning agents,
- steaming or boiling out with suitable agents,
- high impact cleaning with spray or jet for difficult residues,
- sanitizing, disinfecting, sterilizing.

They make access of personnel to narrow confined spaces unnecessary.

Additionally, there are a number of procedures which reduce the necessity for manual cleaning by plant personnel and thus their exposure:

- Flushing, steaming or boiling out tanks, vessels, heat exchangers, pipes etc. from the inside using the process capabilities.
- Tank wash lances/tank washers with rotating fluid or motor driven tank washing nozzles under high pressure.

- Vacuum transfer systems with remote suction of materials through a filtration system into a removal skip.
- Pumping out sludge, water or liquid into a removal skip. This is often employed prior to cleaning, or after cleaning with tank cleaning heads.

However, it should always be borne in mind that high pressure and ultra high pressure jets are capable of easily cutting solid materials. Hence, they lead to severe and often lethal injuries when persons are hit. The high pressure jet liquids are often contaminated and can enter deeply into body tissue thus causing inflammations in addition to injuries. The equipment should therefore only be used by informed and experienced personnel. If possible, mechanically guided jet cleaning devices should be applied.

In any case the necessary protective measures have to be adopted and maintained during work. This includes as well the use of personal protective equipment.

Example 5.4 Repair work at a biogas plant

In order to repair a valve of a biogas plant a worker goes down into a pit. However, hydrogen sulphide had escaped inadvertently from the plant. Since it is a heavy gas (density relative to that of air: 1.2), it had accumulated in the pit. Two minutes later a rescuer arrives who is equipped with a self-contained breathing apparatus (independent from the surrounding air).

What consequences are to be expected?

Data density of hydrogen sulphide at 15 °C $\rho = 1.44 \text{ kg/m}^3$, $M = 34.081 \text{ g/mol}$; $Z = 0.9914$, $p = 100,000 \text{ Pa}$

Solution

Health consequences are assessed using the corresponding probit equation (B20) for death due to exposure to hydrogen sulphide. This requires the concentration to be converted into ppm according to Eq. (2.54), which gives

$$C^* = \frac{1,000 \frac{\text{g}}{\text{kg}} \cdot 0.9914 \cdot 8.3144 \frac{\text{J}}{\text{molK}} \cdot 288.15 \text{ K}}{100,000 \text{ Pa} \cdot 34.081 \frac{\text{g}}{\text{mol}}} \cdot 1,440,000 \frac{\text{mg}}{\text{m}^3} \triangleq 1,003,572 \text{ ppm}$$

The application of Eq. (B20) leads to a probit value of

$$Y = -11.15 + \ln(1,003,572^{1.9} \cdot 2) = 15.45$$

The corresponding probability of death is calculated by evaluating the standard normal distribution for the argument $Y - 5 = 11.49$ (cf. Sect. 2.6.2.2). Equation (2.56) gives

$$P_{\text{death}} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} \exp\left(-\frac{x^2}{2}\right) dx = \phi(Y-5) = \phi(10.45) \approx 1$$

Any help arrives too late. If not equipped with the breathing apparatus the rescuer would die as well. $\square$

5.6 Work with Special Hazards: Permit to Work System

In order to carry out hazardous activities safely a permit to work system is used. It describes the activities, which require a permit to work, and the necessary safety measures as well as their implementation. The notification, communication and authorization of hazardous activities shall apply to both, site and contractor employees. In this way the permit to work is formalized and documented; clear responsibilities are created. Table 5.2 gives some examples of activities which should be authorized in the context of a permit to work system.

The persons who are responsible have to

- clarify the scope of the work activity, location and timing, and ensure that all hazards and precautions are fully described by the permit to work,
- review the scope of the permit to work, requests and confirm that the precautions specified are adequate to control the hazards associated with the work,
- ensure that there are no conflicting concurrent activities,
- ensure that the work activities and authorizations are discussed, clarified and communicated to all persons or groups involved,
- confirm that all relevant parties have been consulted and have provided their input,
- arrange for qualified personnel to implement the defined hazard controls,
- authorize by signature the work to proceed and confirm that all controls are in place and have been signed off,
- provide the necessary system documentation and relevant system control documentation, displaying the copies of signed and “live” permits at a central location as current information,
- ensure that the permit to work is formally issued including the duration of its validity and relating conditions,
- maintain appropriate consultations with the work coordinator and supervisors or contractors’ representatives,
- ensure that the permit holder understands the nature of the hazards and applied controls and the actions to be taken in the event of an emergency,
- cancel or prolong the permit to work and remove the safety measures after being notified of the termination of the work,

Table 5.2 Examples of hazardous activities which should be controlled by permits to work [6]

Activity	Definition	Examples
Hot work	Work with a source of ignition present and a fire or explosion hazard	Welding, cutting, grinding in zones with explosion hazards
		Using non-certified, resp. non explosion-proof tools, machines, vehicles in zones with explosion hazards
		Any heat or spark producing work in zones with explosion hazards
		Welding, cutting, grinding in any enclosed space in equipment (cavities)
Confined space entry	Entry and work in a confined space	Personnel entry into tanks, vessels, silos, ducts, pits, tunnels, sewers, drains, wastewater systems
		Work at places with possible release or presence of suffocating gases
Opening of process equipment and piping	Work to open a closed system, which may cause an unintended or uncontrolled release of hydrocarbons or other flammable or toxic materials or media under pressure	Disconnecting or opening closed pipelines
		Opening of tanks, vessels, equipment parts under pressure
Electrical work	Work on electrical equipment and on low and high voltage systems with the hazard of a dangerous electric shock	Access to electrical installations
		Work at or in electrical installations
		Removal or repair of electric drives
		High voltage switching
		Securing of electrical installations and equipment
Work at heights	Work at elevated or other places with the hazard of falling down, falling through surfaces without sufficient carrying strength or sinking in	Work on roofs
		Work on other elevated places
		Work on scaffolds, scaffolding
		Removal of grid-mesh/floor parts
		Work at places with possible falls to lower locations
		Work over water

(continued)

Table 5.2 (continued)

Activity	Definition	Examples
Excavation work	Excavation and digging work with the hazard of damaging buried pipelines, cables, sewage etc.	Opening of pavements
		Providing access to buried pipeline parts or vessels/tanks for repair
		Underground laying of new cables
Work at or near ionizing radiation emitters	Any kind of work with or near emitters of ionizing radiation	Use of ionizing radiation or radioactive sources for materials or equipment examination
		Removal or repair of instruments with ionizing radiation emitters
		Work in or near equipment with ionizing radiation emitters
Movement of heavy loads near process equipment	Crane hauling or movement of heavy loads or vehicles near process or other equipment containing hazardous materials	Removal or installation of heavy parts of equipment in the process plant by a crane
		Working with a mobile crane in a process plant
		Truck transports into a process plant
Pressure testing of process equipment	Integrity checks with pressure testing of process equipment	Conducting pressure tests as strength testing of equipment before start-up or in recurring inspections
		Gas pressure tests
		Testing gas, vacuum or liquid tightness of pipes or vessels

- verify that the worksite is inspected for the specification of hazard control measures to be sure that the preparatory work and precautions have been carried out and are active,
- verify that the worksite is inspected before the permit to work ends and that it is left in a safe and clean condition,
- archive the permit to work documentation, inform the plant staff of the termination of the work and give clearance for resuming operation.

If several activities are to be carried out concurrently it is recommended to name a coordinator.

An important part of the permit to work system is the isolation of sources of hazards and energy before maintenance, repair or other activities requiring a permit are carried out. Such hazard and energy sources are:

- high pressure or vacuum in parts of equipment;
- high temperatures of walls or connected media;
- hazardous materials, e.g. in scale or deposit build-up;
- explosions and fires;
- lack of oxygen—presence of suffocating or heavier-than-air gases;
- moving parts of machinery or other mechanical hazards (e.g. raised heavy loads or parts that can sink down, auxiliary units under pressure such as hydraulic or pneumatic systems);
- electric shock, electric arc, inadvertent voltage on casings, contact with active conductors;
- ionizing radiation emitters;
- hazard of falling to lower positions.

The measures for isolating or controlling the sources of hazards and energy must account for

- the type of plant and equipment, on which the work is performed,
- nature of the sources of hazards and energy,
- complexity of the isolation (number of necessary steps and activities and locations of the isolation points),
- number of persons involved in the work as well as in the isolation and control,
- duration of the isolation,
- possibility that persons not involved in the work are affected by the isolation.

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In order to safely operate a process plant the desired process conditions have to be set and monitored. The process control engineering (PCE) equipment serves this purpose. It comprises devices for measurement as well as open loop and closed loop control.

Measuring devices measure with the help of sensors in several parts of the plant material properties (density, viscosity, composition etc.) or process parameters (pressure, temperature, flow, level, number of revolutions, valve positions etc.).

Open loop control (non-feedback control) is a procedure by which one or several input variables influence output variables based on a concept of system behaviour (model) and the current status of its parameters. Characteristic is the open chain, i.e. no feedback from the system is integrated into the control process.

Contrary to this closed-loop control adapts the measured material properties and process parameters (current values) to the required values (set values). This is done by converting the signals supplied by the sensors into a controller output which influences final control elements such as control valves. A characteristic of the closed-loop control is the comparison between the current process signals and their respective setpoints. The controlled parameter permanently influences itself via the closed loop.

The equipment for realizing a control task—sensor, controller, final control element—together with the part of the plant (apparatuses, machinery, pipework etc.) lying between the sensor and the final control element form the control loop. This is shown in the block diagram of Fig. 6.1 and in the technical implementations, as for example in Figs. 4.11 and 6.2.

The control of processes is necessary because they are subject to stochastic disturbances, which cause variations of process parameters. The weather may be named (e.g. temperature changes affect the properties of the materials used such as density, viscosity). Switching and human interventions which normally follow a plan but are not always executed at exactly the same moment or to the same degree disturb the process parameters.

Whilst closed-loop control is mostly required for level 1 (normal operation) of the multi-level safety concept shown in Table 4.1, open-loop control is primarily used at levels 2, 3, and 4 (monitoring system, safety system, damage limiting system).

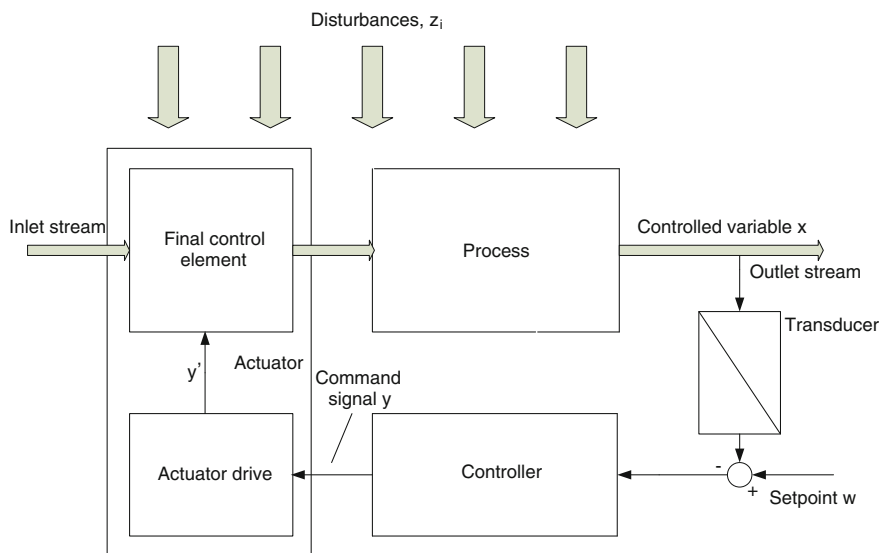


Fig. 6.1 Block diagram for controlling material flows (*closed-loop*)

In what follows the basics of control are presented. Details may be found, for example, in [1, 2].

6.1 Control System Characteristics and P&I Diagrams

The process engineer has to specify the measuring and control tasks in the process flow diagram (PFD) or at the latest in the P&I diagram („piping and instrumentation diagram“, P&ID).

In the first place the degree of automation has to be fixed. Very simple manually operated experimental plants may only need few measuring and indicating instruments placed in the location of the measurement in question, hand-operated controllers and final control elements. With an increasing number of control loops and registers the burden on the personnel decreases. The control system characteristics have to be adapted to the dynamic behaviour of the control loop. Controllers with the following characteristics are distinguished (cf. [1]):

- P-(Proportional) which produces an output proportional to the input;
- I-(Integral) which produces an output proportional to the time integral of the difference between the current and the set value of the input;
- D-(Differential) which produces an output proportional to the rate of change of the input.

Often combinations of the different characteristics such as PI and PID controllers are used.

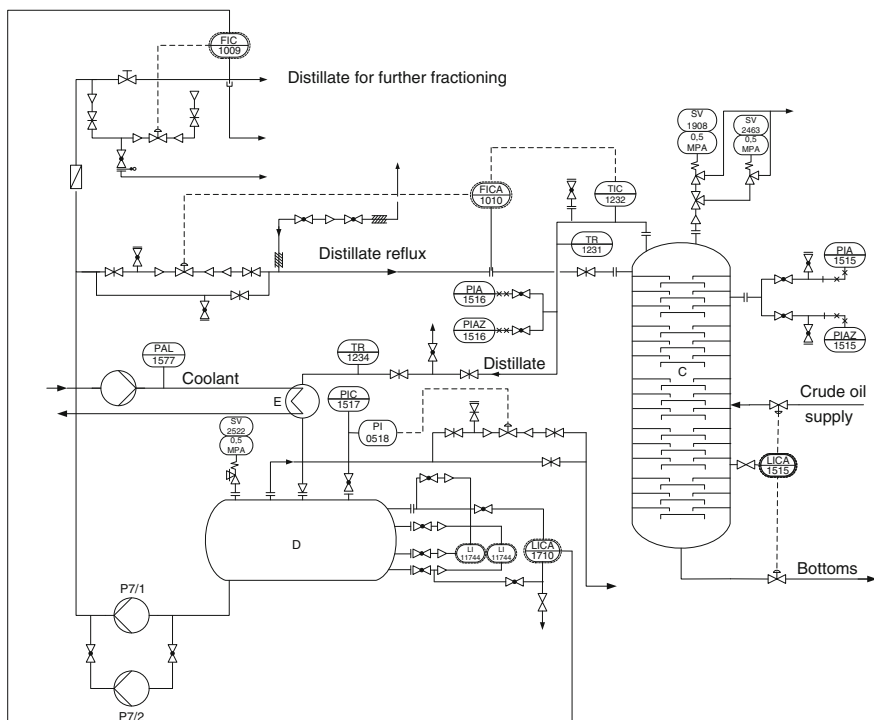


Fig. 6.2 Simplified P&ID for the pre-distillation in a petrol production (*C* rectification column; *D* reflux tank for separating the aqueous phase from the distillate; *P* pumps; *Z* high reliability protective device) [3]

Indication of the measurements is an important part of the P&ID, as shown in Fig. 6.2 and explained below.

The functions of the measuring and control equipment are usually represented by a circle or an oval. If these are inscribed in a square or rectangle, the corresponding function is realized by a programmable logic system (vid. Sects. 6.2 and 6.3). If the letters within the circle or oval are not underlined the measuring readings are in situ. Underlining points to processing in the control room, and double underlining means that the variables are processed in an ancillary control room. The function is identified by a sequence of letters, for example,

- PAHL: pressure alarm high low

Table 6.1 Identifying letters for measuring and control equipment (according to [4]), ANSI/ISA S5.1 and ISO 14617-6 (identification consists of up to five letters)

Letter	Column 1 (measured value)	Columns 2–5 (modifier)
A	Analysis	Alarm
B	Burner, combustion	User's choice
C	User's choice	Control
D	Density	Difference
E	Voltage	–
F	Flow rate	Ratio
G	Gauging, position or length	–
H	Hand (manually initiated operated)	High
I	Current	Indicate
J	Power	–
K	Time or time programme	–
L	Level	Low
M	Moisture or humidity	–
N	User's choice	–
O	User's choice	Orifice, open
P	Pressure or vacuum	–
Q	Quality, for example analysis, concentration, conductivity)	Integral or sum
R	Nuclear radiation	Record
S	Speed or frequency	Switching
T	Temperature	–
U	Multivariable	–
V	Viscosity	–
W	Weight or force	–
X	Unclassified variables	
Y	User's choice	Auxiliary devices
Z	User's choice	Actuator, driver or unclassified final control element

The meaning of the letters is explained in Table 6.1.

Example 6.1 Control characteristics of a P and PI controller

In order to demonstrate the behaviour of different controller types a strongly simplified (linearized model) of an exothermic reaction is used. A more realistic treatment is given in Case Study 4.2.

The process is supposed to be stationary and to receive an input of thermal energy (heat input) at point in time $t = 0$. As a consequence the process temperature begins to rise.

Which variations with time of temperature and mass flow are to be expected if the cooling is controlled by a

- (a) Proportional (P) controller,
- (b) Proportional-plus-Integral (PI) controller?

Data: $a = 3.45 \times 10^{-4} \text{ s}^{-1}$; $b = 2.50 \times 10^{-2} \text{ K kg}^{-1}$; temperature increase due to heat input from $t = 0$ $c = 0.1 \text{ K s}^{-1}$; amplifier gain $K_p = 0.1 \text{ kg (Ks)}^{-1}$; stationary operating temperature $T_s = 289.86 \text{ K}$; $K_I = 0.05 \text{ kg K}^{-2} \text{ s}^{-1}$.

Model

- Time behaviour of temperature T

$$\frac{dT}{dt} = a \cdot T - b \cdot \dot{m} \quad (6.1)$$

- Control of the coolant mass flow $\dot{m}$ as a function of temperature

$$\frac{d\dot{m}}{dT} = K_p \quad (6.2)$$

Stationary Solution

The stationary solution of Eq. (6.1) ($dT/dt = 0$), which applies before heat is input, provides the stationary coolant mass flow $\dot{m}_s$

$$\dot{m}_s = \frac{a}{b} \cdot T_s = \frac{3.45 \cdot 10^{-4} \text{ s}^{-1}}{2.50 \cdot 10^{-2} \frac{\text{K}}{\text{kg}}} \cdot 289.86 \text{ K} = 4.00 \frac{\text{kg}}{\text{s}} \quad (6.3)$$

Solution of the Equation for the Time-Dependent Coolant Mass Flow

The general solution of Eq. (6.2) is

$$\dot{m}(T) = K_p \cdot T + A \quad (6.4)$$

The constant of solution A is determined from the stationary situation

$$\begin{aligned} \dot{m}(T_s) &= K_p \cdot T_s + A = \frac{a}{b} \cdot T_s \text{ whence} \\ A &= \left(\frac{a}{b} - K_p \right) \cdot T_s \text{ and} \\ \dot{m}(T) &= K_p \cdot T + \left(\frac{a}{b} - K_p \right) \cdot T_s \end{aligned} \quad (6.5)$$

Time Dependence of Temperature After Heat Input

Inserting the result for the mass flow rate from Eq. (6.5) in Eq. (6.1) one obtains

$$\frac{dT}{dt} = a \cdot T - b \cdot \left(K_p \cdot T + \left(\frac{a}{b} - K_p \right) \cdot T_s \right) + c \quad (6.6)$$

Equation (6.6) already accounts for the heat input from $t = 0$ via constant c . The Laplace transform of Eq. (6.6) is (cf. [5])

$$s \cdot \tilde{T} - T_s = a \cdot \tilde{T} - b \cdot K_p \cdot \tilde{T} + (K_p \cdot b - a) \cdot \frac{T_s}{s} + \frac{c}{s} \quad (6.7)$$

In order to obtain Eq. (6.7) we used

$$\begin{aligned} \tilde{T} &= \int_0^{\infty} T(t) \exp(-s \cdot t) \text{ and} \\ \int_0^{\infty} \frac{dT}{dt} \cdot \exp(-s \cdot t) dt &= s \cdot \tilde{T} - T_s \end{aligned}$$

Rearrangement of Eq. (6.7) leads to

$$\tilde{T} = \frac{T_s}{s + b \cdot K_p - a} + \frac{K_p \cdot b - a}{s + b \cdot K_p - a} \cdot \frac{T_s}{s} + \frac{1}{s + b \cdot K_p - a} \frac{c}{s} \quad (6.8)$$

After inversion of Eq. (6.8) we have

$$\begin{aligned} T(t) &= T_s + \frac{c}{bK_p - a} \cdot [1 - \exp(-(bK_p - a) \cdot t)] \\ &= 289.86 \text{ K} + 46.40 \cdot [1 - \exp(-0.002155 \cdot t)] \end{aligned} \quad (6.9)$$

Equation (6.9) shows the drawback of P-control. A deviation from the set value always remains. In this case we have: $\lim_{t \rightarrow \infty} T(t) = 336.26 \text{ K}$.

PI Controller

Compared with the foregoing treatment the dependence of the coolant mass flow rate on temperature differs. Instead of Eq. (6.2) one uses

$$\frac{dm}{dT} = K_p + K_I \cdot T \quad (6.10)$$

The general solution of Eq. (6.10) is

$$\dot{m}(T) = K_p \cdot T + \frac{K_I}{2} \cdot T^2 + A \quad (6.11)$$

Equating Eq. (6.11) with (6.1) for the stationary state enables one to determine the constant of solution A. The particular solution then is

$$\dot{m}(T) = K_p \cdot T + \frac{K_I}{2} \cdot T^2 + \frac{a}{b} \cdot T_s - K_p \cdot T_s - \frac{K_I}{2} \cdot T_s^2 \quad (6.12)$$

Inserting Eq. (6.12) in Eq. (6.1) gives

$$\frac{dT}{dt} = a \cdot T - b \cdot \left(K_p \cdot T + \frac{K_I}{2} \cdot T^2 + \frac{a}{b} \cdot T_s - K_p \cdot T_s - \frac{K_I}{2} \cdot T_s^2 \right) + c \quad (6.13)$$

where the heat input represented by c is already incorporated. After rearrangement Eq. (6.13) gives

$$\begin{aligned} \frac{dT}{dt} &= (a - b \cdot K_p) \cdot T - b \cdot \frac{K_I}{2} \cdot T^2 + G \text{ where} \\ G &= c - b \cdot \left(\frac{a}{b} \cdot T_s - K_p \cdot T_s - \frac{K_I}{2} \cdot T_s^2 \right) \end{aligned} \quad (6.14)$$

The non-linear differential Eq. (6.14) is solved by the following assumption (educated guess)

$$T(t) = \frac{u'}{u} \cdot \gamma \quad (6.15)$$

Inserting Eq. (6.15) in Eq. (6.14) gives

$$\frac{u'' \cdot u - u' \cdot u'}{u^2} \cdot \gamma = (a - b \cdot K_p) \cdot \frac{u'}{u} \cdot \gamma - b \cdot \frac{K_I}{2} \cdot \left(\frac{u'}{u} \right)^2 \gamma^2 + G \quad (6.16)$$

In order for the quadratic term on either side of Eq. (6.16) to be cancelled the following has to be true:

$$-\left(\frac{u'}{u} \right)^2 \gamma = -b \cdot \frac{K_I}{2} \cdot \left(\frac{u'}{u} \right)^2 \gamma^2 \quad \text{and hence } \gamma = \frac{2}{b \cdot K_I} \quad (6.17)$$

After rearrangement Eq. (6.16) gives

$$u'' \cdot \gamma = (a - b \cdot K_p) \cdot u' \cdot \gamma + G \cdot u \quad (6.18)$$

Using $u(t) = \exp(\lambda \cdot t)$ in Eq. (6.18) gives

$$\lambda_{1,2} = \frac{a - b \cdot K_p}{2} \pm \sqrt{\frac{G}{\gamma} + \left(\frac{a - b \cdot K_p}{2}\right)^2} \quad (6.19)$$

Applying Eqs. (6.18), (6.19) and (6.15) becomes

$$T(t) = \frac{A \cdot \lambda_1 \exp(\lambda_1 \cdot t) + B \cdot \lambda_2 \exp(\lambda_2 \cdot t)}{A \cdot \exp(\lambda_1 \cdot t) + B \cdot \exp(\lambda_2 \cdot t)} \cdot \frac{2}{b \cdot K_I} \quad (6.20)$$

The initial condition $T(0) = T_s$ leads to

$$B = A \cdot \frac{T_s \cdot b \cdot K_I - 2 \cdot \lambda_1}{2 \cdot \lambda_2 - T_s \cdot b \cdot K_I} \quad (6.21)$$

Thus we have

$$T(t) = \frac{\lambda_1 \exp(\lambda_1 \cdot t) + \frac{T_s \cdot b \cdot K_I - 2 \cdot \lambda_1}{2 \cdot \lambda_2 - T_s \cdot b \cdot K_I} \cdot \lambda_2 \cdot \exp(\lambda_2 \cdot t)}{\exp(\lambda_1 \cdot t) + \frac{T_s \cdot b \cdot K_I - 2 \cdot \lambda_1}{2 \cdot \lambda_2 - T_s \cdot b \cdot K_I} \cdot \exp(\lambda_2 \cdot t)} \cdot \frac{2}{b \cdot K_I} \quad (6.22)$$

Figures 6.3 and 6.4 show the results for temperatures and coolant mass flow rates. It is obvious that in case of the PI controller there is no deviation. The temperature deviation resulting with the P controller would lead to a runaway of the reaction, a fact which does not show here because the Arrhenius relation was linearized for the sake of the example. Furthermore it is evident that the time dependence of the process parameters depends on the controller gains.

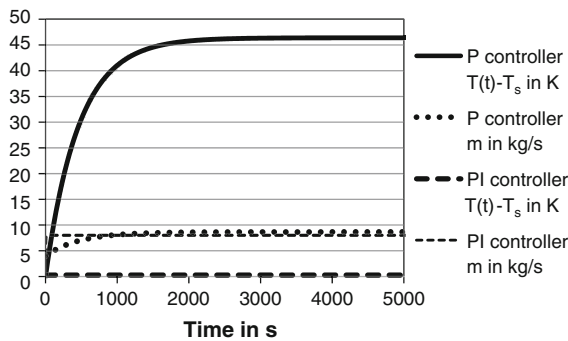
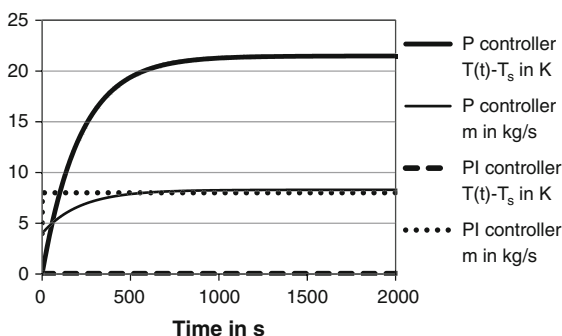


Fig. 6.3 Temperature above the stationary temperature T_s in K and coolant mass flow rate $\dot{m}$ in kg/s ($K_p = 0.1 \text{ kg (Ks)}^{-1}$ and $K_I = 0.05 \text{ kg K}^{-2} \text{ s}^{-1}$)

Fig. 6.4 Temperature above the stationary temperature T_s in K and coolant mass flow rate $\dot{m}$ in kg/s ($K_p = 0.2 \text{ kg (Ks)}^{-1}$ and $K_I = 0.5 \text{ kg K}^{-2} \text{ s}^{-1}$)



□

The description of the dynamic behaviour of the process is fundamental for the design of the control system. The required setpoints of the relevant process parameters must be known for devising the safety function (cf. Case Study 4.2).

Along the material stream several controllers influencing the stream (flow, level, pressure) may be necessary. In order to avoid that the controls interfere with one another a decoupling by sufficiently large buffers is recommended (this may, however, counteract the intention of having small inventories of hazardous substances for safety reasons). For pumps a holding tank with a residence time of 10 min is sufficient to ensure decoupling, unless it may be renounced completely because of apparatuses downstream, e.g. columns, which may serve as buffers.

By connecting several control loops even difficult control tasks may be solved. With cascade control the measured signal serves as input for a master controller. The output of the master controller becomes the setpoint for a slave controller, which in turn receives another measured signal as input. The output of the slave controller then provides the command signal for the final control element in the plant. In a split range configuration a controller provides output signals for several final control elements in response to an input signal or the controller generates a command signal from several sensor inputs.

6.2 Programmable Electronic Systems

With the advent of process computers a transition was initiated in the process industry from pneumatic analogue control (advantageous for reasons of explosion protection) or electrical analogue control to control using microprocessors. This leads to the use of programmable electronic systems (PES). These allow more adequate interventions in the process than conventional control, since they can use all signals from the process for diagnosing its state and generating the response. The use of freely programmable algorithms enables one to attain a high degree of flexibility.

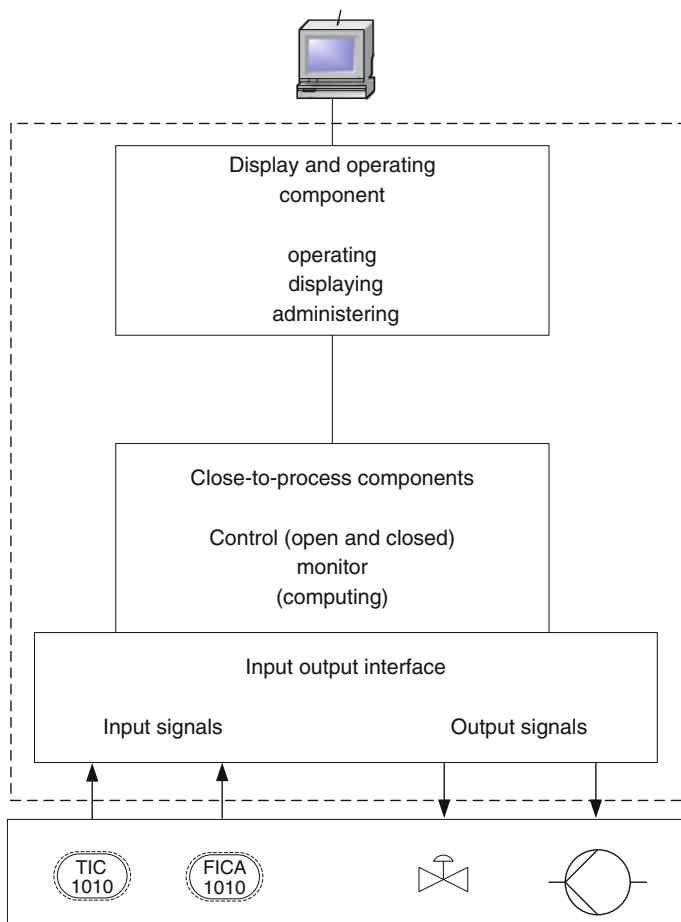


Fig. 6.5 Setup of a PES (after [2])

With a PES the representation and operation of the plant is realized almost entirely via monitors. The basic setup of such a system is shown in Fig. 6.5. It is now briefly commented upon following [2].

In the input/output interface input signals are received and after processing in the PSE output to the final control elements (vid. Fig. 6.6).

Analogue signals arrive as current or voltage values directly from sensors or converters. They must be digitalized in order to be processed. They are input into the PES via an analogue-to-digital converter. The PES outputs digital signals, which may either be used directly as command signals for final control elements or after passing through a digital-to-analogue converter.

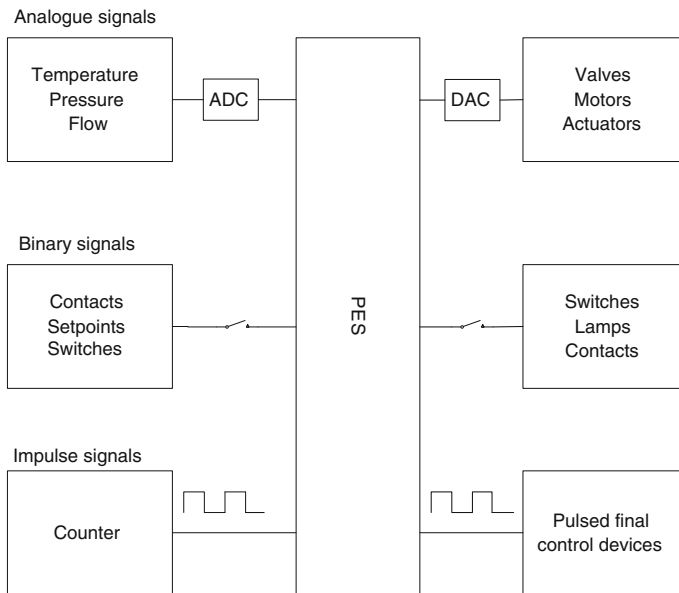


Fig. 6.6 Input and output interfaces of a PES (*ADC* Analogue-to-digital converter, *DAC* Digital-to-analogue converter; after [2])

Binary signals stem from relays, limit monitors, pushbuttons and switches. They can be processed directly and be output to contacts, switches or lamps. All measuring values are cyclically scanned and checked before processing as to their validity. The following distinctions are made.

6.2.1 Components Close to the Process

This part of the computer is the basis of the PES. The fundamental automatized functions are carried out here:

- monitoring,
- closed loop control,
- open loop control.

6.2.1.1 Monitoring

The objective of monitoring is to identify disturbances or dangerous operational states as soon as possible. Reactions of the system can then be

- malfunction alarm on monitor and printer,
- activation of protection and safety systems,
- safety instrumented system (emergency trip of the plant).

6.2.1.2 Closed Loop Control

The control of operational states is an important task of the PES, especially for continuous processes. Software components carry out this task.

6.2.1.3 Open Loop Control

Discontinuous production plants need repetitive procedures. These have to be controlled using pre-programmed function blocks, e.g.

- control function: the control function serves to control and monitor technical equipment such as solenoid valves, motors, positioners etc.
- dosing loop: the dosing loop registers quantities and meter readings during the dosing procedure. After the prefixed volume has been fed the dosing procedure is stopped.

Interlocks which are often required for safety reasons can be implemented in the PES without problems and virtually no additional requirements of equipment. They are realized by fixed programs, which cannot be modified by the operators. In conventional plants with practically independent control loops the interlock function requires additional devices, e.g. relays, to be installed.

Nevertheless in the context of the licensing procedure hardwired activation of safety functions is demanded in addition to PES activation, since it is still difficult to assess the reliability of computer programs. However, in [6] aspects are presented which have to be accounted for if electric/electronic/programmable electronic systems (E/E/PES) are used to realize safety functions. Below some general remarks are made following [7]. The corresponding mathematical and technical treatment is presented in Chap. 11. Since the requirements of [6] can be applied as well to other control systems than (E/E/PES) we speak in what follows of PCE equipment with the understanding that any of the above types of process control is meant.

6.3 Integration of PCE in the Safety Concept

Process control engineering (PCE) is used at all levels shown in Table 4.1, i.e.

- normal operation,
- control of malfunctions,
- avoidance of damage,
- hazard defence.

The area of use, scope and type of the PCE are determined by safety analyses. Simple configurations should be preferred and care should be taken that false alarms do not provoke dangerous states of the plant.

6.3.1 Normal Operation

The PCE equipment controls the specified operation. The system implements the automatic functions required for the production. It measures and controls all the process parameters necessary for the production including auxiliary functions such as logging and report generation.

High level control algorithms, complex control sequences, automated recipe processing, and optimization strategies are increasingly implemented. Many binary, digital, and analogue signals have to be processed if all these tasks are to be performed. Because the functions of PCE systems are called on continuously or frequently during operation these devices are subject to plausibility checks by plant personnel. Hence, failures and malfunctions should be detected immediately.

6.3.2 Monitoring Malfunctions

If a plant leaves its range of specified operation because one or several process variables have left their nominal range the PCE equipment intervenes at the limit between specified operation and tolerable fault conditions, unless there is a reason for plant shut-down.

Alarms are generated to arouse the attention of the plant personnel or prompt a direct intervention. Automatic action of the PCE equipment aimed at returning the process variables to their permissible range are also provided for.

Additionally provisions exist to prevent the triggering of safety systems unless this is definitely required.

6.3.3 Damage Avoidance

The safety-relevant PCE equipment has the mission to avoid impermissible fault states. It is required if the plant has a potential for adopting states which could lead to harm to humans, environment or property.

The PCE equipment monitors the safety-relevant process variables and initiates the following actions if one or more variables leave the permissible fault range:

- limit control;
- alarming the operators so that appropriate countermeasures can timely be initiated.

The functions of the PCE safety instrumented system have priority over the functions of the preceding levels.

6.3.4 Hazard Defence

Measures of hazard defence are intended to mitigate the consequences of accidents. Among them figure the following measures, where of course only the active systems are triggered by PCE equipment.

- Passive protection systems such as dikes, drainage systems, blast walls, bunkers, flame arrestors, structural fire protection.
- Active mitigation systems, which consist of detection, decision and action (e.g. gas detector, which triggers measures like emergency shutdown, segmentation, water or steam/ammonia curtains, or scrubber systems).
- Active fire protection systems (e.g. smoke or heat detectors, deluge sprinkler systems or foam systems).

6.3.5 General Requirements

Activities to be carried out for the operating level and functions for protecting from property damage are indicated in [8]. No detailed requirements are specified. This is different for devices for realizing safety-relevant control, protection functions or limiting damage. Some of the requirements are given below.

The following tasks must be carried out for PCE equipment:

- Safety task statement, safety problem.
- Function of the PCE safety instrumented system.
- Assessment of the availability of the PCE equipment.
- Determination of technical and organizational measures.
- Quantitative risk analysis (vid. Chaps. 8–11).

From this we derive

- Technical design (principle).
- Extent and frequency of scheduled proof testing.
- Other organizational measures (e.g. scheduled maintenance).

The following important principles are to be observed when designing and constructing a PCE safety instrumented system:

- Proven in use, reliable hardware and installation methods shall be implemented.
- The PCE safety device must be simple in construction. Fault effects (e.g. secondary or sequential faults in the PCE safety device) should, if possible, be limited by suitable barriers to fault propagation, e.g. high-impedance decoupling, short-circuit strength, galvanic isolation, etc.

- Harmful effects due to environment and products, e.g. vibration, impact, static strain forces, thermal loads, corrosion, contamination, mechanical wear, and lack of electromagnetic compatibility must be accounted for.
- Effects including those resulting from lightning, ripple content in power supply, grid malfunctions, grid noise, etc., must be taken into account.
- Fail-safe characteristics of equipment shall be utilized, e.g. valve with spring return to the safe position etc. It should be remembered that fail-safe characteristics are generally limited to partial functions of devices.
- If control and monitoring systems are shared in a PCE safety instrumented systems, the safety function shall take priority over other functions and the shared elements must be rated as for the safety device.
- The measurement of process safety variables, processing operations, and the implementation of the safety instrumented function shall be done with accuracy and speed suited to the safety problem.
- The measurement ranges of process safety variables shall be selected to guarantee sufficient resolution. The limit values shall be sufficiently distant from the limits of the measurement range in order to assure safety.
- The setpoints shall be protected against unintentional incorrect settings.
- As a rule, automatic reactivation after initiation of the safety function should be disabled.
- The inference of a process variable from a combination of measurement signals shall be used only if the direct measurement of the process variable is not possible, or if there are no sufficiently reliable measurement methods for a direct measurement.
- Analogue process safety variables should be displayed together with their setpoints in the monitoring (control) room or at local control panels. In this way operating personnel can do plausibility checks, so that fault detection times are kept short and the setpoint setting can be checked easily.
- The design of PCE safety systems must also account for maintenance and start-up needs, ease of inspection and accessibility of all components of the PCE.
- Manual overrides can be provided to allow inspection or repair of PCE safety instrumented systems during normal operation.
- In isolated cases redundant PCE safety instrumented systems should be examined to determine whether fire hazard or the possibility of mechanical damage necessitates a split construction or a protected and/or separate power supply and spatial separation of cable trays.

Additionally

- all important components of the safety PCE system should be designated as such in the documentation and labelled accordingly in situ and in the control room,
- a functional test of the PCE safety system must be carried out before the first start-up.

The use of the safety PCE system requires a number of organizational measures to be implemented. Of special importance are

- continuous monitoring (surveillance),
- functional tests,
- maintenance,
- repair.

6.3.5.1 Continuous Monitoring

Malfunctions of the PCE safety system must be discovered by regularly observing the process variables and checking their plausibility by the operating team. External damage of equipment has to be detected by visual examination. It must be repaired immediately.

6.3.5.2 Functional Tests

Functional tests are necessary in order to detect so-called passive failures, i.e. failures which do not become manifest because of a still functioning redundancy, a missing demand on the system or a lack of self-testing. The intervals between functional tests must be fixed on the basis of a safety analysis. The functional tests are to simulate real demand conditions. For example, the sensor of a control loop should not be simulated by applying a voltage as a substitute for its output. Since it may be necessary to (disable) bridge certain devices during functional tests it must be ensured that the disabled function is taken over by other devices. After the functional test is terminated the disabling must be ended. For example, not enabling a disabled function after maintenance played an important role in the Buncefield accident (vid. Table 1.1).

6.3.5.3 Maintenance

In case of severe service conditions or certain types of measurements (e.g. process analytical instruments) scheduled maintenance may be necessary. Work orders must explain the nature and extent of the periodic maintenance.

6.3.5.4 Repair

Repair of PCE safety devices must be performed without delay by qualified personnel whenever defects are found in the devices and there is no alternative for maintaining the level of safety.

Further important aspects are:

- Documentation: all work on PCE safety devices must be documented.
- Analysis of faults: all faults must be investigated in order to make their occurrence less probable by technical modifications or shorter intervals between tests.

- Disabling: if a device must be disabled during start-up or coast-down or because of repair, measures must be taken to maintain the safety level. The disabling must be clearly recognizable.
- Re-start after activation of the PCE safety system: a restart of components etc., which were turned off by the PCE safety system, must be prevented. Even if the plant has returned to operation, the parts which have been turned off must be tested before returning them to operation.
- Setting of setpoints: limit values may only be modified by order of the plant manager who has to check if safety is affected. The correctness of the new setting must be controlled.

The importance of control for technical processes is demonstrated once again in the following section, where a reaction capable of oscillations is examined in detail.

6.4 Case Study: Iron-Catalyzed Oxidation of Ethanol with Hydrogen Peroxide

The iron (III)-nitrate catalyzed reaction of ethanol with hydrogen peroxide forming acetaldehyde may exhibit temperature oscillations. In what follows the laboratory experiment described in [9] is modelled using the reaction kinetics and details on the experimental reactor given there. The reaction is described by:

$\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}_2 \xrightarrow{\text{cat}} \text{CH}_3\text{CHO} + 2\text{H}_2\text{O}$	$\Delta h_R = -302 \text{ kJ/mol}$
$\text{CH}_3\text{CHO} + \text{H}_2\text{O}_2 \xrightarrow{\text{cat}} \text{CH}_3\text{COOH} + \text{H}_2\text{O}$	$\Delta h_R = -389 \text{ kJ/mol}$
$\text{H}_2\text{O}_2 \xrightarrow{\text{cat}} 0,5 \text{ O}_2 + \text{H}_2\text{O}$	$\Delta h_R = -95 \text{ kJ/mol}$
$\text{cat} + \text{CH}_3\text{COOH} \rightarrow \text{cat}^*$	$\Delta h_R = -0 \text{ kJ/mol}$
$\text{cat}^* \rightarrow \text{cat} + \text{CH}_3\text{COOH}$	$\Delta h_R = -0 \text{ kJ/mol}$

cat* denotes a catalytically inert acetate iron(III) complex

The reaction rates are modelled as follows:

$$r_1 = k_1 \cdot \exp\left(-\frac{E_1}{R_m \cdot T}\right) \cdot c_{\text{cat}} \cdot c_{\text{H}_2\text{O}_2}$$

$$r_2 = k_2 \cdot \exp\left(-\frac{E_2}{R_m \cdot T}\right) \cdot c_{\text{cat}} \cdot c_{\text{H}_2\text{O}_2} \cdot c_{\text{CH}_3\text{CHO}}$$

$$r_3 = k_3 \cdot \exp\left(-\frac{E_3}{R_m \cdot T}\right) \cdot c_{\text{cat}} \cdot c_{\text{H}_2\text{O}_2}$$

$$r_4 = k_4 \cdot \exp\left(-\frac{E_4}{R_m \cdot T}\right) \cdot c_{\text{cat}} \cdot \sqrt{c_{\text{CH}_3\text{CHO}}}$$

Table 6.2 Reaction parameters of the iron-catalyzed reaction of ethanol with hydrogen peroxide

Reaction i	$\Delta H_{R,j}$ in kJ/mol	k_i	$E_{A,j}$ in kJ/mol
1	-302	1.49480×10^{16} in $l \text{ mol}^{-1} \text{ s}^{-1}$	105.5
2	-389	1.95132×10^{20} in $l^2 \text{ mol}^{-1} \text{ s}^{-1}$	126.2
3	-95	6.66600×10^{14} in $l \text{ mol}^{-1} \text{ s}^{-1}$	105.0
4	0	1.17637×10^7 in $l^{0.5} \text{ mol}^{-0.5} \text{ s}^{-1}$	55.69
5	0	3.83330×10^4 in s^{-1}	45.04

$$r_5 = k_5 \cdot \exp\left(-\frac{E_5}{R_m \cdot T}\right) \cdot c_{\text{cat}^*}$$

The corresponding parameter values are given in Table 6.2.

The kinetic equations are as follows:

- water (H_2O)

$$V \cdot \frac{dc_{\text{H}_2\text{O}}}{dt} = \dot{V} \cdot c_{\text{H}_2\text{O},\text{in}} - \dot{V} \cdot c_{\text{H}_2\text{O}} + V \cdot (2 \cdot r_1 + r_2 + r_3) \quad c_{\text{H}_2\text{O}}(0) = 41.61 \frac{\text{mol}}{l}$$

- hydrogen peroxide (H_2O_2)

$$V \cdot \frac{dc_{\text{H}_2\text{O}_2}}{dt} = \dot{V} \cdot c_{\text{H}_2\text{O}_2,\text{in}} - \dot{V} \cdot c_{\text{H}_2\text{O}_2} - V \cdot (r_1 + r_2 + r_3) \quad c_{\text{H}_2\text{O}_2}(0) = 0$$

- ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)

$$V \cdot \frac{dc_{\text{CH}_3\text{CH}_2\text{OH}}}{dt} = \dot{V} \cdot c_{\text{CH}_3\text{CH}_2\text{OH},\text{in}} - \dot{V} \cdot c_{\text{CH}_3\text{CH}_2\text{OH}} + V \cdot r_1 \quad c_{\text{CH}_3\text{CH}_2\text{OH}}(0) = 4.9907 \frac{\text{mol}}{l}$$

- acetaldehyde (CH_3CHO)

$$V \cdot \frac{dc_{\text{CH}_3\text{CHO}}}{dt} = \dot{V} \cdot c_{\text{CH}_3\text{CHO},\text{in}} - \dot{V} \cdot c_{\text{CH}_3\text{CHO}} + V \cdot (r_1 - r_2) \quad c_{\text{CH}_3\text{CHO}}(0) = 0$$

- acetic acid (CH_3COOH)

$$V \cdot \frac{dc_{\text{CH}_3\text{COOH}}}{dt} = -\dot{V} \cdot c_{\text{CH}_3\text{COOH}} + V \cdot (r_2 - r_4 + r_5) \quad c_{\text{CH}_3\text{COOH}}(0) = 0$$

- cat (iron(III)-nitrate)

$$V \cdot \frac{dc_{\text{cat}}}{dt} = \dot{V} \cdot c_{\text{cat},\text{in}} - \dot{V} \cdot c_{\text{cat}} - V \cdot (r_4 - r_5) \quad c_{\text{cat}}(0) = 4.9497 \cdot 10^{-2} \frac{\text{mol}}{\text{l}}$$

- cat* (inert acetate iron(III) complex)

$$V \cdot \frac{dc_{\text{cat}^*}}{dt} = -\dot{V} \cdot c_{\text{cat}^*} + V \cdot (r_4 - r_5) \quad c_{\text{cat}^*}(0) = 0$$

- energy balance for the process

$$\begin{aligned} \sum_{i=1}^5 c_i \cdot M_i \cdot c_{p,i} \cdot V \cdot \frac{dT}{dt} &= \dot{Q} + P_{\text{heat}} + P_{\text{stir}} - \dot{Q}_{\text{cool}} - \dot{Q}_{\text{loss}} \quad T(0) = 294.85 \\ \dot{Q} &= \dot{V} \cdot (c_{\text{H}_2\text{O},\text{in}} \cdot M_{\text{H}_2\text{O}} \cdot c_{p,\text{H}_2\text{O}} \cdot T_{\text{in}} + c_{\text{H}_2\text{O}_2,\text{in}} \cdot M_{\text{H}_2\text{O}_2} \cdot c_{p,\text{H}_2\text{O}_2} \cdot T_{\text{in}} \\ &\quad + c_{\text{CH}_3\text{CH}_2\text{OH},\text{in}} \cdot M_{\text{CH}_3\text{CH}_2\text{OH}} \cdot c_{p,\text{CH}_3\text{CH}_2\text{OH}} \cdot T_{\text{in}} - \sum_{i=1}^5 c_i \cdot M_i \cdot c_{p,i} \cdot T) \\ &\quad + \sum_{i=1}^3 (-\Delta H_{r,i}) \cdot r_i(t, T) \cdot V \end{aligned}$$

In the above relations i denotes the different substances: H_2O ($i = 1$), H_2O_2 ($i = 2$), $\text{CH}_3\text{CH}_2\text{OH}$ ($i = 3$), CH_3CHO ($i = 4$) and CH_3COOH ($i = 5$).

The heat capacity of the catalyst is neglected because of the small quantity present.

$$\dot{Q}_{\text{cool}} = \dot{m} \cdot c_{p,\text{H}_2\text{O}} \cdot (T - T_{c,\text{in}}) \cdot \left[1 - \exp\left(-\frac{F \cdot U}{\dot{m} \cdot c_{p,\text{H}_2\text{O}}}\right) \right]$$

describes the heat removal by the coolant and

$\dot{Q}_{\text{loss}} = 6.6 \cdot 10^{-3} \cdot (T - T_{\text{am}})$ in kW, where T_{am} is the ambient temperature, the heat loss to the surroundings of the reactor.

- PI controller for the coolant mass flow

Table 6.3 Properties of the substances involved in the iron-catalyzed reaction of ethanol with hydrogen peroxide

Substance	Property		
Water H ₂ O	Molar mass	M _{H₂O}	18.016 kg/kmol
	Heat capacity	c _{p,H₂O}	4.187 kJ/(kg K)
	Density	ρ _{H₂O}	999.1 kg/m ³
Hydrogen peroxide H ₂ O ₂	Molar mass	M _{H₂O₂}	34.02 kg/kmol
	Heat capacity	c _{p,H₂O₂}	2.619 kJ/(kg K)
	Density	ρ _{H₂O₂}	1,450 kg/m ³
Ethanol CH ₃ CH ₂ OH	Molar mass	M _{CH₃CH₂OH}	46.07 kg/kmol
	Heat capacity	c _{p,CH₃CH₂OH}	2.44 kJ/(kg K)
	Density	ρ _{CH₃CH₂OH}	789 kg/m ³
Acetaldehyde CH ₃ CHO	Molar mass	M _{CH₃CHO}	44.05 kg/kmol
	Heat capacity	c _{p,CH₃CHO}	2.02 kJ/(kg K)
	Density	ρ _{CH₃CHO}	780 kg/m ³
Acetic acid CH ₃ COOH	Molar mass	M _{CH₃COOH}	60.05 kg/kmol
	Heat capacity	c _{p,CH₃COOH}	2.05 kJ/(kg K)
	Density	ρ _{CH₃COOH}	1050 kg/m ³
Iron(III)-nitrate	Molar mass	M	403.999 kg/kmol
	Density	ρ	1,680 kg/m ³

$$\begin{aligned}
 \frac{dm}{dt} &= \frac{K_1}{\tau} \cdot (\dot{Q} + P_{\text{heat}} + P_{\text{stir}} - \dot{Q}_{\text{cool}} - \dot{Q}_{\text{loss}}) + \frac{K}{\tau} \cdot s_h & \dot{m}(0) &= 2 \\
 \frac{ds_i}{dt} &= \frac{k_c}{p_i} \cdot (K_{mV/T} \cdot T - u_c) & s_i(0) &= 0 \\
 s_h &= K_{mV/T} \cdot T - u_c + s_i & s_h(0) &= 0
 \end{aligned}$$

The properties of the substances involved are contained in Table 6.3. Table 6.4 gives an overview of the process parameters.

In the first place the reactor content is heated to 54 °C. Thereafter the dosing of the feed and the cooling start. On the one hand, the coolant mass flow is fixed to a value of 4.1667×10^{-2} kg/s, on the other the coolant mass flow is controlled by the PI controller described above to produce a constant reaction temperature of 54 °C.

Figures 6.7 and 6.8 show the results of the calculation. Without control of the coolant mass flow the reaction temperature oscillates. However, the coolant mass flow control present in all industrial processes, “smoothens” the oscillations by appropriately adjusting the coolant mass flow. This then leads to stable reactor behaviour.

Table 6.4 Process parameters for the iron-catalyzed reaction of ethanol with hydrogen peroxide

General process conditions	Symbol	Value
Volume of the reaction zone	V	2.4 l
Temperature at reaction onset	T(0)	294.85 K
Mass of the reactor content	—	2.3992 kg
Volumetric flow through the reactor	$\dot{V}$	9.7222×10^{-3} l/s
Concentration of water in feed stream	$C_{H_2O,in}$	42.26 mol/l
Concentration of hydrogen peroxide in feed stream	$C_{H_2O_2,in}$	3.1194 mol/l
Concentration of ethanol in feed stream	$C_{CH_3CH_2OH,in}$	2.3035 mol/l
Concentration of acetaldehyde in feed stream	$C_{CH_3CHO,in}$	1.4872 mol/l
Concentration of catalyst in feed stream	$C_{cat,in}$	5.2546×10^{-2} mol/l
Temperature of feed	T_{in}	288.15 K
Area of the heat exchanger surface (jacket and coil)	F	0.3 m ^{2a}
Overall coefficient of heat transfer	U	0.91 kW/(m ² K)
Power of heating	P_{heat}	1.6 kW
Heat input from stirring	P_{stir}	0.2 kW
<i>Cooling system and control</i>		
Coolant inlet temperature	$T_{c,in}$	277.98 K
Heat capacity of the coolant (water)	$c_{p,k}$	4.18 kJ/(kg K)
Coolant mass flow (uncontrolled)	$\dot{m}$	4.1667×10^{-2} kg/s
Cooler time constant	T	200.0 s
Cooler gain	K	200 kg/(s mV)
Command signal	u_c	327.15 mV
Proportional gain factor	k_c	0.5
Gain of the converter temperature to voltage	$K_{mV/T}$	1.0 mV/K
Converter gain	K_I	1 kg/(s kW)
Integrator coefficient	p_i	4000.0 s

^afor the purpose of calculation the heat transfer area of the coil was increased fictiously in order to simulate the effect of additional condensation cooling

Fig. 6.7 Variation with time of the temperature for the iron-catalyzed reaction of ethanol with hydrogen peroxide

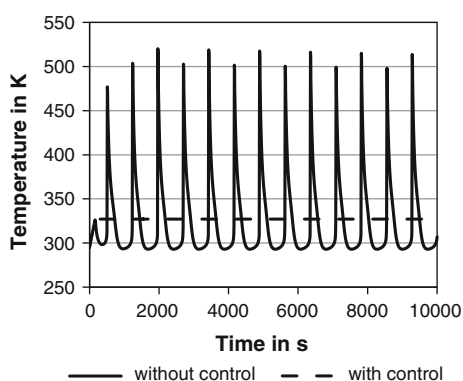


Fig. 6.8 Variation with time of the coolant mass flow for the iron-catalyzed reaction of ethanol with hydrogen peroxide—controlled

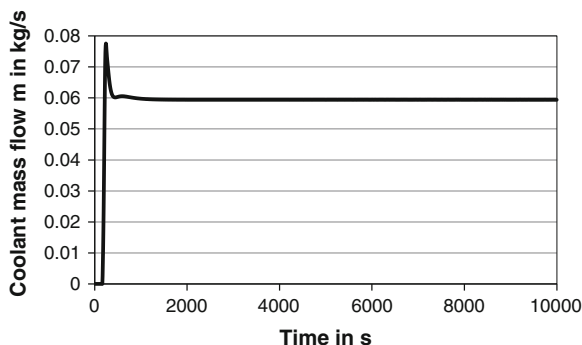
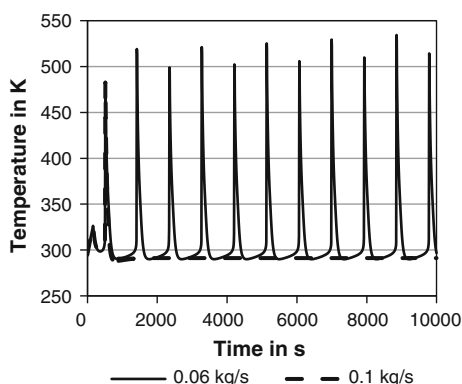


Fig. 6.9 Variation with time of the temperature for the iron-catalyzed reaction of ethanol with hydrogen peroxide after an intervention at $t = 500$ s



Alternatively the effect of an intervention by which the coolant mass flow is increased after $t = 500$ s is assessed. Figure 6.9 shows the result.

Evidently there is either virtually no influence ($\dot{m} = 0.06$ kg/s) or the temperature is permanently lowered to $T = 291$ K ($\dot{m} = 0.1$ kg/s). In the latter case the oscillations disappear, yet the production comes to a virtual standstill since hardly any acetic acid is formed. In order to control the process appropriately feedback control is required.

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After explaining in the preceding chapter the control of processes by means of process control engineering equipment, subsequently safety devices are treated. They should become effective if the process control engineering measures should fail. Since processes take place inside enclosures (vessels, pipework etc.) the objective is to avoid the loss of their integrity (loss of containment, LOC). An important reason for such a loss is a pressure which lies above the failure pressure of the enclosure. This can, for example, result from component failures. Frequently increased pressure is accompanied by increased temperature, which lowers the load limits of materials and hence their failure pressure. Further reasons for a loss of integrity of enclosures are fires and explosions which cause pressure and/or temperature increases.

In what follows the most important technical devices for coping with the above mentioned situations are treated.

In case of overpressure these are:

- safety valves,
- bursting discs,

and for fires and explosions

- flame arresters,
- explosion barriers.

In the first place pressure relief devices are presented in more detail.

7.1 Safety Valves

According to [1] a safety valve is a valve which automatically—without support of any other energy than that of the discharging medium—allows a discharge mass flow such that a predetermined pressure is not exceeded. Its design is such that it closes and impedes the further discharge of the medium once the normal working pressure conditions are restored. The safety valve may either open rapidly or almost continuously (not necessarily linearly) depending on the gradient of pressure increase above its setpoint. The following designs are distinguished:

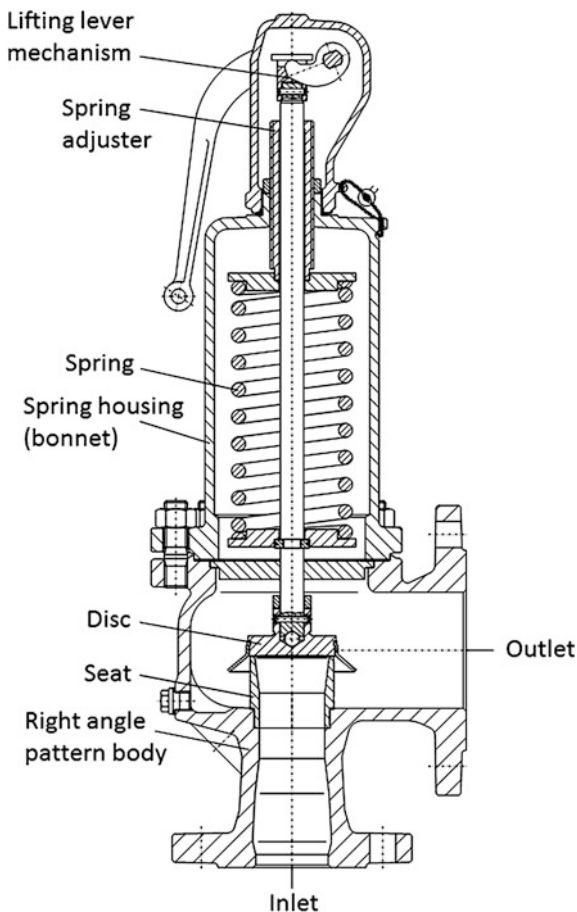
- **Direct loaded safety valve:**
A safety valve where the load exerted by the pressure of the medium on the disc is only counteracted by a direct mechanical load, for example a weight, a lever with a weight or a spring.
- **Assisted opening safety valve:**
A safety valve which can additionally be opened by a mechanically driven auxiliary device at a pressure below its setpoint. Even if the auxiliary device should fail it fulfils all requirements of [1].
- **Supplementary loaded safety valve:**
A safety valve where the tightening pressure is increased by an additional load until the setpoint is reached. The supplementary load is produced by an external power source and is reliably removed as soon as the setpoint pressure is exerted on the entry of the safety valve. The magnitude of the supplementary load is chosen such that the relief valve discharges its recognized mass flow at a load of at the most 1.1 times the permissible load of the object to be protected, even if the supplementary load should not be removed.

The standard [1] furthermore contains amongst others information on materials, type examination, the determination of characteristic parameters, dimensioning and labelling.

The best known type of safety valve is the spring loaded safety valve. Figure 7.1 shows a high performance full lift safety valve [2].

One can recognize the right angle pattern valve body with the valve inlet and outlet as well as the cap volume which accommodates the spring and allows movement. The valve disc prevents the pressurized medium from entering the zone of lower pressure at the outlet, when closed. The disc is held against the nozzle seat (under normal operating conditions) by the spring, which is housed in an open or closed spring housing arrangement (bonnet) mounted on top of the body. The amount of compression on the spring is adjustable by the spring adjuster to alter the pressure at which the disc is lifted off its seat. The compression on the spring is chosen according to the operating pressure of the object to be protected. A seal serves as protection against unwarranted modification of the spring compression. Despite a leak-tight closure small leakage rates are unavoidable.

Fig. 7.1 Full lift safety valve (courtesy of [2])



Should a malfunction cause an increase of the pressure above the setpoint of the valve, it opens and prevents the pressure from rising further. If the pressure drops below the setpoint during the progression of the disturbance, the valve closes again and thus prevents further discharge of the medium.

Correct functioning, as described above, is only to be expected with correct design. On the one hand the dimensions must be chosen such that the maximum mass flow rate occurring during the disturbance can be discharged (vid. Sect. 7.4). On the other hand the valve cross section must not be too large in order to avoid unstable behaviour (e.g. chattering, fluttering).

7.2 Bursting Disc Protection Device

A bursting disc protection device is usually made up of the bursting element (bursting disc) and the corresponding disc mounting. A bursting disc consists of one or several slotted metal foils which are destroyed when the rated pressure is exceeded. It then abruptly opens the entire cross section. However, when pressure drops again discharge is not terminated. After rupture the bursting disc cannot be re-used. It must be replaced by a new one. The bursting disc protection device is practically 100 % leak-tight.

7.3 Combination of Safety Valve and Bursting Disc Protection Device

The combination of a bursting disc protection device and a safety valve, as shown in Fig. 7.2, combines the advantages of both protection devices, viz. the practically 100 % leak-tightness with the re-seating after pressure drop. In case of highly corrosive media or a tendency to polymerize the safety valve can be protected by a bursting disc installed in front of it (vid. Fig. 7.2).

The pressure gauge in Fig. 7.2 serves to monitor the space between the bursting disc and safety valve. It would indicate bursting disc failure. In normal conditions no pressure is signalled whilst after failure the internal pressure is indicated. Furthermore, the space serves for venting in order to prevent possible leakages from building up impermissible backpressure. It must be borne in mind that the bursting pressure changes with temperature.

7.4 Dimensioning of Relief Devices

7.4.1 Energy Balance for the Stationary Flow Process

The energy balance per unit mass for the stationary flow process is as follows (cf. [3]):

$$q_{12} + w_{12} = h_2 - h_1 + \frac{1}{2} \cdot (c_2^2 - c_1^2) + g \cdot (z_2 - z_1) \quad (7.1)$$

In Eq. (7.1) we have

- g acceleration due to gravity in ms^{-2}
- q_{12} heat absorbed from the surroundings in J/kg
- h enthalpy in J/kg
- w_{12} work done on the surroundings in J/kg
- c flow velocity in m/s
- z geometric elevation in m

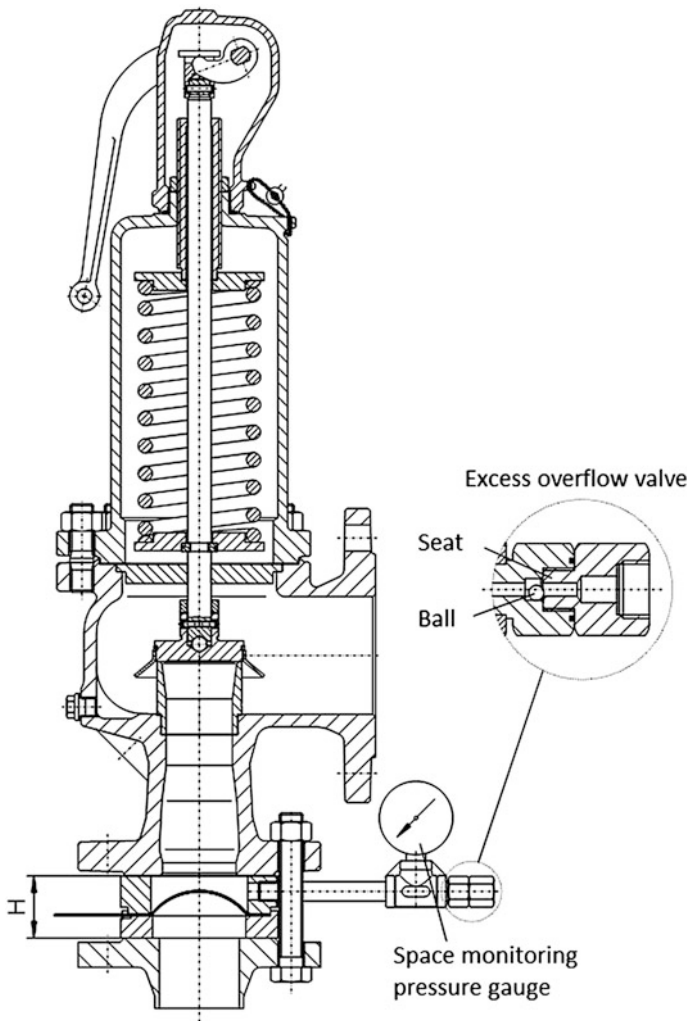


Fig. 7.2 Safety valve with bursting disc (courtesy of [2])

Subscript 1 denotes the initial and subscript 2 the final state, respectively.

The flow processes treated below are considered not to involve any energy losses. Neither heat nor mechanical work are introduced into or output from the process.

Thus Eq. (7.1) becomes

$$h_2 - h_1 + \frac{1}{2} \cdot (c_2^2 - c_1^2) + g \cdot (z_2 - z_1) = 0 \quad (7.2)$$

The enthalpy h can be eliminated from Eq. (7.2) by using the relation

$$h = u + p \cdot v \quad (7.3)$$

In Eq. (7.3) u is the internal energy, p the pressure and v the specific volume of the fluid.

Combining Eqs. (7.1) and (7.2) we have:

$$u_2 - u_1 + p_2 \cdot v_2 - p_1 \cdot v_1 + \frac{1}{2} \cdot (c_2^2 - c_1^2) + g \cdot (z_2 - z_1) = 0 \quad (7.4)$$

If the medium is incompressible (this is, as a rule, a good approximation for liquids), the internal energy only depends on its temperature and its specific volume ($v_1 = v_2 = 1/\rho$). Therefore the internal energy does not change during the flow process and Eq. (7.4) becomes

$$p_1 - p_2 = \frac{1}{2} \cdot \rho \cdot (c_2^2 - c_1^2) + g \cdot \rho \cdot (z_2 - z_1) \quad (7.5)$$

The above relations describe frictionless flow processes. However, the outflow from safety valves and bursting discs is accompanied by friction losses. These are accounted for by the discharge coefficient K_d . This coefficient is determined experimentally in the context of the certification process. It represents the ratio between the ideal and real flow velocities.

According to [4] a certified derated discharge coefficient, K_{dr} , is assigned during the certification process. It may amount to at the most 90 % of K_d , i.e. $K_{dr} \leq 0.9 \cdot K_d$. It must be borne in mind that the discharge coefficient only applies to the specific type of safety valve or bursting disc within defined ranges of pressures and temperatures.

7.4.2 Liquids

The discharge velocity of a liquid can be derived directly from Eq. (7.5). We assume that the pressure difference due to a difference in elevation between inlet and outlet $g \cdot \rho \cdot (z_2 - z_1)$ is negligible compared with the pressure difference between internal and external pressures, $p_1 - p_2$. Furthermore the medium is supposed to be at rest before pressure relief, i.e. $c_1 = 0$. The discharge velocity c_2 (m/s) then is

$$c_2 = \sqrt{2 \cdot \frac{p_1 - p_2}{\rho}} \quad (7.6)$$

The mass flow rate from the discharge opening is obtained as

$$\dot{m} = K_{dr} \cdot K_v \cdot F \cdot \rho \cdot c_2 \quad (7.7)$$

The necessary cross sectional area for discharge is calculated from Eq. (7.7) substituting $\dot{m}$ by the maximum mass flow rate to be discharged, $\dot{m}_{max}$. The (smallest) cross sectional area $F(m^2)$ known as flow area is then obtained by isolating F in Eq. (7.7).

In contrast with the former procedure the viscosity correction factor K_v is provided for in calculating fluid discharge in the draft of standard [4]. It may be read from a diagram or be calculated according to

$$K_v = \left(0.9935 + \frac{2.878}{Re^{0.5}} + \frac{342.75}{Re^{1.5}} \right)^{-1} \quad 35 < Re < 100,000 \quad (7.8)$$

For larger Reynolds numbers $K_v = 1$ applies.

Example 7.1 Dimensioning of a safety valve and a bursting disc for the pressure relief of a liquid

In the course of a potential operational disturbance a mass flow rate of $\dot{m}_{max} = 1 \text{ kg/s}$ has to be discharged from an equipment with an operating pressure of 200,000 Pa. Originally a discharge to the environment was planned. However, it was found later that for reasons of environmental protection a blowdown vessel for safe containment must be installed. The backpressure on pressure relief is thus increased by 20 %.

What are the cross sectional areas of the relief valves? How are the results affected if bursting discs are installed instead of safety valves?

Data: $p_{set \text{ pressure}} = 240,000 \text{ Pa}$; atmospheric pressure $p_2 = p_{atm} = 100,000 \text{ Pa}$ (without blowdown vessel); $p_2 = 120,000 \text{ Pa}$ (with blowdown vessel); $K_d = 0.5$ (safety valve); $K_d = 0.9$ (bursting disc); density of the medium $\rho = 1,260 \text{ kg/m}^3$; dynamic viscosity $\mu = 0.95 \text{ Pa s}$

Pressure tolerance: $\pm 10 \%$ for the safety valve

Bursting tolerance: $\pm 5 \%$ for bursting discs

Solution

(a) Safety valve

Relief pressure:

$$p_1 = p_{set \text{ pressure}} + 0.1 \cdot p_{set \text{ pressure}} + p_{atm} = 364,000 \text{ Pa}$$

The calculation is carried out using $K_v = 1$ and $K_{dr} = 0.9 \cdot 0.5 = 0.45$
From Eq. (7.7) and Eq. (7.6) we have

Table 7.1 Dimensions of the relief devices for the different cases examined

Case	Without blowdown vessel	With blowdown vessel	Size of the relief device to be selected
Safety valve without accounting for viscosity	$8.62 \times 10^{-5} \text{ m}^2$	$8.96 \times 10^{-5} \text{ m}^2$	DN 20
Safety valve accounting for viscosity	$1.40 \times 10^{-4} \text{ m}^2$	$1.47 \times 10^{-4} \text{ m}^2$	DN 20
Bursting disc without accounting for viscosity	$4.90 \times 10^{-5} \text{ m}^2$	$5.11 \times 10^{-5} \text{ m}^2$	DN 15
Bursting disc without accounting for viscosity	$7.05 \times 10^{-5} \text{ m}^2$	$7.40 \times 10^{-5} \text{ m}^2$	DN 15

$$\begin{aligned}
 F &= \frac{\dot{m}_{\max}}{K_{\text{dr}} \cdot K_v \cdot \sqrt{2 \cdot \rho \cdot (p_1 - p_2)}} \\
 &= \frac{1 \frac{\text{kg}}{\text{s}}}{0.45 \cdot 1.0 \cdot \sqrt{2 \cdot 1260 \frac{\text{kg}}{\text{m}^3} \cdot (364,000 - 100,000) \text{ Pa}}} = 8.62 \cdot 10^{-5} \text{ m}^2
 \end{aligned}$$

If viscosity is accounted for one obtains by iteration

$\text{Re} = 100.52$ and $K_v = 0.617$, whence $F = 1.40 \cdot 10^{-4} \text{ m}^2$.

(b) Bursting disc

The bursting disc is treated analogously with $K_d = 0.9$ ($K_{\text{dr}} = 0.9 \cdot 0.9 = 0.81$) and $p_1 = 352,000 \text{ Pa}$.

After installing the blowdown vessel the backpressure becomes

$$p_2 = p_{\text{atm}} + 0.2 \cdot p_{\text{atm}} = 120,000 \text{ Pa}$$

Table 7.1 contains the results for all the cases treated.

If the set pressure is used as relief pressure the values of Table 7.2 are obtained.

Although the lower relief pressure does not lead to different sizing of the relief device to be selected in the present case it is obvious that this might occur, since the minimum cross section is larger than with the higher relief pressure. For this reason there is an industrial practice to deviate from the standard and to choose the set pressure as the basis for dimensioning.

Table 7.2 Dimensions of the relief devices for the different cases examined with modified backpressure

Case	Without blowdown vessel	With blowdown vessel	Size of the relief device to be selected
Safety valve without accounting for viscosity	$9.04 \times 10^{-5} \text{ m}^2$	$9.44 \times 10^{-5} \text{ m}^2$	DN 20
Safety valve accounting for viscosity	$1.48 \times 10^{-4} \text{ m}^2$	$1.57 \times 10^{-4} \text{ m}^2$	DN 20
Bursting disc without accounting for viscosity	$5.02 \times 10^{-5} \text{ m}^2$	$5.24 \times 10^{-5} \text{ m}^2$	DN 15
Bursting disc without accounting for viscosity	$7.26 \times 10^{-5} \text{ m}^2$	$7.64 \times 10^{-5} \text{ m}^2$	DN 15

□

7.4.3 Gases or Vapours

If the discharge of a gas, hence of a compressible fluid, is to be treated the type of fluid and the type of expansion has to be accounted for. Equation (2.28) applies to an ideal gas (vid. [3])

$$p \cdot v = R \cdot T \quad (7.9)$$

and to a real gas

$$p \cdot v = Z \cdot R \cdot T \quad (7.10)$$

In Eqs. (7.9) and (7.10) the following quantities are used

- p pressure in Pa
- v specific volume in m^3/kg
- R specific gas constant in $\text{J}/(\text{kg K})$, where $R = R_m/M$ holds, i.e. the quotient of the molar or universal gas constant and the molar mass of the gas in question
- T absolute temperature in K
- Z compressibility factor at relief pressure and temperature ($Z = 1$ (ideal gas) gives conservative results)

Starting point for the treatment is Eq. (7.2) where the difference in geodetic elevation can normally be neglected in case of gases. We then have

$$h_2 - h_1 + \frac{1}{2} \cdot (c_2^2 - c_1^2) = 0 \quad (7.11)$$

It is usually assumed that the change of state is isentropic (reversibly adiabatic). Hence, one has

$$ds = \frac{dh}{T} - \frac{v \cdot dp}{T} = 0 \quad (7.12)$$

Inserting Eq. (7.9) in Eq. (7.12) and observing that for ideal gases

$$dh = c_p dT \quad (7.13)$$

holds,

$$c_p \cdot \frac{dT}{T} = R \cdot \frac{dp}{p} \quad (7.14)$$

results. By integrating Eq. (7.14) we obtain

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{R}{c_p}} = \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \quad (7.15)$$

In Eq. (7.15) the thermodynamic relations

$$\begin{aligned} R &= c_p - c_v \text{ and} \\ \kappa &= c_p/c_v \text{ (heat capacity ratio, vid. Table 10.14)} \end{aligned} \quad (7.16)$$

were used. By inserting Eq. (7.8) in Eq. (7.14) one obtains

$$\frac{\rho_1}{\rho_2} = \left(\frac{p_2}{p_1} \right)^{-\frac{1}{\kappa}} \quad (7.17)$$

where $\rho = 1/v$ denotes the density in kg/m^3 .

If we use Eqs. (7.13) and (7.15) and assume that the outflow velocity from the valve, c_2 , is much larger than the velocity at its inlet, c_1 , so that the latter can be neglected

$$c_2^2 = 2 \cdot c_p (T_1 - T_2) \quad (7.18)$$

results. Substituting Eqs. (7.9), (7.15) and (7.16) in Eq. (7.18), we obtain

$$c_2 = \left\{ \frac{2 \cdot \kappa}{\kappa - 1} \cdot p_1 \cdot v_1 \cdot \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \right] \right\}^{1/2} \quad (7.19)$$

The mass flow rate of a gas according to Eq. (7.7) (density of the outflowing gas ρ_2 , $K_v = 1$) is obtained by using Eqs. (7.17) and (7.19) as

$$\dot{m} = K_d \cdot F \cdot \left\{ \frac{2 \cdot \kappa}{\kappa - 1} \cdot p_1 \cdot \rho_1 \cdot \left(\frac{p_2}{p_1} \right)^{\frac{2}{\kappa}} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \right] \right\}^{1/2} \quad (7.20)$$

If we define the ratio of external and internal pressures $w = p_2/p_1$ and substitute it in Eq. (7.20) it follows that

$$\dot{m} = K_{dr} \cdot F \cdot \left\{ \frac{2 \cdot \kappa}{\kappa - 1} \cdot p_1 \cdot \rho_1 \cdot \left[w^{\frac{2}{\kappa}} - w^{\frac{\kappa+1}{\kappa}} \right] \right\}^{1/2} \quad (7.21)$$

By differentiating Eq. (7.21) with respect to w and setting the result equal to zero the pressure ratio for the maximum discharge rate, the critical pressure ratio, w_{crit} , is obtained

$$w_{crit} = \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa}{\kappa-1}} \quad (7.22)$$

Replacing w in Eq. (7.21) by w_{crit} according to Eq. (7.22) the maximum mass flow rate is found to be

$$\dot{m}_{max} = K_{dr} \cdot F \cdot \left\{ \rho_1 p_1 \kappa \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa+1}{\kappa-1}} \right\}^{1/2} \quad (7.23)$$

The maximum velocity of flow that can be attained is the speed of sound. It is reached for the critical pressure ratio w_{crit} and true as well if $w < w_{crit}$. The flow rate then only depends on the pressure inside the enclosure, p_1 , and not on the external pressure, p_2 . Equation (7.20) hence applies for discharge processes with velocities below the speed of sound and Eq. (7.23) for all other cases. The latter is usually required if gas under high pressure is discharged.

If friction losses are to be accounted for κ in the foregoing equations is replaced by the corresponding polytropic index n (vid. [3]), which is smaller than κ .

The equations for sub-critical and critical discharges may be summarized by using the discharge function Ψ . One obtains

$$\dot{m} = K_{dr} \cdot F \cdot \sqrt{2 \cdot \rho_1 \cdot p_1} \Psi \quad (7.24)$$

where

$$\Psi = \begin{cases} \left\{ \frac{\kappa}{\kappa-1} \cdot \left(\frac{p_2}{p_1} \right)^{\frac{2}{\kappa}} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \right] \right\}^{1/2} & \text{if } 1 \geq w > \left(\frac{2}{\kappa+1} \right)^{\frac{\kappa}{\kappa-1}} \\ \left\{ \frac{\kappa}{\kappa+1} \left(\frac{2}{\kappa+1} \right)^{\frac{2}{\kappa-1}} \right\}^{1/2} & \text{if } 0 < w \leq \left(\frac{2}{\kappa+1} \right)^{\frac{\kappa}{\kappa-1}} \end{cases} \quad (7.25)$$

The foregoing equations are formulated for ideal gases. For most of them we have

$$1.1 < \kappa < 1.4 \quad (7.26)$$

If the behaviour of the gas discharged is not ideal, the enthalpy difference figuring in Eq. (7.11) is obtained from tables or correlations (cf. [5]).

Example 7.2 Dimensioning of a safety valve for the pressure relief of a gas (critical discharge)

Propylene (C_3H_6) is stored in a vessel at an operating pressure of 4,000,000 Pa. The vessel is to be protected by a safety valve with a set pressure of 4,400,000 Pa. In case of excessive pressure the propylene is relieved with a maximum mass flow rate of $\dot{m}_{\max} = 10 \text{ kg/s}$ into a blowdown vessel; the backpressure amounts to $p_2 = 150,000 \text{ Pa}$. What is the minimal cross sectional area of the safety valve?

Data: molar mass $M = 42.08 \text{ g/mol}$; operating temperature $T = 293.15 \text{ K}$; $\kappa = 1.16$; $Z = 0.98$, $K_{dr} = 0.8$

Solution

Relief pressure:

$$p_1 = p_{\text{set pressure}} + 0.1 \cdot p_{\text{set pressure}} + p_{\text{atm}} = 4,940,000 \text{ Pa}$$

According to Eq. (7.22) the critical pressure ratio is

$$w_{\text{crit}} = 0.5724$$

whilst the pressure ratio amounts to

$$w = \frac{p_2}{p_1} = 3.036 \cdot 10^{-2}$$

Since $w < w_{\text{crit}}$ the discharge is critical. Hence, the minimum cross sectional area is calculated with Eq. (7.23), which gives

$$\begin{aligned} F &= \frac{\dot{m}_{\max}}{K_{dr} \left\{ \rho_1 p_1 \kappa \left(\frac{2}{\kappa+1} \right)^{\frac{\kappa+1}{\kappa-1}} \right\}^{1/2}} \\ &= \frac{10 \frac{\text{kg}}{\text{s}}}{0.8 \cdot \left(87.03 \frac{\text{kg}}{\text{m}^3} \cdot 4,940,000 \text{ Pa} \cdot 1.16 \cdot 0.9259^{13.5} \right)^{1/2}} = 9.41 \cdot 10^{-4} \text{ m}^2 \end{aligned}$$

where ρ_1 was calculated from Eq. (7.10).

If the set pressure is used as relief pressure, the latter amounts to

$$p_1 = p_{\text{set pressure}} + p_{\text{atm}} = 4,500,000 \text{ Pa}$$

and

$$F = 9.67 \cdot 10^{-4} \text{ m}^2$$

is then obtained.

□

Example 7.3 Dimensioning of a safety valve for the pressure relief of a gas (subcritical discharge)

The Example 7.2 is repeated with a backpressure of $p_2 = 3,500,000 \text{ Pa}$.

Solution

We now obtain

$$w = \frac{p_2}{p_1} = 0.7085$$

and thus subcritical discharge because of $w > w_{\text{crit}}$. Equation (7.20) is used to give

$$\begin{aligned} F &= \frac{\dot{m}}{K_d \cdot \left\{ \frac{2 \cdot \kappa}{\kappa - 1} \cdot p_1 \cdot \rho_1 \cdot \left(\frac{p_2}{p_1} \right)^{\frac{2}{\kappa}} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\kappa - 1}{\kappa}} \right] \right\}^{1/2}} \\ &= \frac{10 \frac{\text{kg}}{\text{s}}}{0.8 \cdot [14.5 \cdot 4,940,000 \cdot 86.92 \cdot 0.7085^{1.7241} \cdot (1 - 0.7085^{0.13793})]^{1/2}} = 9.90 \cdot 10^{-4} \text{ m}^2 \end{aligned}$$

With a relief pressure of 4,500,000 Pa we obtain

$$F = 1.17 \cdot 10^{-3} \text{ m}^2$$

□

7.4.4 Two-Phase Flow

In treating disturbances in process plants problems like the pressure relief of superheated liquids which evaporate on depressurization have to be dealt with. Then two-phase flow results, i.e. the liquid and vapour phase are discharged together. Most work in the area refers to mixtures of water and steam, which are of special importance in nuclear reactor accidents. The much more complex task to treat flow processes of multi-component two phase mixtures, which are a characteristic of process plants, still requires intense research.

The basic problem in modelling two-phase flow is the question to what extent equilibrium exists between the phases. In general, there is no equilibrium. Yet, as a rule equilibrium is assumed, since this simplifies the analytical treatment of the problem. Fundamental considerations on two-phase flow can, for example, be encountered in [6]. In what follows the model of Leung [7, 8] is described. The presentation draws upon [8].

Leung distinguishes between the following initial states:

- saturated liquid,
- two-phase gas-liquid mixture,
- subcooled liquid,
 - weak subcooling,
 - strong subcooling.

For the model the parameter ω is important; it determines the equation of state:

$$\frac{v_2}{v_1} = \omega \cdot \left(\frac{p_1}{p_2} - 1 \right) + 1 \quad (7.27)$$

The parameter is given by

$$\omega = \frac{x_1 \cdot v_{g1}}{v_1} + \frac{c_{f1} \cdot p_1 \cdot T_1}{v_1} \cdot \left(\frac{v_{g1} - v_{f1}}{h_{g1} - h_{f1}} \right)^2 \cdot N \quad (7.28)$$

where

$$N = \left(x_1 + c_{f1} \cdot p_1 \cdot T_1 \cdot \frac{v_{g1} - v_{f1}}{(h_{g1} - h_{f1})^2} \cdot \ln \frac{1}{w_{\text{crit}}} \right)^a$$

If $N = 1$ in Eq. (7.28) we speak of the homogeneous equilibrium model. If the expression for N given above, which was derived in [9], the model is referred to as non-equilibrium.

The specific volume at the valve inlet, v_1 , appearing in Eq. (7.28) is given by

$$v_1 = x_1 \cdot v_{g1} + (1 - x_1) \cdot v_{f1} \quad (7.29)$$

In the foregoing equations we use:

- x mass fraction of vapour
- v specific volume in m^3/kg
- h enthalpy in J/kg
- c specific heat in $\text{J}/(\text{kg K})$

Subscript “g” denotes the gas phase and “f” the liquid phase; “1” indicates before and “2” after release.

The homogeneous model shows a tendency to calculate small discharge mass flow rates, especially if short pipes are treated [9]. The factor N corrects this drawback, where

$$a = \begin{cases} 0.6 & \text{for orifices, control valves and short nozzles} \\ 0.4 & \text{for pressure relief valves, high-lift control valves} \\ 0 & \text{for long nozzles and orifices with large area ratio} \end{cases}$$

has to be used.

7.4.4.1 Flow of Saturated Liquids and Two-Phase Flow

If the liquid at the inlet of the relief valve is saturated, x_1 is equal to 0, i.e. there is no vapour and the first term on the right-hand side of Eq. (7.28) is equal to 0. If both phases are present, $x_1 \neq 0$. In both cases the following approach is applied.

Using the value for ω from Eq. (7.28) the critical pressure ratio, w_{crit} , is determined iteratively from

$$w_{crit}^2 + (\omega^2 - 2\omega) \cdot (1 - w_{crit})^2 + 2\omega^2 \ln w_{crit} + 2\omega^2 \cdot (1 - w_{crit}) = 0 \quad (7.30)$$

If $p_{crit} < p_2$ there is no limitation of flow („unchoked flow“). The flow is subcritical and the mass flow rate is obtained from

$$\dot{m} = K_{dr} \cdot F \cdot \sqrt{\frac{p_1}{v_1}} \cdot \frac{\left\{ -2 \cdot \left[\left(\omega \cdot \ln \frac{p_2}{p_1} \right) + (\omega - 1) \cdot \left(1 - \frac{p_2}{p_1} \right) \right] \right\}^{1/2}}{\omega \cdot \left[\left(\frac{p_1}{p_2} \right) - 1 \right] + 1} \quad (7.31)$$

Otherwise there is a limitation on flow (“choked flow”) and we have for the critical mass flow rate

$$\dot{m} = K_{dr} \cdot F \cdot \sqrt{\frac{p_1}{v_1}} \cdot \frac{w_{crit}}{\omega^{1/2}} \quad (7.32)$$

7.4.4.2 Subcooled Liquid

If the liquid at the inlet of the valve is subcooled, a distinction is made between weak and strong subcooling.

In the case of weak subcooling ω_s (the index “s” denoting subcooling) is obtained from

$$\omega_s = \frac{c_{f1} \cdot p_s \cdot T_1}{v_{f1}} \cdot \left(\frac{v_{g1} - v_{f1}}{h_{g1} - h_{f1}} \right)^2 \quad (7.33)$$

The subcooling is weak if

$$w_s \geq \frac{2\omega_s}{1 + 2\omega_s} \quad (7.34)$$

applies, where $w_s = p_s/p_1$, is the ratio between saturation and internal pressure.

The critical pressure ratio is obtained in this case, for example by Newton's root finding method or by bracketing and bisection, from

$$\frac{\omega_s + \frac{1}{\omega_s} - 2}{2\omega_s} \cdot w_{\text{krit}}^2 - (2\omega_s - 1) \cdot w_{\text{krit}} + w_{\text{krit}} \cdot \omega_s \ln \frac{w_{\text{krit}}}{w_s} + \frac{3}{2} \omega_s \cdot w_s - 1 = 0 \quad (7.35)$$

The mass flow rate is then given by

$$\dot{m} = K_{\text{dr}} \cdot F \cdot \sqrt{\frac{p_1}{v_{f1}}} \cdot \frac{\{2 \cdot (1 - w_s) + 2 \cdot [w_s \cdot \omega_s \cdot \ln \frac{w_s}{w} - (\omega_s - 1) \cdot (w_s - w)]\}^{1/2}}{\omega_s \cdot \left[\left(\frac{w_s}{w}\right) - 1\right] + 1} \quad (7.36)$$

In the case of strong subcooling the critical pressure ratio is determined by

$$w_{\text{crit}} = \frac{p_s}{p_1} \quad (7.37)$$

The corresponding mass flow rate then is

$$\dot{m} = K_{\text{dr}} \cdot F \cdot \sqrt{2 \cdot \rho_{f1} \cdot (p_1 - p_s)} \quad (7.38)$$

7.4.4.3 Non-condensable Gas and Liquid

In the case of the flow of a non-condensable gas and a liquid the parameter ω is approximately calculated from [5]

$$\omega = \frac{x_1 \cdot v_{g1}}{v_1 \cdot \kappa} \quad (7.39)$$

The critical pressure ratio is then determined iteratively from Eq. (7.30) using the value for ω from Eq. (7.39). The mass flow rate results from Eq. (7.32).

Example 7.4 Dimensioning of a safety valve for pressure relief with two-phase flow—critical (choked) discharge.

Saturated water at 250 °C is to be discharged via a safety valve. The corresponding saturation pressure is 3,973,600 Pa and the maximum mass flow rate is 100 kg/s.

Data: $v_g = 0.05011 \text{ m}^3/\text{kg}$; $v_f = 0.00125 \text{ m}^3/\text{kg}$; $\Delta h_v = 1,715.4 \text{ kJ/kg}$; $c_p = 4,857 \text{ J/kg}$; $K_{\text{dr}} = 0.8$; $p_2 = p_{\text{atm}} = 100,000 \text{ Pa}$

Solution

Relief pressure:

$$p_1 = p_{\text{set pressure}} + 0.1 \cdot p_{\text{set pressure}} + p_2 = 4,470,960 \text{ Pa}$$

ω is determined from Eqs. (7.28) and (7.29) with $x_1 = 0$, since only water is present before pressure relief.

$$\begin{aligned} \omega &= \frac{x_1 \cdot v_{g1}}{v_1} + \frac{c_{f1} \cdot p_1 \cdot T_1}{v_1} \cdot \left(\frac{v_{g1} - v_{f1}}{h_{g1} - h_{f1}} \right)^2 = \frac{0 \cdot 0.05011 \frac{\text{m}^3}{\text{kg}}}{0 \cdot 0.0511 \frac{\text{m}^3}{\text{kg}} + 1 \cdot 0.00125 \frac{\text{m}^3}{\text{kg}}} \\ &\quad + \frac{4,857 \frac{\text{J}}{\text{kg K}} \cdot 4,470,960 \text{ Pa} \cdot 523.15 \text{ K}}{0 \cdot 0.05011 \frac{\text{m}^3}{\text{kg}} + 1 \cdot 0.00125 \frac{\text{m}^3}{\text{kg}}} \cdot \left(\frac{0.05011 \frac{\text{m}^3}{\text{kg}} - 0.00125 \frac{\text{m}^3}{\text{kg}}}{1,715,400 \frac{\text{J}}{\text{kg}}} \right)^2 \\ &= 0 + 9.0884 \cdot 10^{15} \cdot 2.8483 \cdot 10^{-8^2} = 7.373 \end{aligned}$$

Bracketing and bisection gives the following solution of Eq. (7.30):

$$\begin{aligned} w_{\text{crit}} &= 0.8245 \text{ and hence } p_{\text{crit}} = w_{\text{crit}} \cdot p_1 = 0.8245 \cdot 4,470,960 \text{ Pa} \\ &= 3,686,306.5 \text{ Pa} \end{aligned}$$

Since $p_{\text{crit}} > p_2$ the flow is choked. Hence the necessary minimum cross sectional is obtained from Eq. (7.32)

$$F = \frac{\dot{m}}{K_{\text{dr}} \sqrt{\frac{p_1}{v_1} \cdot \frac{w_{\text{crit}}}{\omega^{1/2}}}} = \frac{100 \frac{\text{kg}}{\text{s}}}{0.8 \cdot \sqrt{\frac{4,470,960 \text{ Pa}}{0.00125 \frac{\text{m}^3}{\text{kg}}} \cdot \frac{0.8245}{7.373^{1/2}}}} = 6.88 \cdot 10^{-3} \text{ m}^2$$

The necessary cross section obtained by using the non-equilibrium model is $F = 4.57 \times 10^{-3} \text{ m}^2$.

□

Example 7.5 Dimensioning of a safety valve for a pressure relief with two-phase flow—subcritical (unchoked) discharge

The backpressure in Example 7.4 is increased to $p_2 = 3,800,000 \text{ Pa}$. What is the minimum cross sectional area of the safety valve?

Solution

Since the backpressure does not play any role when determining ω and w_{crit} , the values of Example 7.4 apply, i.e.

$$p_{\text{crit}} = w_{\text{crit}} \cdot p_1 = 0.8278 \cdot 4,470,960 \text{ Pa} = 3,701,060.7 \text{ Pa}$$

Since now $p_{\text{crit}} < p_2$, the flow is unchoked. Hence, the necessary minimum cross sectional area is obtained from Eq. (7.31) as

$$\begin{aligned}
 F &= \frac{\dot{m}}{K_{\text{dr}} \cdot \sqrt{\frac{p_1}{v_1}}} \cdot \frac{\omega \cdot \left[\left(\frac{p_1}{p_2} \right) - 1 \right] + 1}{\left\{ -2 \cdot \left[\left(\omega \cdot \ln \frac{p_2}{p_1} \right) + (\omega - 1) \cdot \left(1 - \frac{p_2}{p_1} \right) \right] \right\}^{1/2}} \\
 &= \frac{100 \frac{\text{kg}}{\text{s}}}{0.8 \cdot \sqrt{\frac{4,470,960 \text{ Pa}}{0.00125 \frac{\text{m}^3}{\text{kg}}}}} \cdot \frac{7.373 \cdot \left[\left(\frac{4,470,960 \text{ Pa}}{3,800,000 \text{ Pa}} \right) - 1 \right] + 1}{\left\{ -2 \cdot \left[\left(7.373 \cdot \ln \frac{3,800,000 \text{ Pa}}{4,470,960 \text{ Pa}} \right) + (7.373 - 1) \cdot \left(1 - \frac{3,800,000 \text{ Pa}}{4,470,960 \text{ Pa}} \right) \right] \right\}^{1/2}} \\
 &= 2.0901 \cdot 10^{-3} \text{ m}^2 \cdot \frac{2.3018}{0.6964} = 6.91 \cdot 10^{-3} \text{ m}^2
 \end{aligned}$$

The necessary cross section obtained by using the non-equilibrium model is $F = 4.98 \times 10^{-3} \text{ m}^2$. □

Example 7.6 Dimensioning of a safety valve for pressure relief with two-phase flow—sub-cooled liquid

Ethyl acetate is stored at 450 K and 1,200,000 Pa. The maximum required discharge rate for pressure relief is 10 kg/s, the backpressure amounts to $p_2 = p_{\text{atm}} = 100,000 \text{ Pa}$. What is the required minimum cross sectional area of the safety valve, which has a set pressure of 1,300,000 Pa?

Data: saturation pressure at 450 K $p_s = 1,172,000 \text{ Pa}$; $v_{g1} = 0.02817 \text{ m}^3/\text{kg}$; $v_{f1} = 0.001493 \text{ m}^3/\text{kg}$; $\Delta h_v = 267.9 \text{ kJ/kg}$; $c_{f1} = 2,640 \text{ J/(kg K)}$; $K_{\text{dr}} = 0.65$

Solution

Relief pressure:

$$p_1 = p_{\text{set pressure}} + 0.1 \cdot p_{\text{set pressure}} + p_2 = 1,530,000 \text{ Pa}$$

Firstly it must be found out whether the subcooling is strong or weak. This requires ω_s to be determined according to Eq. (7.33), which gives

$$\begin{aligned}
 \omega_s &= \frac{c_{f1} \cdot p_s \cdot T_1}{v_{f1}} \cdot \left(\frac{v_{g1} - v_{f1}}{h_{g1} - h_{f1}} \right)^2 \\
 &= \frac{2,640 \frac{\text{J}}{\text{kg K}} \cdot 1,172,000 \text{ Pa} \cdot 450 \text{ K}}{0.001493 \frac{\text{m}^3}{\text{kg}}} \cdot \left(\frac{0.02817 \frac{\text{m}^3}{\text{kg}} - 0.001493 \frac{\text{m}^3}{\text{kg}}}{267,900 \frac{\text{J}}{\text{kg}}} \right)^2 \\
 &= 9.3258 \cdot 10^{14} \frac{\text{kg}^2}{\text{m}^2 \cdot \text{s}^4} \cdot 9.9578 \cdot 10^{-8} \frac{\text{m}^2 \cdot \text{s}^4}{\text{kg}^2} = 9.2472
 \end{aligned}$$

By applying Eq. (7.34) we find that

$$\frac{p_s}{p_1} < \frac{2\omega_s}{1 + 2\omega_s}, \text{ just as } 0.77 < \frac{2 \cdot 9.2472}{1 + 2 \cdot 9.2472} = 0.95$$

Hence, we are dealing with strong subcooling and according to eq. Gl. (7.38) the minimum cross-sectional area of the safety valve amounts to

$$F = \frac{\dot{m}}{K_{dr} \cdot \sqrt{2 \cdot \rho_{f1} \cdot (p_1 - p_s)}} = \frac{10 \frac{\text{kg}}{\text{s}}}{0.65 \cdot \sqrt{\frac{2}{0.001493 \frac{\text{m}^3}{\text{kg}}} \cdot (1,530,000 \text{ Pa} - 1,172,000 \text{ Pa})}} \\ = 7.03 \cdot 10^{-4} \text{ m}^2$$

□

Example 7.7 Dimensioning of a safety valve for pressure relief with two-phase flow—water and air

A safety valve is to discharge a mixture of water and air ($x_1 = 0.3$) at a backpressure of $p_2 = p_{\text{atm}} = 100,000 \text{ Pa}$. Its pressure amounts to $1,000,000 \text{ Pa}$ and its temperature to $T_1 = 298.15 \text{ K}$. What is the minimum cross-sectional area if 20 kg/s have to be discharged?

Data: $v_{g1} = 0.0854 \text{ m}^3/\text{kg}$; $v_{f1} = 0.001 \text{ m}^3/\text{kg}$; $\kappa = 1.4$; $K_{dr} = 0.8$

Solution

Relief pressure:

$$p_1 = p_{\text{set pressure}} + 0.1 \cdot p_{\text{set pressure}} + p_2 = 1,200,000 \text{ Pa}$$

The value of ω is obtained from Eq. (7.39), which gives

$$\omega = \frac{x_1 \cdot v_{g1}}{v_1 \cdot \kappa} = \frac{0.3 \cdot 0.0854 \frac{\text{m}^3}{\text{kg}}}{\left(0.3 \cdot 0.0854 \frac{\text{m}^3}{\text{kg}} + 0.7 \cdot 0.001 \frac{\text{m}^3}{\text{kg}}\right) \cdot 1.4} = 0.6953$$

The critical pressure ratio is obtained from Eq. (7.30) by bracketing and bisection resulting in

$$w_{\text{krit}} = 0.559$$

The minimum cross section is calculated from Eq. (7.32) to give

$$F = \frac{\dot{m}}{K_{dr} \cdot \sqrt{\frac{P_1}{V_1}} \cdot \frac{w_{crit}}{\omega^{1/2}}} = \frac{20 \frac{\text{kg}}{\text{s}}}{0.8 \cdot \sqrt{\frac{1,200,000 \text{ Pa}}{0.3 \cdot 0.0854 \frac{\text{m}^3}{\text{kg}} + 0.7 \cdot 0.001 \frac{\text{m}^3}{\text{kg}}}} \cdot \frac{0.559}{0.6953^{1/2}}} = 5.52 \cdot 10^{-3} \text{ m}^2$$

□

7.4.5 Mass Flow Rate to Be Discharged

The mass flow rate to be discharged following malfunctions depends on the process parameters, the nature of the malfunction and the pertinent boundary conditions. It is useful to determine these by a systematic safety analysis, for example a HAZOP study (vid. Sect. 9.1.2.3). In such an analysis special attention should be paid to identifying sequences leading to overpressure. Basically the following causes of overpressure can be distinguished (cf. [8]):

7.4.5.1 Mechanical

A substance flows from a higher-pressure system into a system designed for lower pressure. The mass flow rate to be relieved depends on the pressure difference.

A substance is supplied to a system, for example by a pump or a compressor. The mass flow rate then depends on the capacity of the pump, respectively the compressor. If its stagnation pressure lies above the failure pressure of the system, its failure must be assumed. The mass flow rate to be relieved corresponds to the flow rate which results from the pressure difference after opening the relief device according to the characteristic of the pump or compressor.

7.4.5.2 Thermal

A cooling system or the control of a heating system fail or a fire occurs. The system is heated. Pressure builds up due to the thermal expansion of the substance involved, the rising vapour pressure or the release of dissolved gases. The mass flow rate to be discharged then depends on the maximum thermal power supplied to the system. External heating can cause large amounts of vapour to be discharged. In case of thermal expansion usually only relatively small amounts of liquid or gas to be discharged are involved. However, the thermal expansion of liquids may cause large pressures given their virtual incompressibility.

7.4.5.3 Chemical

This includes runaway reactions (vid. Chap. 3) due to cooling failure, wrong dosing, heat input from outside, too large quantities of catalyst etc. Three categories are distinguished:

(a) vapour producing systems (“tempered systems”):

The pressure rises along the vapour pressure curve of the reaction mixture due to an increase of reaction heat following a temperature rise. When the safety valve opens, vapour is removed from the system and the pressure drops. The system cools down due to expansion and the use of its energy for providing the latent energy to evaporate the liquid phase.

(b) gas producing systems (“gassy system”):

The pressure increases because a non-condensable gas is produced in the process, for example following decomposition or synthesis reactions. The partial pressure of the liquid in the mixture then is comparatively low. For design calculations the solubility of the gas in the liquid phase has to be taken into account. Pure gassy systems are very rare in the process industry since the influence of vapour pressure increases with rising temperatures.

(c) hybrid systems

In hybrid systems the pressure rise is caused by both gas production and evaporation.

In what follows some easy-to-use formulae are presented. A detailed treatment can be found in [6, 10]:

- External heat input into liquid with evaporation and flow of a gas only through the relief device

$$\dot{m} = \frac{\dot{Q}_{in}}{\Delta h_v} \quad (7.40)$$

In Eq. (7.40) $\dot{m}$ is the mass flow rate resulting from evaporation in kg/s, $\dot{Q}$ is the thermal power introduced into the system in W and Δh_v the enthalpy of evaporation of the substance involved in J/kg. The energy which may be necessary to heat up the substance to its boiling temperature is neglected in Eq. (7.40) because it is small compared to the energy of evaporation.

- External heat input into a liquid with evaporation and two-phase flow through the relief device

$$\dot{m} = \frac{M_R \cdot \dot{Q}_{in}}{\left[\left(\frac{V_R \cdot \Delta h_v}{M_R \cdot (V_g - V_f)} \right)^{1/2} + (c_{pf} \cdot \Delta T)^{1/2} \right]^2} \quad (7.41)$$

In Eq. (7.41) M_R is the mass of the reactor or vessel contents in kg, V_R the corresponding volume in m^3 , Δh_v the enthalpy of evaporation in J/kg, c_{pf} the heat capacity of the liquid in J/(kg K) and ΔT the temperature difference between the states at set pressure and relief pressure in K. All material properties refer to the set pressure.

Heat input can be caused by control failure of a heating system, impact from a fire or a runaway reaction.

In case of fire impinging on a vessel the thermal power input can be assessed according to

$$\dot{Q}_{in} = 43,200 \cdot F \cdot A_b \quad (7.42)$$

In Eq. (7.42) $F = 1$ is used, if the vessel is not clad with a fire resistant insulation and $F < 1$, if there is such an insulation. A_b denotes the wetted inner surface of the vessel in m^2 up to an elevation of 8 m above the fire level respectively up to the largest diameter in case of a spherical vessel. $\dot{Q}_{in}$ is then obtained in W.

Example 7.8: Pressure relief of a gas-filled tank in case of fire

A vertical cylindrical storage vessel with an internal diameter of $D = 4$ m and a height of $H = 10$ is filled with methane at a pressure of $p_{op} = 700,000$ Pa. Its supporting columns measure 1 m, so that the bottom of the vessel is 1 m above ground. The vessel is not insulated. It is equipped with a safety valve with a set pressure of 780,000 Pa which discharges into a blowdown tank at a backpressure of $p_2 = 150,000$ Pa. What is the minimum cross-sectional area, so that the valve can discharge the mass flow rate following a fire?

Note: it is assumed that the geometry of vessel is not changed and that it does not fail due to fire impact.

Data: molar mass $M = 16.04$ g/mol; operating temperature $T_{op} = 293.15$ K; $c_v = 1745.6$ J/(kg K); $\kappa = 1.3$; $Z = 0.998$; specific gas constant $R = R_m/M = 0.51826$ J/(g K); $K_{dr} = 0.8$

Solution

Determination of the relief pressure p_1 :

$$p_1 = p_{set\ pressure} + 0.1 \cdot p_{set\ pressure} + p_2 = 870,000 \text{ Pa}$$

Determination of the relief temperature T_1 :

The process is isochoric; hence we have (cf. [3])

$$\frac{p_1}{p_{op}} = \frac{T_1}{T_{op}} \quad \text{and thus} \quad T_1 = T_{op} \cdot \frac{p_1}{p_{op}} = 293.15 \text{ K} \cdot \frac{870,000 \text{ Pa}}{700,000 \text{ Pa}} = 364.34 \text{ K}$$

Determination of the mass flow rate to be relieved:

- Thermal power input

According to Eq. (7.42) we have ($H' = 8$ m, since $H > 8$ m)

$$\dot{Q}_{\text{in}} = 43,200 \cdot F \cdot A_b = 43,200 \cdot 1 \cdot \pi \cdot \left(\frac{D^2}{4} + D \cdot H' \right) = 4,885,804.9 \text{ W}$$

- Specific volume for relief conditions v_1

From Eq. (7.10) we obtain

$$v_1 = \frac{Z \cdot R \cdot T_1}{p_1} = \frac{0.998 \cdot 518.26 \frac{\text{J}}{\text{kg K}} \cdot 364.34 \text{ K}}{870,000 \text{ Pa}} = 0.2166 \frac{\text{m}^3}{\text{kg}}$$

- Determination of the mass flow rate $\dot{m}$

From thermodynamic considerations (relief at constant pressure p_1) we obtain

$$\dot{Q}_{\text{in}} = p_1 \cdot \dot{V}$$

where $\dot{V}$ is the volumetric flow rate in m^3/s discharged via the safety valve. Thus the corresponding mass flow rate becomes

$$\dot{m} = \frac{\dot{Q}_{\text{in}}}{p_1 \cdot v_1} = \frac{4,885,804.9 \text{ W}}{870,000 \text{ Pa} \cdot 0.2166 \frac{\text{m}^3}{\text{kg}}} = 25.93 \frac{\text{kg}}{\text{s}}$$

- Determination of the minimum cross-sectional area F

According to Eq. (7.22) the critical pressure ratio is

$$w_{\text{crit}} = 0.5457$$

whilst the existing pressure ratio is

$$w = \frac{p_2}{p_1} = \frac{150,000 \text{ Pa}}{870,000 \text{ Pa}} = 1.724 \cdot 10^{-1}$$

Since $w < w_{\text{crit}}$ the discharge is critical. Therefore the minimum cross-sectional area is obtained from Eq. (7.23)

$$F = \frac{\dot{m}_{\max}}{K_{dr} \left\{ \rho_1 P_1 \kappa \left(\frac{2}{\kappa+1} \right)^{\frac{\kappa+1}{\kappa-1}} \right\}^{1/2}}$$

$$= \frac{25.93 \frac{\text{kg}}{\text{s}}}{0.8 \cdot \left(4.6168 \frac{\text{kg}}{\text{m}^3} \cdot 870,000 \text{ Pa} \cdot 1.3 \cdot 0.8696^{7.6667} \right)^{1/2}} = 2.42 \cdot 10^{-2} \text{ m}^2$$

where $\rho_1 = 1/v_1$.

- Assessment of the time between the start of the fire and the initiation of relief t^* (without accounting for the heating of the vessel; hence a time shorter than in reality is calculated)

Determination of the mass of methane stored in the vessel using Eq. (7.10)

$$\rho_{op} = \frac{p_{op}}{Z \cdot R \cdot T_{op}} = \frac{700,000 \text{ Pa}}{0.998 \cdot 518.28 \frac{\text{J}}{\text{kg K}} 293.15 \text{ K}} = 4.62 \frac{\text{kg}}{\text{m}^3}$$

$$m = V \cdot \rho_{op} = \frac{\pi \cdot D^2}{4} \cdot H \cdot \rho_{op} = 580.6 \text{ kg}$$

Assessment of the time until the beginning of discharge:

The heat balance is (the fire is supposed to start at point in time $t = 0$)

$$m \cdot c_v \frac{dT}{dt} = \dot{Q}_{in}$$

with the solution

$$T(t) = T_{op} + \frac{\dot{Q}_{in}}{m \cdot c_v} \cdot t$$

Now the time t^* is determined at which the temperature $T_1 = 364.34 \text{ K}$ (see above) is reached

$$t^* = \frac{(T_1 - T_{op}) \cdot m \cdot c_v}{\dot{Q}_{in}} = \frac{(364.34 \text{ K} - 293.15 \text{ K}) \cdot 580.6 \text{ kg} \cdot 1745.6 \frac{\text{J}}{\text{kg K}}}{4,885,804.9 \text{ W}}$$

$$= 14.8 \text{ s}$$

□

Example 7.9 Pressure changes inside a vessel following temperature changes

A cylindrical vessel for storing petrol with a volume of 2,000 m³ is filled to 90 % with liquid at an outside temperature of 20 °C. The internal pressure amounts to 100,000 Pa. How does the internal pressure change, provided there is no breather valve, if

- (a) the inside temperature rises to 30 °C due to an increase of the outside temperature,
- (b) the inside temperature drops to 0 °C due to a decrease of the outside temperature?

Data: coefficient of volumetric expansion $\beta = 950 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$; molar mass 100 g/mol

Assumption: the mass of gas does not change on temperature change

Solution

The volume above the liquid level available for accommodating the gaseous phase, V_G , amounts to

$$V_G = 0.1 \cdot 2,000 \text{ m}^3 = 200 \text{ m}^3$$

- (a) by the temperature increase from 20 to 30 °C this volume is reduced due to the expansion of the liquid by

$$R = (2,000 - 200) \text{ m}^3 \cdot 950 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1} \cdot 10 \text{ }^{\circ}\text{C} = 17.1 \text{ m}^3$$

- (b) following a temperature drop from 20 to 0 °C the gas volume is increased by

$$G = (2,000 - 200) \text{ m}^3 \cdot 950 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1} \cdot 20 \text{ }^{\circ}\text{C} = 34.2 \text{ m}^3$$

The mass of gas results from the ideal gas law

$$m_G = \frac{p \cdot V_G \cdot M}{R_m \cdot T} = \frac{100,000 \text{ Pa} \cdot 200 \text{ m}^3 \cdot 100 \frac{\text{kg}}{\text{kmol}}}{8,314.51 \frac{\text{J}}{\text{kmol K}} \cdot 293.15 \text{ K}} = 820.55 \text{ kg}$$

The corresponding pressures are

$$p = \frac{m_G \cdot R_m \cdot T}{(V_G - R) \cdot M} = \frac{820.55 \text{ kg} \cdot 8,314.51 \frac{\text{J}}{\text{kmol K}} \cdot 303.15 \text{ K}}{(200 - 17.1) \text{ m}^3 \cdot 100 \frac{\text{kg}}{\text{kmol}}} = 113,079.94 \text{ Pa}$$

$$p = \frac{m_G \cdot R_m \cdot T}{(V_G - R) \cdot M} = \frac{820.55 \text{ kg} \cdot 8,314.51 \frac{\text{J}}{\text{kmol K}} \cdot 273.15 \text{ K}}{(200 + 34.2) \text{ m}^3 \cdot 100 \frac{\text{kg}}{\text{kmol}}} = 79,571.22 \text{ Pa}$$

□

7.4.6 Relief and Retention Systems

The substances discharged on pressure relief must be handled in such a way that no harm to humans or environment is caused. In the first place, it must be determined if one or two-phase relief takes place. In case of doubt it is recommendable to separate the liquid phase in order to avoid further reactions. After the separation has taken place, e.g. in impingement separators or cyclones, the reaction is stopped by a large quantity of cold water containing a reaction inhibitor, if necessary.

The safe disposal of gases and vapours must be achieved as well. Three possibilities are available; the choice depends on the quantity and nature of the substances involved:

- discharge into the atmosphere,
- retention by treatment systems,
- retention in closed recovery systems.

Figures 7.3 and 7.4 give an overview.

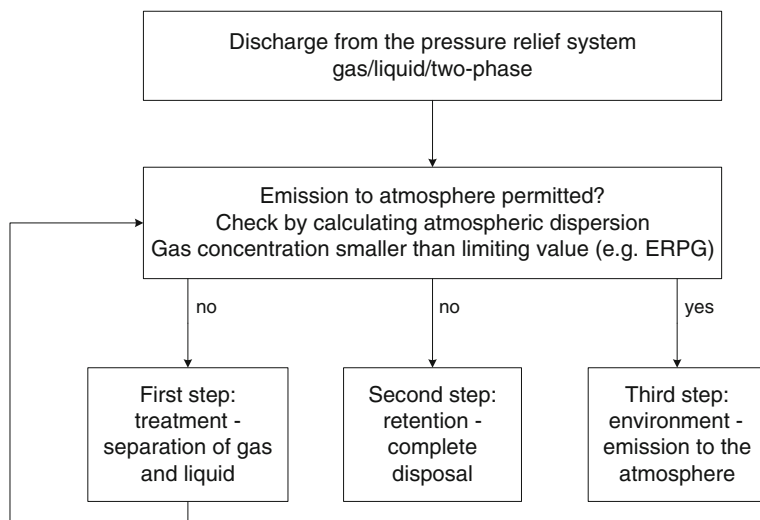


Fig. 7.3 Possibilities for treating substances released on pressure relief (courtesy of [11])

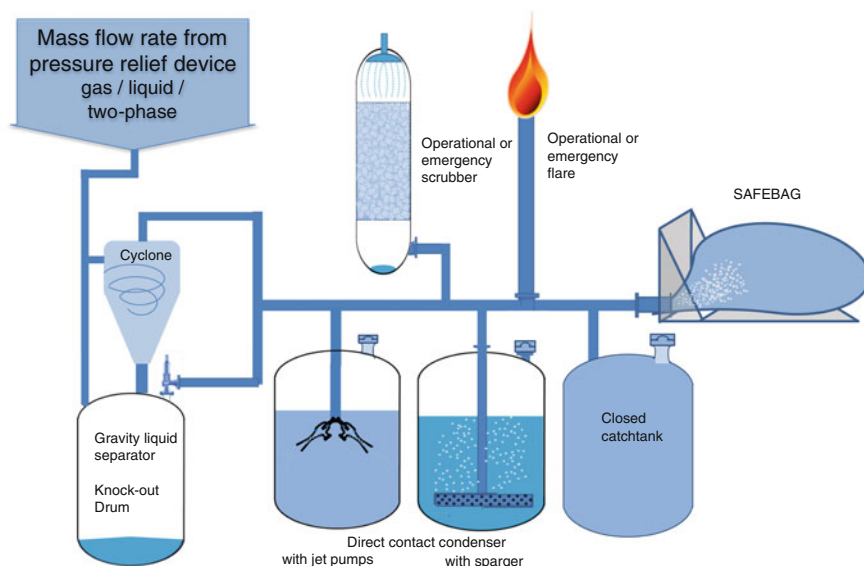


Fig. 7.4 Technical alternatives for retention systems (courtesy of [11])

Substances may only be released to the atmosphere if it was proved, e.g. by a dispersion calculation (vid. Sect. 10.5), that their negative impact remains within acceptable limits. Otherwise the substances have to be treated. This can be done by thermal cleanup systems, flare systems, scrubbers as well as dip-tube and other condensation units.

In doing this it has to be controlled whether the hazard potential is sufficiently reduced or not, since both untreated substances and the final products of the treatment are ultimately released into the environment. It may happen that the hazard potential is merely shifted. A scrubber may clean up exhaust air, but then generate highly contaminated wastewater. Additionally, it must be demonstrated that the disposal systems are not damaged by the reaction forces and momentum transfer occurring during discharge.

If no satisfactory solution is found, the substances must be discharged into a closed retention system. This may be a static vessel or a bag that can be blown up (SAFE BAG). However, these systems may quickly reach their limitations because of the large quantities that have usually to be retained.

A reduction of volume can be achieved by dissolving, condensing or chemically fixing the discharged substance. Often this can be done by discharging the gases and vapours into a liquid (often water) filled vessel. The effectiveness of the condensation or absorption process can be enhanced by introducing the substance into the vessel through nozzles or distributor pipes and thus dispersing them.

Furthermore the effectiveness of condensation or absorption is influenced by the temperature of the fluid in the liquid filled vessel, its filling level, which influences the bubble rise time and the pressure. The latter should be as high as possible in accord with the requirements of the pressure relief device.

The design of a safe pressure relief system together with an appropriate handling of the discharged substances may be a time-consuming iterative process. An alternative to pressure relief can be pressure containment, i.e. the load limit is chosen in such a way that no event sequence in the plant leads to pressures exceeding it (passive safety, vid. Sect. 4.2.2).

Furthermore, a pressure relief device is not required if pertinent process control equipment reliably prevents impermissibly high pressure from occurring. Yet it must be ensured that such equipment copes with all conceivable scenarios. For example, a reliable protection against overfilling a vessel does not protect against a pressure rise caused by heating, e.g. from fire or exposure to sun radiation.

The best solution has to be found observing the pertinent boundary conditions. It is conceivable as well that the required mass flow rate for relief is so big that adequate openings cannot be provided for because equipment geometry does not permit one to do so.

7.5 Constructive Measures of Explosion Protection

Explosions can occur in process plants. They may endanger humans and the environment. If explosions cannot be prevented or rendered sufficiently improbable by measures of preventative explosion protection, constructive measures of explosion protection must be considered. They do not prevent explosions but offer protection. In particular we can apply [12]:

- explosion-proof design for the maximum explosion pressure;
- explosion-proof design for the reduced maximum explosion pressure in conjunction with explosion pressure relief;
- explosion-proof design with explosion suppression.

Furthermore, the propagation of the explosion pressure to adjacent parts of the plant must be prevented by explosion isolation or explosion suppression.

Explosion-proof design implies that all structures potentially affected by an explosion can withstand the maximum pressure and the maximum pressure rise caused by a confined explosion. Details on confined explosions of flammable gases are found in Sect. 2.1.1.10 and of flammable dusts in Sect. 2.4.6. In considering this it must be kept in mind that the initial pressure of an explosion can be above atmospheric depending on process conditions. This leads to a corresponding increase of the maximum pressure. Explosion-proof design is an example for a passive safety measure.

With explosion pressure relief the maximum possible explosion pressure is lowered by opening a relief vent after explosion initiation. This can be a bursting disc, explosion panel or explosion vent, with the latter allowing repeated use. In extreme cases the side wall or the roof of the industrial hall may serve as vent opening. By explosion relief the confined explosion becomes a partially confined one with a corresponding lower maximum pressure. Pertinent calculation procedures can be found in [12, 13].

Explosion suppression is achieved by a device consisting of a detector, which already detects the explosion at its early stage, and a tank containing an extinguishing agent under pressure. The detector activates a fast opening valve allowing the extinguishing agent to be rapidly injected from its tank into the vessel to be protected. This interrupts the explosion process. Hence, the pressure only rises to a value below the maximum pressure. This is an example for an active protection system.

In process plants apparatuses are connected by pipes. Therefore pressure waves generated by an explosion in an apparatus can cause pressure loads in other apparatuses. In order to avoid this, isolation of apparatuses can be achieved by flame arresters (or other devices). They are described below following [14–16]. These impede the propagation of an explosion and hence reduce its consequences (level 4 of Table 4.1). They can be applied to mixtures of flammable gases or vapours with oxidants (usually the oxygen in air) or mixtures of dusts and oxidants.

Mechanical flame arresters are based on the fact that small gaps reduce flame propagation, the flame is quenched (vid. Sect. 2.1.1.6).

The length of the gap required to extinguish a flame approximately amounts to

$$L = \frac{v_{\text{burn}} \cdot d_h^2}{100 \cdot \nu} \quad (7.43)$$

In Eq. (7.43) L is the length in cm, v_{burn} the initial speed of flame propagation in cm/s (vid. Sect. 2.1.1.5), d_h the hydraulic diameter in cm (4 times the cross section/perimeter) and ν the kinematic velocity of the material mixture in the flame in cm^2/s .

7.5.1 Deflagration and Detonation Arresters for Gases

During normal plant operation flame arresters permit the unhindered passage of explosive mixtures. If ignition occurs, however, they block the passage of the flame by preventing the ignition from being propagated to the protected equipment. Different types of flame arresters are distinguished depending on the nature of the combustion process (stable combustion, deflagration, detonation) and the place of installation, which can be inside the pipe (in-line), at the opening of an apparatus to its connecting pipe (volume) or at the end of the pipe (end-of-line). The latter serves to stop a transfer of ignition from the outside into the system. The following types of flame arresters are distinguished:

- static dry flame arresters,
- static liquid seal flame arresters,
- dynamic flame arresters.

Independently of its design the effect of a flame arrester derives from one or several of the following mechanisms.

7.5.1.1 Flame Quenching in Narrow Channels: Static Dry Flame Arresters

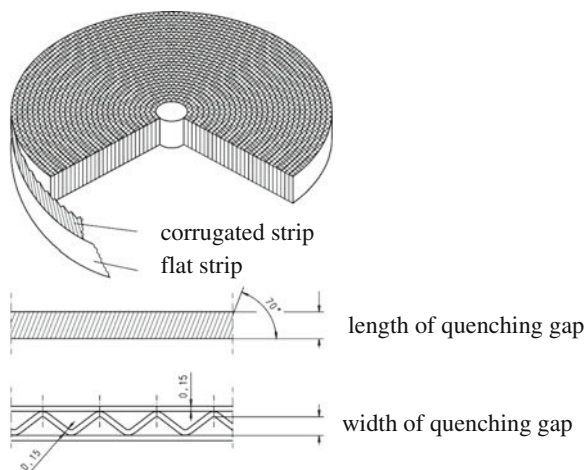
Through intimate contact with the cold walls of a filter element comprising many narrow channels heat and free radicals are withdrawn from the combustion process, and the flame is extinguished. This mechanism is employed in dry flame screens (e.g. the crimped-ribbon flame arrester shown in Fig. 7.5).

The element consists of wound corrugated metal strips. The quenching gap size can be adjusted in accordance with the flash-back capability of the explosive mixture. The principle of flame quenching in small gaps is applied in end-of-line flame arresters and in-line flame arresters.

The working principle of a crimped ribbon type dry flame arrester element is shown in Fig. 7.6. If a mixture of gases ignites in a gap between two walls, the flame spreads towards the non-combusted mixture. The volume expansion accompanying the combustion compresses the non-combusted gases and accelerates the flame. The flame is extinguished because of heat loss to the boundary layer 's' caused by heat transfer to the large gap surface, which is mainly due to gap length. The gas mixture is cooled below its ignition temperature.

Gap width and length of the flame arrester element determine its extinguishing capability. The narrower and the longer the gap the better is the extinguishing effectiveness. The wider and the shorter the gap the lower is the pressure loss. The optimum is determined by experiment.

Fig. 7.5 Flame arresting element made of flat and corrugated metal strips (courtesy of [17])



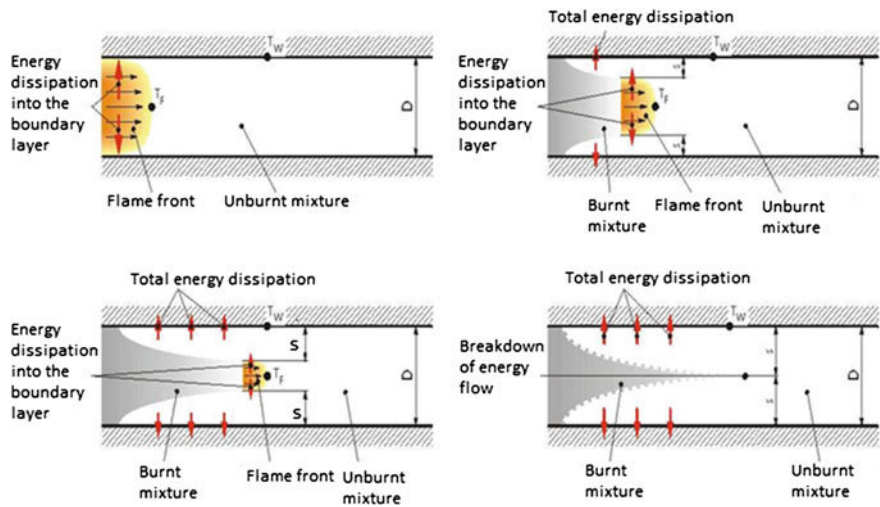


Fig. 7.6 Mechanism of flame quenching: extinguishing by heat dissipation in the temperature boundary layer from *left to right* (courtesy of [17])

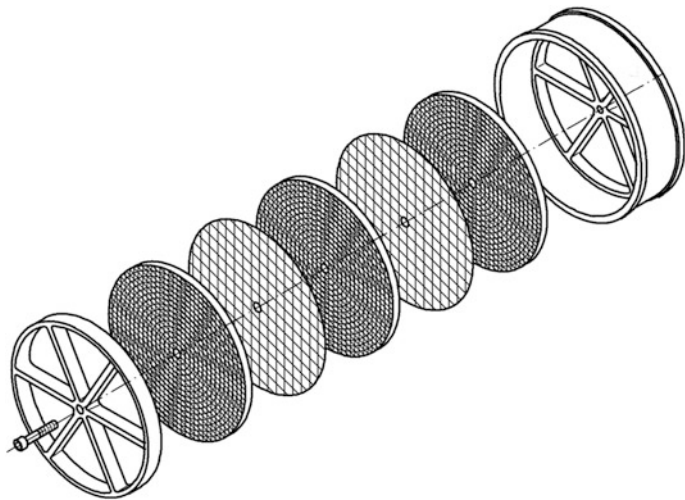


Fig. 7.7 Typical flame arrester unit with several elements (courtesy of [17])

Figure 7.7 shows how several flame arrester elements are combined forming a flame arrester unit which provides the required gap length. The final configuration of a flame arrester is shown in Fig. 7.8. It consists of a pressure shock resistant housing and the appropriate flame arrester unit.

Fig. 7.8 Typical detonation flame arrester with built-in flame arrester unit and temperature switches for triggering additional safety functions (courtesy of [17])

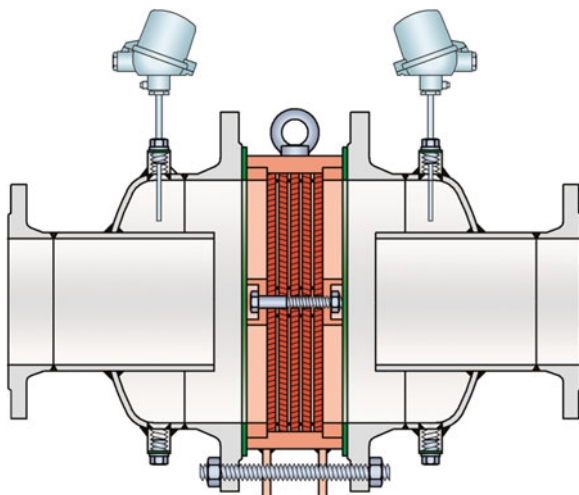


Fig. 7.9 Liquid product flame arrester for the filling line of storage vessels (courtesy of [17])

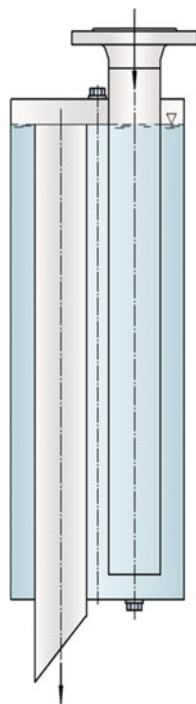
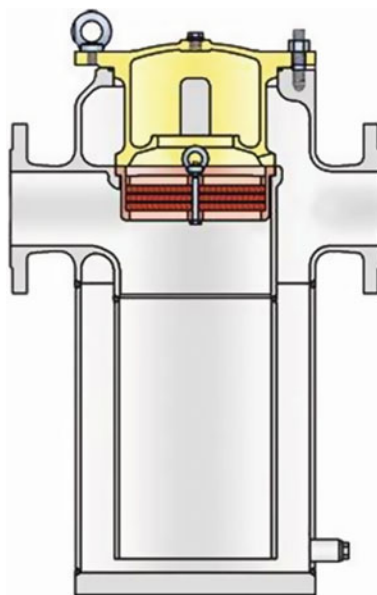


Fig. 7.10 Liquid product flame arrester for the filling and emptying lines of storage vessels (external installation) (courtesy of [17])

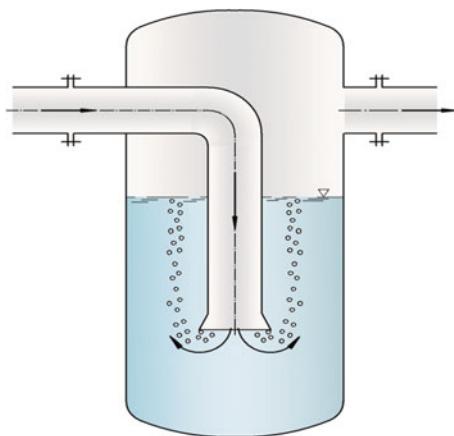


7.5.1.2 Blocking by Liquids: Liquid Seal Flame Arresters

There are two main types of liquid-type flame arresters:

- the liquid seal in a kind of siphon or in form of a siphon built into a liquid transporting pipe, which forms a barrier against flame transmission from a deflagration or a detonation (vid. Figs. 7.9 and 7.10), and
- the hydraulic flame arrester in which a stream of gas passes through a dip tube and is divided into non-coalescing bubbles (vid. Figs. 7.11 and 7.12).

Fig. 7.11 Hydraulic flame arrester (principle) (courtesy of [17])



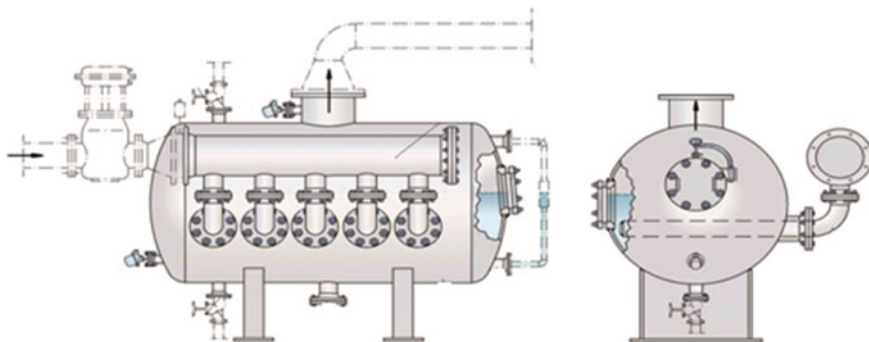


Fig. 7.12 Hydraulic flame arrester (courtesy of [17])

7.5.1.3 Dynamic Blocking: Dynamic Flame Arresters

The dynamic flame arrester has a cross section which is so small that the flow velocity is always greater than the turbulent flame velocity (combustion velocity) of the flammable mixture. An upstream propagation of the explosion is thus prevented as long as the flow is fast enough.

Safe flow velocities in the described device depend on the diameter of the pipe and the explosion properties of the gas involved. The location of installation has to be considered, for example, at an open outlet (e.g. high velocity vent valve) or enclosed, e.g. at the burner inlet of an incinerator, where the heat flux from the surroundings has an influence. In both cases turbulence shall not be increased, because that would accelerate the combustion process. This is achieved by the high velocity vent valve shown in Fig. 7.13.

7.5.2 Use of Flame Arresters in Practice

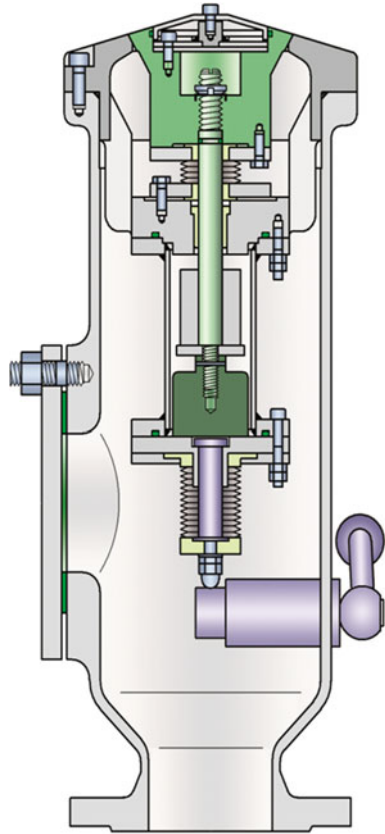
A hazard analysis, for example a HAZOP study (vid. Sect. 9.1.2.3, serves to identify the necessary preventative or protective safety measures. Constructive measures of explosion protection are necessary if the occurrence of flammable atmospheres and sources of ignition cannot be totally avoided.

The selection of a flame arrester depends on a number of boundary conditions. Only intimate knowledge of the system to be protected and the process within it enable one to select appropriate and economic barriers.

The hazard analysis allows one to determine which parts of the plant have to be protected against which type of hazard, i.e.

- What is to be protected?
- Where and of what type are the potential ignition sources?
- Can ignition be due to external or internal sources?

Fig. 7.13 High velocity vent valve (courtesy of [17])



- What is the chemical composition of the explosive atmosphere?
- What are the operating conditions? (Deviations from standard atmospheric temperature and pressure?)

These questions have to be clarified in order to determine the place and type of installation as well as the type of flame arrester.

If installed inside a pipe (in-line) deflagration and detonation (vid. Sects. 2.1.1.9 and 2.1.1.10) have to be considered. Often a few meters of a pipe are sufficient to effect a transition from deflagration to detonation (DDT). Therefore usually detonation-type flame arresters are used for installation inside pipes.

If installed at the end of a pipe (end-of-line), e.g. for protecting tank vents, deflagration flame arresters can be used, if the formation of a stable flame on the flame arrester is not to be expected. Otherwise a flame arrester certified for stable burning must be chosen.

In the next step the type of flame arrester is determined. In doing this a number of boundary conditions have to be considered. Among them figure, for example, contamination with solids, solidification temperature and condensation or

Table 7.3 Classification of materials in explosion groups based on their maximum experimental safe gap (MESG) according to [1, 14, 16]

Explosion group	Maximum experimental safe gap $w_{\max}$ in mm	Test gas
IIA1	$1.14 \leq \text{MESG}$	Methane
IIA	$0.9 < \text{MESG} < 1.14$	Propane
IIB1	$0.85 \leq \text{MESG} \leq 0.9$	Ethene
IIB2	$0.75 \leq \text{MESG} < 0.85$	Ethene
IIB3	$0.65 \leq \text{MESG} < 0.75$	Ethene
IIB	$0.50 \leq \text{MESG} < 0.65$	Ethene/hydrogen
IIC	$\text{MESG} < 0.5$	Hydrogen

Note Equipment group I applies to equipment intended for use in underground parts of mines, and in those parts of surface installations of such mines liable to be endangered by firedamp and/or combustible dust, Equipment group II applies to equipment intended for use in other places liable to be endangered by explosive atmospheres [18]. The degree of hazard increases from A to C; the sub-division into 1–3 is done in [16].

solidification of impurities from the stream. Additionally, the arrester must be capable of withstanding the expected pressure. Details can be found in [12, 15].

In order to correctly choose the flame arrester, the maximum gap width (cf. Sect. 2.1.1.6) must be known. This parameter serves to categorize materials in explosion groups, as shown in Table 7.3.

In Europe the use of equipment in flammable atmospheres is regulated in [18]. Flame arresters are also covered there.

7.5.3 Safety Concept

According to [16] risk must be assessed in order to develop a safety concept for the system to be protected. In the informative part of [16] an assessment is carried out for an in-line detonation arrester, which is based on a qualitative estimate of risk.

In doing this the following factors must be accounted for:

- the probability (preferably: the expected frequency of occurrence; vid. Chap. 9) of the undesired event (e.g. flame propagation from the source of ignition) and
- the extent of the accompanying consequences (e.g. destructions caused by explosion pressure waves; vid. Chap. 10).

The assessment may suggest the conclusion that more than one protective measure must be installed in order to sufficiently reduce the probability of flame propagation. A relevant safety concept may consist, for example, of an inline detonation arrester, which is located as closely as possible to the installation to be protected, and (as an additional measure) an inline deflagration arrester close to the potential source of ignition.

This principle is demonstrated in Table 7.4. In that table the probability of ignition is combined with the probability of the existence of a flammable mixture.

Table 7.4 Number of independent measures against flame propagation, if considerable consequences are to be expected (from [16])

Source of ignition	Flammable atmosphere			
	Permanently	Occasionally	Rarely	Never
Permanently	3	2	1	0
Occasionally	2	1	0	–
Rarely	1	0	–	–
Never	0	–	–	–

The required number of independent measures leads to the same safety level. One of the measures of Table 7.4 is an in-line detonation arrester.

7.5.4 Flame Arresters for Dusts

The flame arresters described above are not suitable for use in equipment and pipework where the hazard of a dust explosion exists. Other procedures must be adopted there. Among the devices used for isolation figure star-wheel feeders or rotary valves, active barriers with extinguishing media, rapid-closing valves (explosion isolation valves) and doors, as well as explosion vents. These are described in detail in [19].

If star-wheel feeders are to be used, it must be established beforehand whether they impede flame propagation and withstand the explosion pressure or not. In order to avoid that combustion gases are transported to parts of the plant lying downstream, the star-wheel feeder must be closed automatically in case of an explosion, for example triggered by a pressure switch.

If barriers of extinguishing agents are used, the agent is injected within a few milliseconds into the flame front. The injection is triggered by a flame detector. In case of doors the flame detector activates their closing function. The effectiveness of the measures must be demonstrated experimentally.

Explosion valves working without auxiliary sources of energy close at the higher velocities of flow occurring during explosion pressure relief. Thus they automatically block the pipe and prevent the explosion from propagating.

When explosion vents are used, the formation of long flames and the release of large quantities of combustion products, possibly with negative environmental impact must be expected.

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*Doch mit des Geschickes Mächten ist kein ew'ger Bund zu
flechten. (Against misfortune's might! covenants with powers of
fate will—alack—not always last.)*

Das Lied von der Glocke, Friedrich Schiller 1759–1805

8.1 Overview of Risk and Safety Analyses

In modern technology, which is characterized amongst others by the use of nuclear power, the operation of complex process plants and air and space travel, failure can hardly be tolerated because its consequences may be large. They can be economic, such as unplanned shut-downs or destruction of plants, or endanger humans and environment. Accidents do happen despite the numerous safety measures described in the preceding chapters. The reason is that technical measures and human interventions for avoiding accidents can never be perfect. They fail with a certain probability. This is the rationale for the barrier concept presented in Sect. 4.2.

Therefore safety of plants is an important issue already from the beginning of the planning phase. This is especially true for plants which are subject to the Major Accident Ordinance [1]. For these plants, amongst others, a safety assessment has to be performed. According to the second administrative regulation [2], which is no longer valid but by no means obsolete, the assessment is to be made using methods such as Hazard and Operability Studies (HAZOP) [3], Failure Mode and Effect Analysis (FMEA) [4], Event Tree Analysis (ETA) [5] or Fault Tree Analysis (FTA) [6, 7]. These methods are treated in detail in Chap. 9. They mainly serve to identify potential accidents and weak points in the design of a plant. They differ as to the approach (e.g. inductive, deductive) and the degree detail (depth) of the analysis. Most of all a distinction between qualitative and quantitative approaches must be made. In this context it has to be recalled that all methods are qualitative in the first place and that they only become quantitative if probabilities

are assigned, as far as the method in question permits this to be done. Event tree and fault tree analyses are particularly suited for quantification.

Accidents in technical systems are rare events. Therefore their risk can in general not be derived directly from operating experience (actuarial approach) and then be applied to judge the future development, as is, for example, possible with occupational accidents. Instead engineering risks are usually assessed using an approach called risk assessment based on the knowledge of details. Figure 8.1 shows the procedure, starting from the initiating events up to the determination of damage and risk numbers. Four steps are distinguished:

- (1) Event sequences
- (2) Characteristics
- (3) Exposure sequences
- (4) Damage and risk

The first step “event sequences” deals with conceivable event sequences, so-called scenarios, and the determination of the corresponding expected frequencies of occurrence (Example: release of chlorine following pipe rupture due to overpressure with an expected value for the frequency (expected frequency) of 10^{-6} a^{-1}). Starting point are the initiating events, $D_1, \dots, D_k$. They usually represent the failure of an operational (duty) component (here: component failure which caused the overpressure). An initiating event leads to an accident, if it is not coped with by the monitoring and safety systems of the plant (vid. Sect. 4.2). Which of the monitoring and safety systems are required and how their functioning, respectively their failure, affects the event sequence, is investigated in this step.

The second step “characteristics” comprises the initial and boundary conditions for assessing the consequences of the event sequence for employees and the population at large (Example: leak cross section 10 cm^2 , elevation of release point 10 m, pressure difference 500 kPa). It makes sense to assign the different sequences to categories (e.g. small leaks, medium leaks, large leaks, fires, explosions etc.), each of them representing several event sequences by one set of initial and boundary conditions. This set must lead to the most severe consequences of all the event sequences covered by the category and hence be conservative. The boundary conditions usually are stochastic, i.e. at most the probability of occurrence, for example for the above mentioned leak, may be indicated. It is normally not equal to 1, as supposed in the deterministic approach. Other leak sizes and locations are, of course, possible.

The two steps described above represent the analysis of engineered systems of the plant. In the first place the analysis is done qualitatively, for which methods like HAZOP (Sect. 9.1.2.3) and FMEA (Sect. 9.1.2.4) can be used. The result of the investigation is then represented by means of event and/or fault trees. Chains of events leading to the different end points of the accident sequences shown in the event tree (e.g. leaks of different sizes) are systematically arranged. Thus probabilities can be assigned to them on the basis of reliability data for the failure of

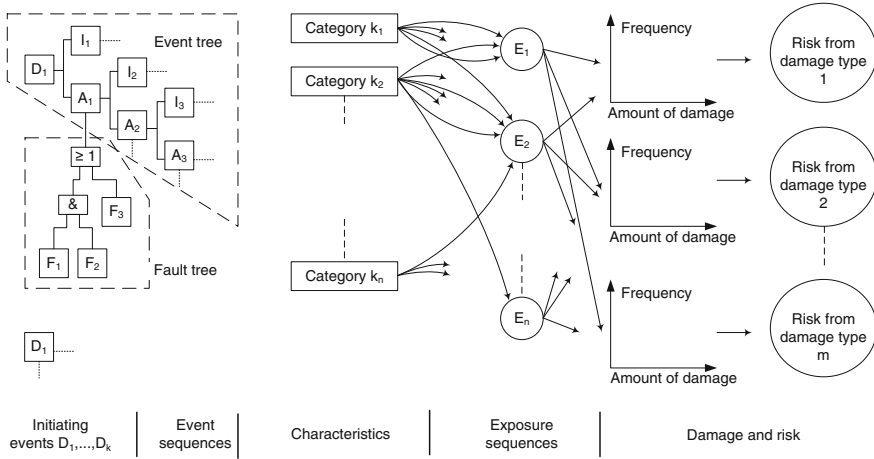


Fig. 8.1 Outline of a risk assessment based on detailed knowledge of event and exposure sequences [8]

technical components and human error. Results are the expected frequencies of occurrence of the different categories $k_1, \dots, k_n$ in Fig. 8.1.

If the investigation ends here we speak of a probabilistic safety analysis (PSA). Its main objective is to identify possibly existing weak points in the plant design and to show how they are efficiently removed.

We arrive at a probabilistic risk assessment (PRA) if the accident consequences are assessed as well and frequency and consequence are combined. This is done in the following steps.

The third step “exposure sequences” describes how the harmful agent (chlorine in this case) impacts the object to be protected (Example: dispersion calculation for determining how many people in the surroundings of the point of release are exposed during which period of time to which concentrations of chlorine; measures like staying indoors or evacuation can be accounted for).

The fourth step “damage and risk” firstly comprises the damage, i.e. the consequences of the accident (Example: x fatalities following chlorine exposure, y cases of grave acne from chlorine).

In order to assess the risk damage and its expected frequency of occurrence are then combined (Example: $x \cdot 10^{-6} \text{ a}^{-1}$ fatalities following chlorine release, $y \cdot 10^{-6} \text{ a}^{-1}$ cases of acne).

The assessment of accident consequences is treated in Chap. 10. It requires numerous phenomena to be modelled such as discharge, atmospheric dispersion or heat radiation of fires. Additionally, relations are needed which relate the intensity of exposure of humans and environment with probabilities for certain volumes of damage. This is often done using probit equations (vid. Sect. 2.6.2.2 and Appendix B).

The methods of calculation employed are those which are used as well for deterministic analyses. The difference is that stochastic boundary conditions, which are closer to reality, are used for the calculations. For example, instead of a fixed leak size a whole spectrum of leak sizes is treated with pertinent expected frequencies of occurrence being assigned to the different leak sizes. Instead of calculating the dispersion of a toxic substance based on a specific weather situation, different possible weather situations with their corresponding probabilities of occurrence are accounted for. This is reasonable, since the instant in time of the accident and the weather condition, which then prevails, are not known beforehand.

The analyses outlined above cannot be performed without fixing certain parameter values and making simplifications. This is in reality a specific characteristic of deterministic analyses. However, the assumptions and simplifications made in probabilistic analyses are generally closer to reality than in deterministic assessments. Their extent depends on the focus and degree of detail specified for the analysis.

A PSA serves the objective of establishing the probability of failure of technical systems and to point out ways for reducing it. It increasingly becomes a complement of traditional procedures of safety design. This applies, in particular, for the area of nuclear power, where the safety of almost all plants worldwide has been assessed probabilistically. The periodic safety review in the Federal Republic of Germany [9] with the corresponding guidelines [10, 11] firmly establishes probabilistic safety analyses as part of the valuation of the safety of nuclear power stations. In the meantime the safety of all German nuclear power plants has been investigated according to this procedure. For process plants a number of probabilistic safety analyses have been performed as well, e.g. [12–17].

As already mentioned, in risk studies the determination of the expected frequencies for the occurrence of damaging events by means of event and fault tree analyses is complemented by an assessment of their consequences. These are radioactive releases in the case of nuclear power stations and for process plants generally fires, explosions or releases of toxic substances whose impact on

Table 8.1 Risk studies which substantially contributed to the development of the methodology of assessing engineering risks

Study	Object
Reactor safety study (“Rasmussen study”) (1975) [22]	Pressurized and boiling water reactors of U.S. design
NUREG-1150 (1989) [23]	Several pressurized and boiling water reactors of U.S. design
German risk study nuclear power plants (phases A and B) (1979) [24] and (1990) [25]	Nuclear power station Biblis B (pressurized water reactor)
Canvey island study (1978) [26]	Process plants in the Thurrock area (U.K.)
Rijnmond study (1982) [27]	Process plants in the mouth of the river Rhine (Netherlands)

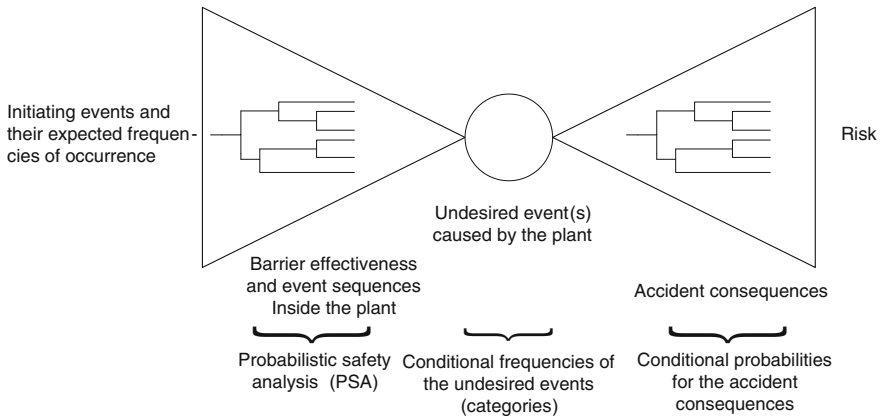


Fig. 8.2 Bow-tie diagram as an overview of a complete risk analysis

humans, the environment and property is assessed. Procedures and results of studies for nuclear power stations are described in detail in [18] and for process plants in the subsequent Chaps. 9 and 10.

In Table 8.1 several studies are listed, in which important contributions to the development of the methodology of risk assessments were made. Contrary to the risk studies which are performed in the Netherlands [19], France [20] and Switzerland [21] in the context of the licensing of process plants they are published.

The risk analysis procedure is outlined once again in Fig. 8.2 using the so-called bow-tie diagram, which is frequently found in the literature.

The left-hand side of Fig. 8.2 symbolizes the detailed event and fault tree analyses of the engineered systems of the plant. The right-hand side, on the other hand, represents the event tree analyses of the accident consequences as well as their impact on humans, environment and valuable property.

As already mentioned, the scope and depth of the analyses may differ. If only the left-hand side of the bow-tie diagram is treated, we are dealing with a probabilistic safety analysis. Its results are the expected frequencies of undesired events. The objectives then are to identify weak points and imbalances in the engineered safety systems as well as to indicate ways for eliminating them. This is the most work-intensive part of a risk analysis.

The main tool of a probabilistic analysis is fault tree analysis. It is based on deriving deductively the failure of a system from the failure of its sub-systems and sub-sub-systems and so forth. The failure of the latter is in turn derived from the failure of its components. The result of this analysis is represented by the so-called fault tree, which shows the logical relationships between the failure of a system and that of its components. In general, only two states of the system and its components are admitted: functioning and failure. These states occur with a certain probability. The probability of failure of the system then results from a

Table 8.2 Expected frequencies for a loss of containment in 10^{-6} a^{-1} [28] (before use the footnotes in [28] should be observed)

Installation (part)	Instantaneous release of the total contents	Continuous release of the total contents within 10 min	Continuous release from hole with a diameter of 10 mm
Pressure vessel	0.5	0.5	10
Process vessel (change of physical properties)	5	5	100
Reactor vessel (change of chemical properties)	5	5	100

mathematical evaluation of the fault tree on the basis of the probabilities for the failure of its components and the probabilities for the occurrence of operator errors and external impacts on the system.

The functioning or failure of a technical system depends on the values of the chemical and physical parameters such as temperatures, pressures and concentrations of the process which takes place in it. Hence, the fault tree model is a simplification. Yet this simplification has the advantage that the connections between the individual components and the system and the impact of their failures on the process as a whole can be represented.

Fault tree analysis is a complete procedure. If consistently applied it generates all event combinations leading to failure. Limitations do not derive from the procedure but from the knowledge and scrupulousness of the analyst. It goes without saying that phenomena not known at the time of analysis cannot be identified.

The procedure used, for example, in the Netherlands in the context of the licensing of process plants places the focus on accident consequences (right-hand side of Fig. 8.2). The detailed investigation of the engineered systems is then replaced by indicating expected frequencies for the loss of containment (LOC). These frequencies have to cover, apart from spontaneous failures (developing without apparent predictable causes), failures of all failure modes, for example, failures caused by overpressure, too high temperatures, corrosion etc. The fault tree analysis of the engineered systems is replaced by using these frequencies. Such an analysis is called risk-based. In what follows several of the failure mechanisms which may lead to a loss of containment are listed:

- internal corrosion (e.g. selectively, locally, tensile crack corrosion, elongation corrosion, abrasion);
- external corrosion (weather impacts, droplets from neighbouring systems, contact corrosion, friction corrosion, destruction of protective surfaces);
- alternating stresses (mechanical and thermal);
- operating and handling errors (e.g. erroneous opening of valves, wrong threads, wrong bolting, wrong sealing material etc.);
- hazards from maintenance and repair work;

Table 8.3 Expected frequencies for a loss of containment in $10^{-6} \text{ m}^{-1} \text{ a}^{-1}$ [28] (before use the footnotes in [28] should be consulted)

Installation (part)	Full bore rupture (release from both open ends)	Leak with a diameter of 10 % of the nominal diameter, maximum 50 mm
Pipeline, nominal diameter < 75 mm	1	5
Pipeline, $75 \leq$ nominal diameter $\leq$ 150 mm	0.3	2
Pipeline, nominal diameter > 150 mm	0.1	0.5

- mechanical impacts (handling, transport, dropping loads, assembly etc.);
- overload from over or under pressure due to system malfunctions.

Tables 8.2 and 8.3 present the expected frequencies of failure for vessels and pipework as used in risk-based analyses.

The leak sizes are the starting point for accident consequence calculations. If the results of the latter are combined with the corresponding expected frequencies of leak occurrence we obtain an estimate of the risk.

Safety deals with stochastic events (for example, the moment of occurrence of an accident) and with stochastic boundary conditions (for example, the weather at the point in time of accident occurrence). This together with lack of knowledge on some of the phenomena to be treated and flaws in models and input data lead to uncertainties, which are often compensated by safety factors and lead to procedures based on conventions. This was already pointed out in Chap. 1.

In line with the two elements, which make up risk, the methods of qualitative and quantitative analysis of plant engineered systems are treated in Chap. 9. Their results are the expected frequencies for the occurrence of the categories of Fig. 8.1. This is followed by the description of the methods for assessing the extent of damage in Chap. 10. Chapters 11 and 12 are dedicated to two important applications, functional safety and the determination of appropriate distances between industry and residential areas.

8.2 Risk Limits

Since hazardous industrial activities cannot be totally free from risk, the question arises whether the determined risk is sufficiently small or not. This is often put into perspective by the question “how safe is safe enough”. A yardstick for measuring the result of a risk analysis is required.

This yardstick, often called a safety goal, may have different degrees of bindingness. Safety goals may be

- fixed by the analyzing engineer himself,
- fixed within an industrial firm,
- used by public administration for valuating results,
- determined by an administrative act,
- fixed by the parliament of a country.

Since there is no risk limit which can be derived from the laws of nature, often measured values or values tolerated by society serve as a guideline, for example, the frequency of occupational accidents or the frequency of cancer cases. The tolerable risk from industrial activities is then chosen to be one or two orders of magnitude smaller. Considerations leading to limit values are described in detail in [29].

Limit values may refer to different levels, for example, to

- the failure probability of safety barriers,
- the expected frequency of the occurrence of undesired events or
- the risk.

Concerning the latter one has to differentiate between the risk of an individual and that of a group of the population (collective, group or societal risk).

Instead of directly specifying requirements concerning failure probabilities of barriers recently risk limits are used from which these requirements are derived. This is done in the context of “functional safety”, which is treated in detail in Chap. 12.

In Germany so far no risk limits for technical installations have been specified which can be used to judge calculated risks. Other European states, on the other hand, have been using such limits for quite some time. Yet, their binding power and legal consequences differ (vid. [30]). The highest binding power corresponds to the limit values in the Netherlands, which result from a parliamentary decision.

Risk limits have always to be regarded in relation with the procedure used for risk assessment. The degree of conservativeness, of detail etc. in determining risks influence the calculated result (vid. Chaps. 9 and 10). In order to ensure equitable treatment the application of risk limits requires a largely unified, convention-based procedure of analysis. This is achieved, for example in the Netherlands, by using the computer program PHAST [31]. It contains algorithms for the methods of analysis and default values for many of the required input parameters.

The concept of risk is used with the following differentiations:

- individual risk: the expected annual frequency for an individual to suffer damage;
- location risk: the expected annual frequency to suffer damage at a certain location, which is independent of whether a person is present at this location or not; it coincides with the individual risk if the person is present during 24 h;
- group, collective or societal risk: the expected frequency for more than a certain number of people to suffer damage;

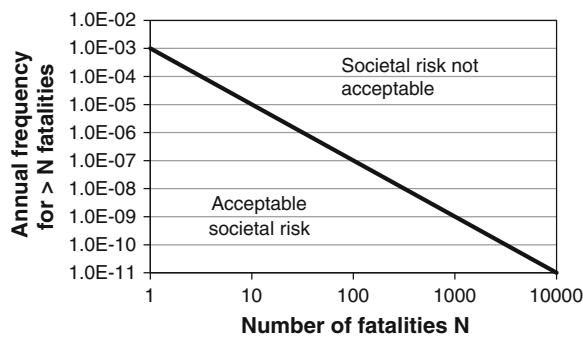


Fig. 8.3 Criterion for societal risk in the Netherlands (after [19])

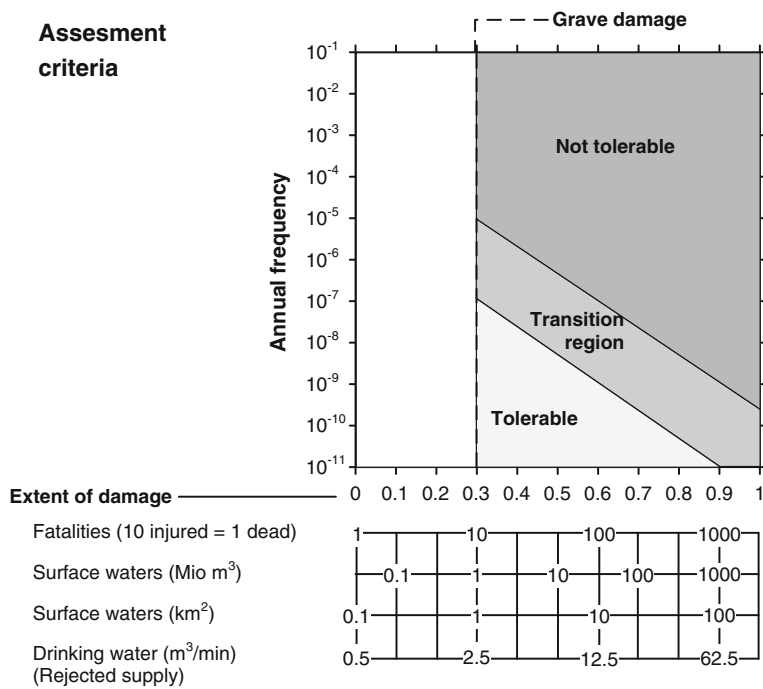


Fig. 8.4 Risk limits in the canton of Zürich (courtesy of [33])

The damage type usually is death. Of course, it is possible to assess the risk of permanent health damage, damage to the environment or property.

In particular, risks of the contamination of land or water can be assessed as well. In Switzerland limit values for these types of damage have been specified (vid. Fig. 8.4).

Table 8.4 Risk limits in several countries

Country	Limit value for individual risk in 10^{-6} a^{-1}
Netherlands	1 for new plants 10 for existing plants
Switzerland (canton Zürich)	10
Great Britain	<1 no action required 100 – 1 further action required observing the ALARP principle (as low as reasonably practical)

8.2.1 Individual Risk

A recent development in Germany in the field of risk limits is a proposal by the committee on hazardous materials (AGS). It specifies the risk limits given below. They concern the individual risk of death from handling carcinogenic materials [32]:

accepted risk: for the period of transition 4:10000
at the latest from 2018 onwards 4:100000

Values below these limits are acceptable. If a risk lies above them, it is tolerated observing measures specified in a catalogue as long as it lies below the limit of tolerable risk of 4:1000.

A risk above the tolerable risk limit is not tolerated. All risk limits refer to an entire working life of 40 years duration and continuous daily exposure. The stipulation is action-oriented and closely tied to a concept of staggered measures for risk reduction.

In what follows several risk limits for industrial installations are given. In the U.K. the following values apply:

- maximum tolerable workplace risk: $10^{-3}/\text{a}$
- maximum tolerable risk for the public: $10^{-4}/\text{a}$
- generally accepted risk: $10^{-6}/\text{a}$

Further values are listed in Table 8.4.

8.2.2 Collective Risk

The tolerable collective, group or societal risk is usually fixed using the relation

$$R = h \cdot x^n \quad (8.1)$$

In Eq. (8.1) h is the annual frequency for the occurrence of the damaging event and x the volume of damage associated with it (e.g. number of fatalities); n is the coefficient of risk aversion, which is usually chosen to be >1 . In this way a larger weight is assigned to the volume of damage, which has a special impact for catastrophes involving many fatalities.

In the Netherlands the relationship for the risk limits shown in Fig. 8.3 applies. The corresponding coefficient of risk aversion is $n = 2$.

In Switzerland (canton Zürich or e.g. Basel as well) the limit values of Fig. 8.4 are in use.

It is evident that three regions are distinguished in Fig. 8.4, viz.

- tolerable (also “acceptable”, but recently normally denoted by “tolerable”, since no risk is deemed acceptable).
- transition region: within certain periods of time measures for upgrading have to be implemented. In doing this the ALARP principle is applied, which comprises cost benefit considerations.
- not tolerable (a license cannot be granted).

As long as there are no official values in Germany the author proposes to use the individual risk value (location risk) of the Netherlands, i.e. 10^{-6} a^{-1} , and for the societal risk the limits applied in Switzerland (Zürich). The latter were used as well by the German Major Accident Commission in its expert opinion on the extension of the Frankfurt Airport [34].

Example 8.1 Determination of the risk aversion coefficient in Switzerland.

In order to determine the risk aversion coefficient two points are taken from the risk curve of Fig. 8.4 and then applies Eq. (8.1) to them.

Solution

For example, the curve gives 10^{-7} a^{-1} for 10 fatalities and 10^{-11} a^{-1} for 1,000 fatalities.

From these values we obtain:

$$R = h_1 \cdot x_1^n = h_2 \cdot x_2^n$$

After inserting the numerical values we have

$$10^{-7} \cdot 10^n = 10^{-11} \cdot 1000^n \quad \text{order} \quad 10^4 = 100^n$$

whence $n = 2$ results. □

8.3 Representation of Risks

In addition to indicating numerical values pictorial representations of risk are used. By way of example Fig. 8.5 shows the location risk as lines on a map. These lines around the investigated plant are lines of equal risk, the so-called iso-risk contours.

Collective risks are represented by so-called complementary frequency distributions. These indicate the expected frequencies for the occurrence of a damage which is larger than a certain value. For example, Fig. 8.6 shows the frequency

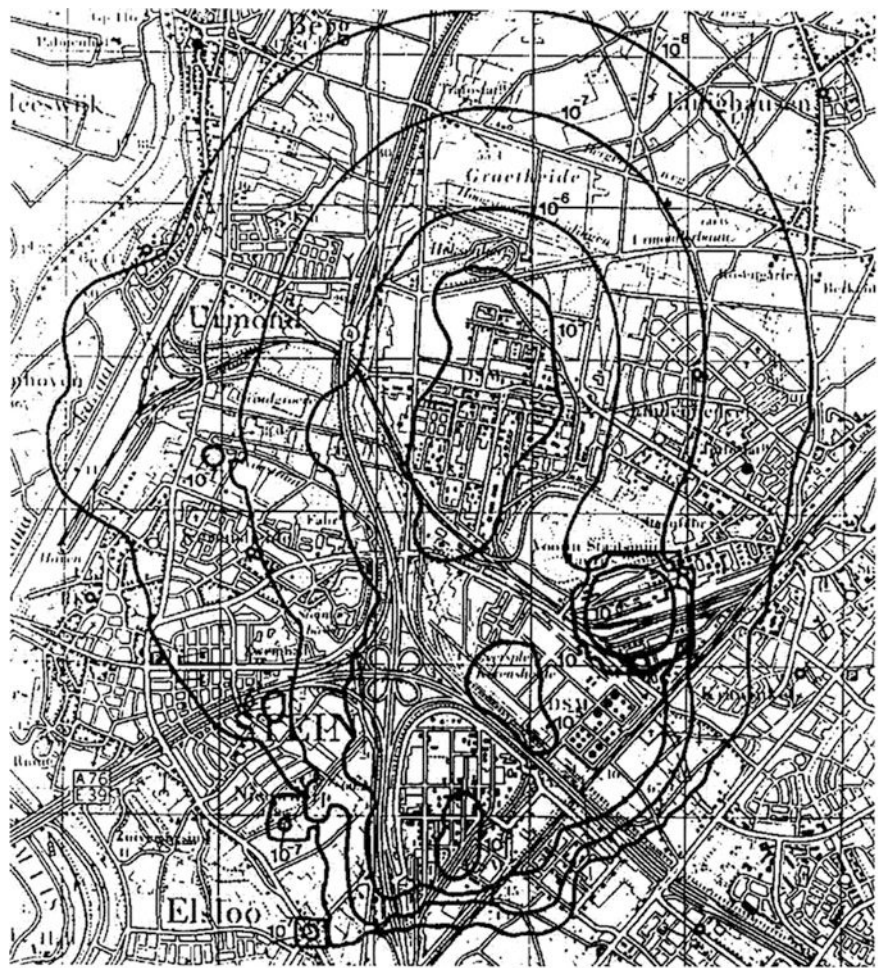
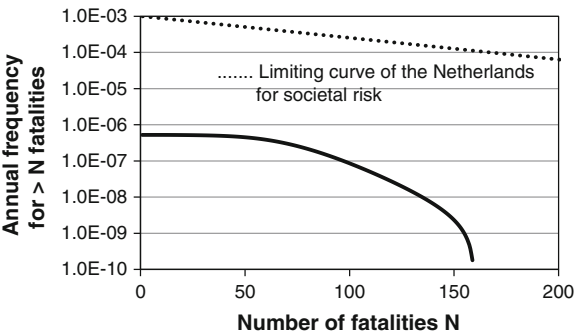


Fig. 8.5 Iso-risk contours in the surroundings of an industrial site (DSM Geleen) (courtesy of [19])

Fig. 8.6 Complementary frequency distribution of the collective risk caused by the failure of a pipeline (result of Case study of Sect. 10.11)



(ordinate) for more than N fatalities (abscissa) being caused by the failure of the gas pipeline treated in the Case study of Sect. 10.11.

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How safe is safe enough?

9.1 Fundamentals

A process plant functions properly, if the containment (pipework, apparatuses, vessels etc.) of the materials is intact and all parameters, which characterize its state such as temperatures, mass flows, pressures, concentrations etc. are within their design tolerance ranges. A prerequisite is, of course, the correct design of the plant, whose fundamentals were treated in the preceding chapters. It must be pointed out that the tolerance ranges mentioned above can vary with different operational states such as start-up, coast-down and full or partial load.

If deviations outside the tolerance range occur in one or several process parameters their consequences depend on the type of system, the extent of the deviations, the type and number of parameters affected and the functioning, respectively failure, of the monitoring and safety systems provided for such a case. Consequences can be: restricted operation, standstill or an accident, which results in an explosion, a fire or the release of toxic or radioactive substances depending on the nature of the plant affected. Several of the consequences mentioned may occur simultaneously.

Obviously, the relationship between deviations of the process parameters from their nominal values and the accompanying consequences can only be dealt with in concrete cases. Their treatment generally requires the interplay of several areas of knowledge, as shown in Fig. 9.1.

One has to observe that safety-related issues provide impulses for the underlying areas of knowledge. Interrelationships exist. It should be noted that the requirements on the systems and the decision of whether a certain state is to be assigned to functioning or failure depends on the required system function (totality of systems, which have to work in order to fulfil the required task). This decision may differ depending on whether full or partial load operation, shut-down or start-up are to be investigated.

Objective: Identification and valuation of weak points, proposals for improvement, demonstration of their effectiveness and implementation in order to achieve a balanced safety design

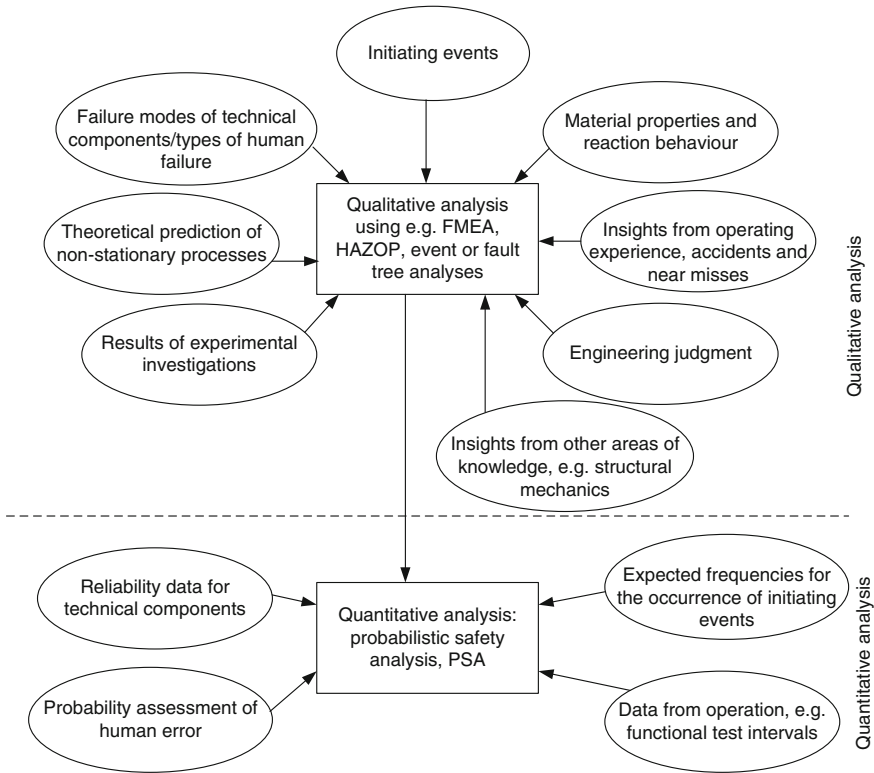


Fig. 9.1 Safety analyses and required input information (based on a process engineer as analyst) (after [2])

Given their importance as potential initiating events for an accident (cf. Sect. 8.1) a classification of conceivable failures of technical components and systems is given below [1].

1. Classification according to the technical impact of the failure (based on consequences)

- partial failure
- total failure
- catastrophic failure

2. Classification according to the variation with time of the main parameters until the occurrence of the failure

- spontaneous failure
- drift failure

3. Classification according to the causality between cause and effect

- systematic failure (early or late)
- random failure

4. Classification according to failure causes

- design-related failures
- manufacture-related failures
- utilization-related failures

5. Classification according to the relationship between failures

- dependent failure (functional dependence, secondary, common cause)
- independent failure

6. Classification according to the possibility of repair

- repairable
- non-repairable

Failures occurring in technical installations can usually be assigned to the attributes given above and be characterized in this way. Several terms and definitions of importance for safety analyses are listed in Table 9.1.

9.1.1 Failures and Safety Factors

The physicochemical processes leading to component failure are very complex. Therefore, it is difficult or even impossible to formulate a general theory describing their occurrence. Nevertheless, it is possible to describe a broad class of failures with the statistical model explained below.

Failures of technical components occur if the load to which they are exposed exceeds their resistance. The load can be mechanical, electrical, chemical, and biological or be caused by the environment. Combinations of different types of loads are, of course, conceivable. Technical components are designed in such a way that they can resist a certain load. Because of stochastic influences during the production of their structural materials (materials, for example, do not have homogeneous properties, e.g. hairline cracks may exist) and the manufacture of the components themselves (e.g. size tolerances) the resistance is a random variable. Such a variable is described by a statistical distribution. Similar considerations apply to the load. Factors like varying operating loads (e.g. fluctuations of pressures in pipes, loads in lifts) as well as varying environmental conditions (e.g. fluctuations of air temperature and humidity) or differing operating interventions by operators are of influence. Hence, the load is also described by a random

Table 9.1 Definitions of terms used in the safety analysis of engineered systems (expressions in brackets are often used, but do not stem from the standards [3–5]; author’s translation)

Term	Definition
Object of analysis	The object of analysis is the object of a statement on reliability. Object of analysis could be e.g. systems, sub-systems, components, functional elements. Technical objects of analysis have to be distinguished from functional ones.
System	A system is the assembly of technical and organizational means for autonomously realizing a task. A distinction must be made between technical and organizational systems. In accordance with its different functions a system comprises one or several functional elements.
Subsystem	A technical subsystem is the combination of components for realizing coherent tasks within a technical system. A functional subsystem is the combination of functional elements for realizing coherent tasks within a functional system.
Component	A component is a unit at the lowest level in a technical system for which a statement on reliability can be made. One or several functional elements are assigned to every component.
Functional element (subcomponent)	A functional element is the lowest level unit considered in a functional system. It may only describe basic functions as e.g. switching, turning, shutting-off, opening, supplying with energy.
Procedure	A procedure is a convention applying to normal operation or accident situations, to maintenance, handling, transport, flow of information etc.
Failure	A failure of a technical object of analysis occurs if a tolerable deviation from a performance target of this object is exceeded. In a functional system such a failure represents the loss of a functional element, which is called its failure. Failures may be divided into the following categories: (a) primary or basic failure (failure while admissible operating conditions of a component prevail) (b) secondary or consequential failures (failures as a consequence of inadmissible operating conditions for a component) (c) failure due to functional dependence (failure of a functioning component as a consequence of a wrong or missing activation or the failure of support equipment).
Failure mode	The different modes of failure of a component, e.g. control valve stuck or restrictions in movement, are called failure modes.
Maintenance	Measures for preserving or restoring the correct state as well as for establishing and judging the actual state of the technical equipment of a system (these measures comprise functional tests, maintenance and repair and include the “harmonization” of the maintenance objectives with company objectives and the determination of maintenance strategies).
Service	Measures to delay the consumption of the existing lifetime working potential.

(continued)

Table 9.1 (continued)

Term	Definition
Inspection	Measures for determining and valuating the actual state of a technical unit of a system including the causes for wear and the determination of the necessary consequences for its future use.
Repair	Measure for restoring the technically correct state of a technical unit of a system.
Survival probability (reliability)	The survival probability is the property of a technical system to satisfy the requirements of its mission within defined boundary conditions for a certain period of time.
Availability	The availability is the property of a technical system to function at a future randomly selected point in time, i.e. the capability of fulfilling the requirements of its mission.

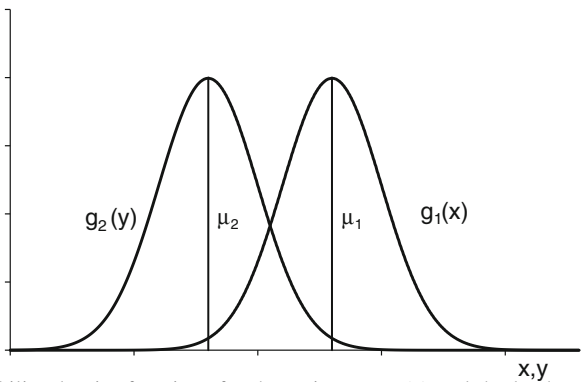


Fig. 9.2 Probability density functions for the resistance $g_1(y)$ and the load $g_2(y)$ of a technical component (μ_1 : mean value of the resistance; μ_2 : mean value of the load; for simplicity's sake a normal distribution was chosen; of course, other distribution types are used as well, especially those which are only defined on the positive half-axis, as is in fact required for both resistance and load)

variable. Figure 9.2 shows the situation just explained. Normally the resistance is larger than the load. Hence, the component does not fail. Yet, there is an area, where both probability density functions overlap. There the load is larger than the resistance and the component fails. The corresponding probability of failure¹ is represented by the area of overlap.

Hence, one of the objectives of a good design is to keep the area of overlap small. This is achieved by making the difference of the nominal values of load and resistance, which are given by the expected values of their respective distributions, big. Traditionally, the load is divided by a safety factor $S > 1$ in order to achieve this. In the present context this procedure, which reduces the probability of failure,

¹ Complement of the survival probability (reliability) of Table 9.1.

can be interpreted probabilistically (cf. [6, 7] and the Example 9.1). An alternative approach for reducing the probability of failure consists in reducing the variances of the distributions. This can be achieved by choosing especially good materials and keeping the tolerances in manufacturing the components as well as in building and operating the plant small.

The model outlined is particularly suited for treating the failure of passive components. Such components fulfil their function by their mere presence, for example vessels, pipes and walls. Contrary to this active components have to move in order to fulfil their function. Examples are control valves and pumps. Yet, active components usually have a passive ancillary function. Thus, the pump casing serves as well to contain the transported medium.

Example 9.1 Probabilistic interpretation of the safety factor

A pipe is designed to withstand a certain pressure. Its resistance is represented by the normal distribution $g_1(x)$ with an expected value of $\mu_1 = 20,000$ kPa and the standard deviation $\alpha_1 = 3,000$ kPa. The pressure to which the pipe is exposed varies according to the normal distribution $g_2(y)$ with an expected value of $\mu_2 = 15,000$ kPa and the standard deviation $\alpha_2 = 4,000$ kPa. Both distributions are mutually independent, which is supposed to apply here but does not necessarily have to be true in general.

Determine:

- the mathematical expression for calculating the probability of failure;
- the numerical value of the probability of failure;
- the safety factor which lowers the probability of failure to 10^{-3} .

Figure 9.2 shows the situation. The probability of failure is given by the region of overlap of the two probability density functions. This region is characterized by the condition that $z = x - y \leq 0$. Hence, the probability $P\{z = x - y \leq 0\}$ is to be calculated, i.e.

$$P\{z \leq 0\} = \int_{-\infty}^{\infty} \int_{-\infty}^{z+y} g_1(x) \cdot g_2(y) dx dy = \int_{-\infty}^{\infty} G_1(z+y) \cdot g_2(y) dy \quad (9.1)$$

The probability density function for z results from the convolution integral of Eq. (9.1) by differentiation with respect to z , i.e.

$$\frac{dP\{z \leq 0\}}{dz} = f(z) = \int_{-\infty}^{\infty} g_1(z+y) \cdot g_2(y) dy \quad (9.2)$$

Equation (9.2) is true in independence from the choice of the probability distribution. Since, for example's sake, the normal distribution (vid. Eq. (C.24) in

Appendix C) was chosen here, its probability density function is inserted in Eq. (9.2) to obtain

$$f(z) = \frac{1}{2\pi\sigma_1\sigma_2} \int_{-\infty}^{\infty} e^{-\frac{(z+y-\mu_1)^2}{2\sigma_1^2}} \cdot e^{-\frac{(y-\mu_2)^2}{2\sigma_2^2}} dy \quad (9.3)$$

Using the abbreviations $b = y - \mu_2$ and $a = z + \mu_2 - \mu_1$ Eq. (9.3) becomes

$$f(z) = \frac{1}{2\pi\sigma_1\sigma_2} \int_{-\infty}^{\infty} e^{-\frac{1}{2} \left[\frac{(a+b)^2}{\sigma_1^2} + \frac{b^2}{\sigma_2^2} \right]} db \quad (9.4)$$

The expression in square brackets can be written as

$$\gamma = \frac{b^2(\sigma_1^2 + \sigma_2^2) + 2ab\sigma_2^2 + a^2\sigma_2^2}{\sigma_1^2 \cdot \sigma_2^2} \quad (9.5)$$

Introducing the new variable

$$t = b \cdot \frac{\sigma}{\sigma_1\sigma_2} + a \cdot \frac{\sigma_2}{\sigma\sigma_1} \quad (9.6)$$

where $\sigma^2 = \sigma_1^2 + \sigma_2^2$, Eq. (9.5) becomes

$$\gamma = t^2 + a^2 \frac{\sigma^2 - \sigma_2^2}{\sigma^2 \cdot \sigma_1^2} = t^2 + \frac{a^2}{\sigma^2} \quad (9.7)$$

Observing that according to Eq. (9.6) $\frac{dt}{db} = \frac{\sigma}{\sigma_1 \cdot \sigma_2}$ holds, Eq. (9.4) is converted into

$$f(z) = \frac{1}{2\pi\sigma} e^{-\frac{a^2}{2\sigma^2}} \cdot \int_{-\infty}^{\infty} e^{-\frac{t^2}{2}} dt \quad (9.8)$$

The integral on the right hand side of Eq. (9.8) has the value $\sqrt{2\pi}$, so that we obtain

$$f(z) = \frac{1}{\sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}} \cdot e^{-\frac{[z-(\mu_1-\mu_2)]^2}{2(\sigma_1^2 + \sigma_2^2)}} \quad (9.9)$$

Integration of Eq. (9.9) leads to

$$F(z) = \Phi \left(\frac{z - (\mu_1 - \mu_2)}{\sqrt{\sigma_1^2 + \sigma_2^2}} \right) \quad (9.10)$$

In Eq. (9.10) ϕ is the standard normal distribution, whose values can be obtained from the usual tables.

The desired probability of failure follows from Eq. (9.10), if z is set equal to 0, i.e.

$$F(0) = \phi(-1) = 0.16$$

The safety factor which lowers the probability of failure to 10^{-3} results from the condition that

$$\phi\left(-\frac{\mu_1 - \frac{\mu_2}{S}}{\sqrt{\sigma_1^2 + \sigma_2^2}}\right) = 0.001 \quad (9.11)$$

i.e.

$$-\frac{\mu_1 - \frac{\mu_2}{S}}{\sqrt{\sigma_1^2 + \sigma_2^2}} = -3.091$$

since the standard normal distribution adopts the value 10^{-3} for the argument -3.091 . Using the input data of the problem we have $S \approx 3.3$, from which a permissible load of 4545.5 kPa results.

Aging, which not considered here, can lead to a widening of the probability density functions of Fig. 9.2 and to a reduction of the mean value of the strength of the material. For example, a material suffers from cyclical loads. In this way, the region of overlap will grow larger in the course of time. $\square$

9.1.2 Input Information and Methods of Analysis

In order to carry out a safety analysis fundamental information on the plant and the hazards associated with its process and operation is needed. In general, knowledge of the following issues is required:

- plant and system structure,
- operating conditions and procedures,
- hazardous materials,
- distribution of the mass of materials inside the plant,
- hazardous plant states,
- existing protection and safety systems.

The information on plant and system structure comprises a description of the plant, its layout, and the design and construction characteristics of equipment, systems and components. Furthermore, operating and handling procedures are included.

Before analyzing a technical system it makes sense to define the boundary conditions of the analysis. This implies fixing the outer boundary for the object of analysis defined in Table 9.1 and the degree of detail (depth) of the analysis. The way of doing this is illustrated by the following example of a telephone [8].

A telephone stands on a table. Does it suffice to regard the telephone alone (earphone, microphone etc.) as a system or does the cable to the socket in the wall have to be included? Does the socket in the wall belong to the system as well as the lines connecting with the telephone exchange or even with the rest of the world? These few questions put into perspective how important it is to fix the outer boundary of the system. The choice depends on the objective of the investigation. If, for example, the telephone does not ring loud enough to arouse attention the investigation can be limited to the telephone itself. If, on the other hand, interferences in the connection are to be analyzed, the outer boundary must be fixed such that connecting lines and switchboards are included as well.

Apart from the outer boundary the inner boundary, i.e. the degree of detail of the analysis, must be determined. With reference to the telephone example this implies the question whether screws, coils, cables etc. have to be considered or not. Does the analysis have to address the molecular or atomic level or go even further? Obviously not. In practical cases the degree of detail is determined by the objective of the analysis. If we intend to find out the consequences of a pump failure, it suffices to consider the pump as a unit. This unit comprises the motor, the impeller, the power transmission and the casing as well as the local control boards and the cables to the sockets in the wall. Should, however, the failure of the pump itself be examined, the piece-parts mentioned must be considered individually or even be broken down to smaller units.

The adequate choice of the inner and outer boundaries is important for the success of the investigation. Whatever has an impact on the objective of the investigation must be considered without clouding the view on the essentials by too much detail. The outer boundary fixes the scope of the analysis, the inner boundary its detail (depth).

In addition to the physical boundaries the time horizon to be considered in the analysis has to be fixed. It makes a substantial difference if a system has to survive a few weeks only or to last for years. The maintenance strategy, for example, would be strongly influenced by this.

Although the system boundary and the degree of detail must be fixed before the analysis begins, their determination is done iteratively. A tentative initial determination is updated in view of the analysis results during work progress.

There are several methods for analysis, which can be classified as follows:

1. According to the procedure of conclusion:

- inductive methods,
- deductive methods.

2. According to the scope:

- qualitative methods,
- quantitative methods.

3. According to the objective:

- methods for identifying hazard potentials,
- methods to value hazard potentials.

The methods of analysis can often not be characterized by one of above attributes alone. A method may be both, inductive and deductive, qualitative and quantitative and serve to identify and to value hazard potentials.

An inductive procedure starts with a single event in order to arrive at more general conclusions. A certain failure in a system is postulated and its consequences are found out. For example, one may suppose the failure of one jet of a three-jet plane and deliberate what the consequences for its flight capability are (cf. Example C.8).

In contrast, in deductive procedures the investigation proceeds from general to specific. The undesired or unwanted event is postulated, for example the release of a toxic substance, and the reasons for this to occur are conceived.

In the following sections several qualitative methods of safety analysis are described. Among them hazard indices and HAZOP studies were specifically devised for analyses of process plants.

It is fundamental for all of the methods that they require thought experiments. These have to be nourished by a solid background knowledge of chemistry, physics and engineering as well as other areas of knowledge related to the plant under investigation (e.g. biology in case of biotechnological plants).

The method then enables one, in words or quantitatively, to process input information in such a way that answers to safety technological questions are given. In this sense it does not differ so much from mathematically formulated models, which also pursue the objective to process input information in a way that they provide answers to the problem at hand.

9.1.2.1 Check Lists

Check lists serve to draw one's attention to safety relevant issues. They reflect to a large extent the experiences with the design, building and operation of plants and the corresponding safety analyses. Apart from the normal operation the lists should cover start-up and shut-down as well as other possible plant states. In what follows a checklist for process plants is presented. Further information can be found in the relevant literature, for example also in [9].

- Are the operation and surveillance of apparatuses, pipework and valves as well as access and possibility of replacement on repair ensured?
- Can the plant be purged, dewatered, vented and bled? Do the necessary connections and valves exist (e.g. leak or pressure tests)?
- Can products not in accord with their specification—e.g. produced during start-up or shut-down—be eliminated from the process (discharged, flared off)?
- Which by-products can be formed by:

- impurities,
 - difference in feed composition
 - changes in operating conditions?
- Can by-products cause deposition or obstruction?
- What are the effects of changes of state of the media in case of deviations from nominal operating conditions (e.g. state of aggregation, viscosity, interfacial tension)?
- Are the plant and its parts designed properly as to process conditions, structural strength and materials for the cases: normal operation, start-up, shut-down and emergency shut-down?
- Can closed tanks for solids and liquids “breathe” during changes of filling level, ambient pressure or temperature? Is the breather pipe properly dimensioned? Can underpressure or ingress of air and humidity occur?
- How does potential scale or dirt affect the function and performance of plant equipment? Can endangered zones be inspected and cleaned?
- Is equipment prone to wear? Can the endangered equipment be inspected and exchanged, if necessary? What is the effort involved?
- What is the influence of leaks (e.g. ingress of air, water, steam, heat exchanger medium) on the process, corrosion progression or self-ignition?
- Can parts of the plant be reliably isolated from others by line blinds in order to carry out maintenance and repair work, leak and pressure tests?
- Are flammable gases, vapours, liquids or solids (dust) present? To which ignition group and hazard class do they have to be assigned?
- Are health-damaging substances present or can they be formed after the release of feed, intermediate or final products through leaks etc. by reaction with air or water (toxicity, radioactivity, hazard of skin absorption or infection, limit values to be observed)?
- What are the temperature and composition of off-gases during start-up, normal operation, extreme operating conditions, shut-down, emergency shut-down or malfunctions? Is the safe discharge and removal of pollutants from off-gases ensured? Are off-gas stacks and flares etc. properly dimensioned?
- Can feed, auxiliary, intermediate and final products enter pipes or parts of the plant where they should not be, due to operator mistakes or malfunctions (e.g. cooling water or products in drinking water pipes, oxygen or air in inert gas pipes etc.)? What safety measures are implemented to prevent this (e.g. check, valves, double shut-off valves with a vent, interlocks of valves etc.)?
- Which safety measures are implemented against fires and explosions (explosion protection, inert gas protection, sprinkler, steam curtain etc.)?
- Are all parts of the plant protected against impermissible overpressure due to operator error, fire, failure of the supply of electricity, water, heater medium, instrument air, inert gas or some feed or auxiliary materials, malfunctions in other plants, blockage of product discharge etc.?
- Can safety equipment fail because of obstruction, freezing, wear or corrosion? Can the availability of safety equipment be tested during plant operation?
- Do interlocks impede wrong operator actions, which counteract plant safety? Can operators easily deactivate interlocks serving plant safety?

9.1.2.2 Hazard Indices

A hazard index is obtained by recording the hazardous inventory of the plant under investigation and by valuating the substances and the production processes using empirical factors. The methodology was originally developed for insurance purposes. It enables one to assess the hazard potential of a plant by calculating a numerical value.

There are a number of hazard indices, for example [10, 11]. Yet, the best-known is the “Fire and Explosion Index (F&EI)” of the Dow Company (Dow Index) [9], which is the only one to be treated here. It is based on experience and data on past accidents, the energy potential of the material to be considered and the state of the measures for preventing accidents.

In applying the index the following objectives are pursued:

1. **Quantify** the expected damage of potential fire, explosion and reactivity incidents in realistic terms.
2. **Identify** equipment that would be likely to contribute to the creation or escalation of an incident.
3. **Communicate** the F&EI potential to the management.

Despite the use of numbers the crucial element of the F&EI is the objective to visualize the hazard potential of the different plant areas to the engineer and to enable him to find ways for minimizing the hazard as well as the associated material loss in an efficient and cost-effective way.

The index was originally developed for plants where flammable or reactive materials are stored, handled or processed. Yet it may also be used in analyzing the loss potential of sewage treating facilities, distribution systems, pipelines, rectifiers, transformers, boilers, thermal oxidizers and certain elements of power plants. The procedure can also be used for risk evaluations of small processes with modest inventories of potentially hazardous materials. Its application to pilot plants is strongly recommended. The procedure can be applied if a minimum of approximately 454 kg (1,000 lb) of a flammable or reactive material is handled.

Common sense and good judgement must be used during the actual calculation and in the interpretation of the results.

The process of calculating the index is shown in Fig. 9.3; it is briefly commented upon below. For any concrete application, however, [9] should be consulted. Penalty factors are assigned to hazardous elements and credit factors to good safety features.

The following working steps are carried out for a risk analysis according to [9]:

- **Selection of pertinent process units:** A process unit is defined as any major item of process equipment. The following units could be identified, for example, in a furnace/quench section in a vinyl chloride monomer/ethylene dichloride plant: ethylene dichloride pre-heater, ethylene dichloride evaporator, furnace, quench column, ethylene dichloride absorber and tar pot. Important factors for selecting pertinent process units include:

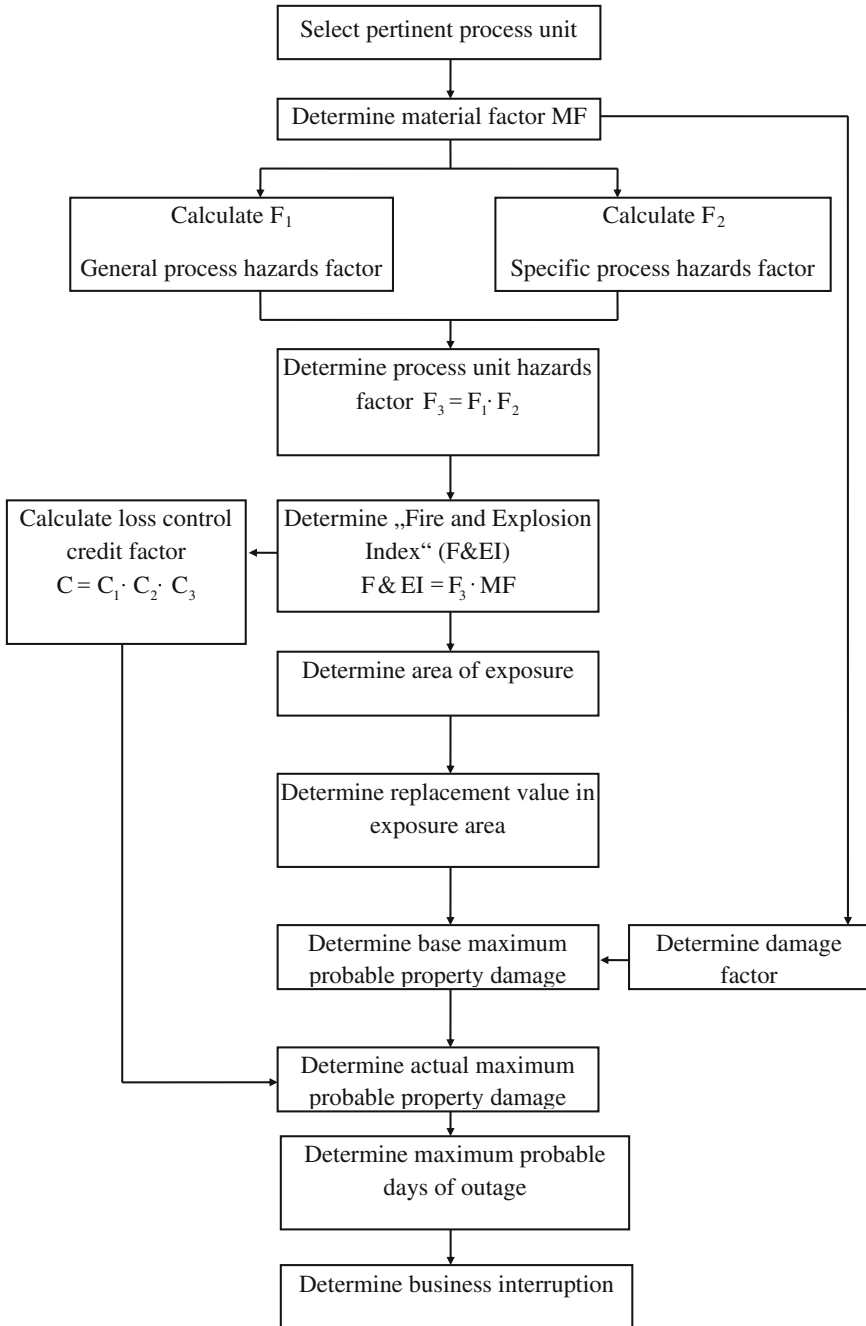


Fig. 9.3 Procedure for calculating the “fire and explosion index” and further information for a risk analysis according to [9]

Table 9.2 Examples for the material factor MF (from [9])

Material	Material factor MF
Chlorine dioxide	40
Cyclohexane	16
Chlorine	1

- Chemical energy potential (material factor),
- Quantity of hazardous material in the process unit,
- Capital density (dollars per square foot),
- Process pressure and process temperature,
- Past history of problems that resulted in a fire and explosion incident,
- Units critical to plant operation, e.g. thermal oxidizer.

The more vigorous any of these factors is the larger is the probability that the process unit in question has to be analyzed.

- **Material factor:** This factor, denoted by MF (vid. Table 9.2), is a measure of the intrinsic rate of potential energy release from fire or explosion produced by combustion or chemical reaction. It describes the flammability and reactivity (instability) of a material and is obtained from tables given in [9]. Its value lies between 1 and 40 and refers to ambient temperature. It is modified if materials are present at higher temperature in order to cater for the resulting increase in hazard potential.
- **General process hazards:** In this context six items are considered which played a major role in past accidents:
 - **Exothermic chemical reactions:** Mild exotherms like hydrolysis or isomerization require a penalty of 0.3, moderate exotherms such as oxidation or polymerization one of 0.5. A penalty of 1.0 is assigned to critical-to-control exotherms like halogenations and a penalty of 1.25 to particularly sensitive exotherms like nitration.
 - **Endothermic processes:** By way of example the following penalties are assigned: calcination (0.40), electrolysis (0.20), pyrolysis or cracking (0.4).
 - **Material handling and transfer:** This item is evaluated with regard to the potential for fire involving the pertinent process unit during the handling, transfer and warehousing of materials. For example transfer of a liquefied petroleum gas (LPG) where transfer lines are connected and disconnected has a penalty of 0.50.
 - **Enclosed or indoor processes:** Enclosure implies an increase of the hazard potential. For example: dust filters inside an enclosed area, penalty of 0.50; processes in which flammable liquids are handled above their flash point, penalty 0.30 and if more than 3.79 m³ are involved a penalty of 0.45; processes in which LPG or any flammable liquid are handled above their boiling point within an enclosed area require a penalty of 0.6, which is increased to

0.90 if more than 4,535 kg are handled. Where properly designed mechanical ventilation has been installed, the above penalty factors may be reduced by 50 %.

- **Access:** Emergency teams and equipment must have ready access to the area housing the pertinent process unit. Access from at least two sides is considered the “minimum requirement”. Strong consideration should be given to this penalty for major process units located in enclosed areas. Judging the specific situation a penalty of 0.20 or 0.35 is required if access is not adequate.
- **Drainage and spill control:** This section lists penalties for design conditions that could cause large spills of flammable or combustible liquids to be retained around or near process equipment (as a rule a penalty of 0.50 is used).
- **Special process hazards:** Special process hazards are factors that contribute primarily to the probability of a loss incident. They consist of specific process conditions that have shown that they are major causes of fire and explosion incidents. Twelve items are listed:
 - **Toxic materials:** The presence of toxic materials complicates the response of emergency personnel by reducing their ability to investigate or mitigate damage during an incident. A penalty factor of $0.2 \times NH$ is used, where NH describes the health effect of toxic substances according to pertinent U.S. guidelines.
 - **Sub-atmospheric pressure:** Sub-atmospheric pressure is important for processes where ingress of air may cause a hazard. A penalty factor of 0.5 is used.
 - **Operation in or near the flammable range:** There are certain operating conditions which can cause air to enter and be entrained into the system. The ingress or entry of air could lead to the formation of a flammable mixture and create a hazard. The penalty factor amounts in this case to 0.30, 0.50 or 0.80 depending on the situation.
 - **Dust explosion:** The maximum rate of pressure rise and maximum pressure generated by a dust explosion are largely influenced by the particle size. In general both quantities increase with decreasing particle size. The penalty factor ranges from 0.25 to 2 depending on particle size.
 - **Relief pressure:** Where operating pressures are above atmospheric, a penalty is applied for the higher discharge rates caused by higher pressure in the event of a leak. Depending on the situation the penalty factor lies between 0.86 and 1.50.
 - **Low temperature:** Low temperatures lead to a penalty if carbon steels or other metals are exposed to temperatures at or below their ductile/brittle transition temperatures. A factor of 0.2 or 0.3 is assigned.
 - **Quantity of flammable or unstable materials:** This considers the additional exposure of an area as quantities of flammable and unstable materials in a process unit are increased. Detailed considerations, in which experience-based diagrams are used, lead to fixing the penalty.

Table 9.3 Ranges of the F&EI and corresponding degree of hazard

F&EI index range	Degree of hazard
1–60	Light
61–96	Moderate
97–127	Intermediate
128–158	Heavy
159 and larger	Severe

- **Corrosion and erosion:** Although good design makes allowances for corrosion and erosion, corrosion or erosion problems may still occur in certain processes. A possible cause may be impurities in process streams. Penalty factors between 0.10 and 0.75 are used depending on the situation. The latter is applied if stress-corrosion cracking might develop.
- **Leakage—joints and packing:** Gaskets, seals of joints or shafts can be sources of leaks of flammable or combustible materials. Depending on the quality of the design of the process unit and the type of material involved penalty factors between 0.1 and 1.5 are assigned.
- **Use of fired equipment:** The penalties for the use of fired equipment are determined applying the tables in [9]. Depending on the quantities of substances and their temperatures of ignition penalty factors between 0.25 and 1.15 are used.
- **Hot oil heat exchange systems:** Since most hot oil (heat exchange) fluids will burn and are frequently used above their flash points or boiling points, they represent an additional hazard in any process unit that uses them. A penalty factor between 0.25 and 1.15 is applied depending on quantity and temperature.
- **Rotating equipment:** A penalty factor of 0.50 is assigned for hazards due to equipment with rotating parts (e.g. compressors or pumps with large powers).

The penalty factors applicable to the process unit considered are summed up resulting in the factor for general process hazards F_1 and that for specific process hazards F_2 . The starting point is a base factor of 1 for both F_1 and F_2 , which is the final word if no penalties have to be considered. A value of 0 is used for items, which are not applicable.

Based on the foregoing considerations the Fire and Explosion Index (F&EI) is calculated. Table 9.3 shows the assignment of the degree of hazard resulting from the numerical value of the index.

After classifying a process unit according to the index the possibility of giving credit for an especially good design exists. This leads to a credit which is related amongst others to the existence of the safety equipment and safety-related properties listed below.

The credit is represented by the credit factor $C = C_1 \cdot C_2 \cdot C_3$, where the factors C_1 , C_2 and C_3 are obtained by multiplying the individual credits within their corresponding group (a credit of 1 is assigned to non-existent equipment or

properties) with one another. The equipment and credit factors (in parenthesis) are merely listed below; necessary explanations and justifications for the assessment are found in [9].

Process control credit factor (C_1)

- Emergency power—(0.98)
- Cooling—(0.97–0.99)
- Explosion control—(0.84)
- Emergency shutdown—(0.96–0.99)
- On-line computer control—(0.93–0.99)
- Inerting—(0.94–0.96)
- Operating instructions and procedures—(0.91–0.99)
- Reactive chemical review—(0.91–0.98)
- Process hazard analyses in addition to F&EI—(0.91–0.98).

Material isolation credit factor (C_2)

- Remote control valves—(0.96–0.98)
- Emergency dump or blowdown—(0.96–0.98)
- Drainage—(0.91–0.97)
- Interlock—(0.98).

Fire protection credit factor (C_3)

- Leak detection—(0.94–0.98)
- Fireproof coated structural steel—(0.95–0.98)
- Fire water supply—(0.94–0.97)
- Special systems (e.g. flame detectors)—(0.91)
- Sprinkler systems—(0.74–0.97)
- Water curtains—(0.97–0.98)
- Foam injection systems—(0.92–0.97)
- Hand extinguishers—(0.93–0.98)
- Cable protection systems—(0.94–0.98).

Example 9.2 Determination of the DOW F&I Index

A reactor for a nitration reaction is located inside a hall, which has three doors for entry and exit. The reactor is cooled and disposes of an emergency shutdown and dump system. The material factor is $MF = 40$.

The F&EI as well as the index value for the actual maximum probable damage are to be determined.

Solution

The calculation of the factors for the general and specific hazards from the process is shown in Table 9.4, that of the credit factors in Table 9.5.

Table 9.4 Calculation of the factors for the general and specific process hazards

	Value or range	Value used
<i>General process hazards</i>		
Minimum value	1.0	1.0
Exothermic reaction	0.3–1.25	1.25
Endothermic process	0.2–0.4	0
Material handling and transfer	0.25–1.05	0
Enclosed or indoor process units	0.25–0.9	0.7
Access	0.2–0.35	0
Drainage and spill control	0.5	0
Factor for general process hazards F_1		2.95
<i>Special process hazards</i>		
Minimum value	1.0	1.0
Toxic materials	0.2–0.8	0.7
Sub-atmospheric pressure	0.5	0
Operating parameters close to the explosion range	0.5–0.8	0.8
Dust explosion	0.25–2	0
Relief pressure	0.16–1.5	0
Low temperature	0.2–0.3	0
Quantity of flammable and unstable materials	0–2.18	1.5
Corrosion and erosion	0.1–0.75	0.5
Leakage—joints and packings	0.1–1.5	0.2
Use of fired equipment	Diagrams from [9]	0
Hot oil heat exchanging equipment	0.25–1.15	0
Rotating equipment	0.5	0
Factor for specific process hazards F_2		4.7

Hence we obtain the F&EI according to Fig. 9.3

$$F\&EI = FM \cdot F_1 \cdot F_2 = 40 \times 2.95 \times 4.7 = 554.6$$

Thus, we are dealing with a severe hazard according to Table 9.3.

The calculation of the credit factors is contained in Table 9.5 (for increased transparency only existing equipment is accounted for, because non-existing equipment figures in the calculation with a multiplying factor of 1).

Table 9.5 Calculation of the credit factors

Credit factors	Value or range	Value used
<i>Process control factor (C₁)</i>		
Default value	1.0	1.0
Cooling	0.97–0.99	0.99
Emergency shut-down	0.96–0.99	0.96
Reactive chemical review	0.91–0.98	0.91
Process hazard analyses in addition to F&EI	0.91–0.98	0.91
Factor C₁		0.79
<i>Material isolation credit factor (C₂)</i>		
Default value	1.0	1.0
Emergency dump system	0.96–0.98	0.96
Factor C₂		0.96
<i>Fire protection credit factor (C₃)</i>		
Default value	1.0	1.0
Factor C₃		1.0
Factor C = C₁ · C₂ · C₃		0.76

Hence, we assess the actual maximum probable material damage by

$$F\&EI \cdot C = 554.6 \times 0.76 = 421.5$$

This would still fall into the category “severe hazard” of Table 9.3.

Therefore additional safety measures have to be implemented. This implies the question to which of the categories of Table 9.3 the hazard would have to be reduced (cf. Sect. 8.2). $\square$

9.1.2.3 Hazard and Operability (HAZOP) Studies

The hazard and operability (HAZOP) study [12, 13] developed during the 1970s by ICI in the U.K. has proved to be particularly suited for safety analyses of process plants. The procedure was taken over in Germany where it became known under the name of *Prognose, Auffinden der Ursachen, Abschätzung der Auswirkungen, Gegenmaßnahmen* (PAAG) [14].

The basic concept of a HAZOP study is to take a full description of the process and to question every part (functional unit) of it in order to discover what deviations from the intention of the design can occur. Furthermore conceivable causes for these deviations, for example of temperature or mass flow, and their consequences are sought. This is done systematically by applying the guidewords of Table 9.6 to process conditions, plant functions, materials as well as time and space.

The analysis can be carried out for continuous and batch processes. It should address conceivably safety-relevant situations of the plant, in particular start-up

Table 9.6 Guidewords for a HAZOP study

Guideword	Meaning
NO or NOT	Negation of intention
MORE	Quantitative increase
LESS	Quantitative decrease
AS WELL AS	Qualitative increase
PART OF	Qualitative decrease
REVERSE	Logical opposite of intention
OTHER THAN	Complete substitution

Table 9.7 Time-related guidewords

Guideword	Meaning
SOONER	Relative to the clock time
LATER	Relative to the clock time
BEFORE	Relating to order or sequence
AFTER	Relating to order or sequence

and shut-down. For the latter and for batch processes the time-related guidewords of Table 9.7 are of use.

In general the guidewords apply to the plant functions and—possibly with the exception of “reverse”—to materials as well. Occasionally they have to be modified analogously.

It is reasonable to have the study carried out by a group of analysts with different educational backgrounds. Disciplines like process and mechanical engineering, control and electrical engineering, safety engineering, plant design and operation should be represented. The group should be headed by a person who is conversant with the technique of analysis but not necessarily specialized in the process in question.

The basis for the safety analysis of a plant is its P&I diagram and a detailed description of the process. The plant is contemplated pipe by pipe. In each pipe the guidewords are applied to process parameters such as mass flow, pressure, temperature and concentration. Possible causes and consequences of deviations analyzed by thought experiments are identified. This enables one to decide on the necessity and type of possibly required countermeasures. The process of analysis may be supported by estimates of the frequency of occurrence of deviations and the extent of the accompanying consequences.

The focus is directed primarily on pipes. The rationale is that problems with an apparatus generally manifest themselves as causes or consequences of deviations of process parameters from their nominal values in the connecting pipework.

The procedure is illustrated below by two simple examples.

Example 9.3 Application of the HAZOP technique to a simple system

Figure 9.4 shows a system of two pumps, which transport water. Its intended function is to cool a reactor for an exothermic reaction. This requires the mass flow of exactly one of the pumps. This requirement is called “success criterion”.

The results of the HAZOP study are summarised in Table 9.8, where guide-words which do not proceed nor provide additional insights for this specific case have already been omitted.

Fig. 9.4 Two-train system for transporting a reactor coolant

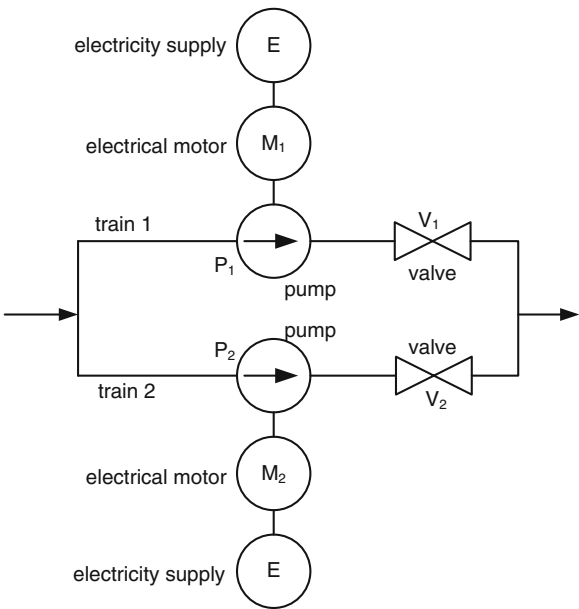


Table 9.8 HAZOP study for the system of Fig. 9.4

Functional unit: Coolant transport				
Intended function: Cooling of the reactor				
Guide-word	Deviation	Possible causes	Consequences	Required action(s)
NO or NOT	No flow	(1) Pump failure	No cooling, reaction temperature rises	(1) Start-up reserve train
		(2) Non-isolatable pipe rupture		(2) Emergency trip
		(3) Valve erroneously closed		(3) Open valve and if stuck start-up reserve train
NO or NOT	No electricity supply	Grid failure, transformer failure and such like	No cooling, reaction temperature rises	Emergency trip
MORE	Too much flow	Both pumps in operation	No optimal reaction conditions	Turn off one pump
AS WELL AS	Impurities in coolant	(1) Carelessness when filling	Corrosion, in case of ingress into the reactor possibly influence on reaction	Control and correction during maintenance
		(2) Loss of lubricant from bearings		
OTHER THAN	Wrong coolant	Carelessness when filling	Heat transfer not according to design	Exchange

In carrying out the analysis one must observe that

- for realizing the required action the information about its necessity must be available, e.g. by an alarm and that the necessary technical equipment is actually installed (if not, upgrading is necessary),
- it is important to ensure that the time for detection and realizing the required action is sufficiently large to prevent a dangerous state. □

Example 9.4 Application of the HAZOP study technique [15]

A HAZOP study is to be carried out for the system described below.

System Description

The cooling system, which is shown in Fig. 9.5, consists of two loops, the coolant tank (1), two redundant pumps in each loop (P1A, P1B and P2A, P2B), and the heat exchanger (2). The latter is connected to a refrigerating unit. In one of the loops the coolant, whose temperature is -5°C , is pumped by one of the pumps P2A or P2B from the cold side of the coolant tank to the consumers of the production process. After removing heat from the consumers the coolant is pumped back into the warm side of the coolant tank.

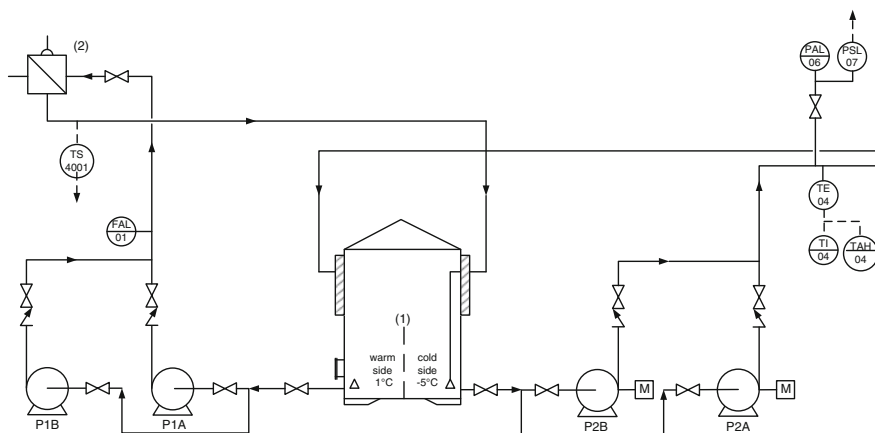


Fig. 9.5 R&I diagram of the cooling system of a plant for producing hexogen

The second loop serves to transport the coolant from the warm side of the coolant tank through the evaporator (2) where it is cooled down to -5°C . The transport is effected either by pump P1A or P1B. After passing through the heat exchanger the coolant is returned to the cold side of the coolant tank.

The coolant temperature is lowered from 1 to -5°C in the heat exchanger. The heat is removed by the evaporation of a halogenated hydrocarbon in the refrigerating unit, whose details are not shown in Fig. 9.5.

The cooling unit is controlled by temperature switch TS 4001. It ensures the appropriate temperature of the coolant (-5°C), which is returned from the refrigerating unit to the cold side of the coolant tank.

The flow in the warm loop is monitored by flow switch FAL 01, which provides an alarm in the control room on low flow. Both temperature and pressure of the cold loop are monitored as well. The instrument TI04 indicates the temperature in the control room giving an alarm signal for high temperature via TAH04. In case the pressure in the loop should be too low the instrument PAL 06 would give an alarm. The operating handbook contains the instructions for actions to be taken after perceiving any of the alarms. Additionally, pressure switch PSL 07 would stop the supply of one of the feed materials to the process downstream (level 2 of Table 4.1).

Failures of the cooling, if undiscovered or unattended, would lead to the exothermic process downstream not being cooled adequately. This would cause a runaway reaction if the reactor safety devices failed as well.

HAZOP Study

The HAZOP study is shown in Tables 9.9, 9.10, 9.11, 9.12.

Table 9.9 HAZOP study for the system of Fig. 9.5 (guide words which do not proceed were left out after examination)

Functional unit: Transport of coolant from the refrigerating unit to the cold side of the coolant tank				
Intended function: Transport into the cold side of the coolant tank				
Guideword	Deviation	Possible causes	Consequences	Action required
NO or NOT	No flow	Failure of pump P1A	Depletion of contents of cold side; flow alarm via FAL01	Activation of reserve pump P1B
MORE	Abnormally high temperature	Refrigerating unit failed	Cold side gradually warms up; alarm via TAH 04	Shut-down of plant; repair of refrigerating unit
LESS	Less flow	Pipe leak	Depletion of contents of cold side: detection on walk-around	Shut-down of plant; repair of pipe

Table 9.10 HAZOP study for the system of Fig. 9.5 (guide words which do not proceed were left out after examination)

Functional unit: Transport of coolant from the cold side of the coolant tank to the process				
Intended function: Transport of coolant to the process				
Guideword	Deviation	Possible causes	Consequences	Action required
NO or NOT	No flow	Pump P2A fails	No supply of coolant to the process; pressure alarm via PAL06, PSL07 interrupts supply of one of the feed materials	Activation of reserve pump P2B
LESS	Less flow	Pipe leak	Insufficient cooling of the process	Emergency shut-down of the plant; repair of pipe

Table 9.11 HAZOP study for the system of Fig. 9.5 (guide words which do not proceed were left out after examination)

Functional unit: Transport of coolant from the process to the warm side of the coolant tank				
Intended function: Coolant flow from the process to the warm side of the coolant tank				
Guideword	Deviation	Possible causes	Consequences	Action required
NO or NOT	No flow	Pump P2A fails	No return to tank, gradual depletion of warm side; pressure alarm via PAL06; PSL07 interrupts supply of one of the feed materials	Activation of reserve pump P2B
LESS	Less flow	Pipe leak	Depletion of warm part of tank; detection on walk-around	Repair of pipe

Table 9.12 HAZOP study for the system of Fig. 9.5 (guide words which do not proceed were left out after examination)

Functional unit: Transport of coolant from the warm side of the coolant tank to the refrigerating unit				
Intended function: Coolant flow from the warm side of the coolant tank to the refrigerating unit				
Guideword	Deviation	Possible causes	Consequences	Action required
NO or NOT	No flow	Pump P1A fails	Gradual depletion of contents of the cold side; flow alarm via FAL01	Activation of reserve pump P1B
LESS	Less flow	Pipe leak	Gradual depletion of contents of the cold side; detection by FAL01, if leak before instrument, otherwise on walk-around or via TS 4001	Shut-down of plant; repair of pipe

It is emphasized once again that in analyzing attention should be paid to the remarks at the end of Example 9.3. □

9.1.2.4 Failure Mode and Effect Analysis

The failure mode and effect analysis (FMEA) [16] is an inductive method, which is normally used qualitatively, but may serve as well for quantifying. The method is applied for identifying the failure modes of components of systems or subsystems, hazardous states and the associated consequences. The following information is required for its use:

- Description of the system to be analyzed.
- Description of the function of the system.

- Overview of potential failure modes of technical components and conceivable human errors.
- Description of the conditions in the surroundings of the plant.

The system is divided into its components, for example pumps, valves, and measuring gauges. For any one of these components a form sheet has to be filled in containing the following details:

- type of component,
- function of the component,
- failure mode (for example, a valve may fail in open or closed position, leak across the seat or leak to the outside),
- failure mechanism,
- effect of the failure on the system,
- way of failure detection,
- possible countermeasures,
- remarks.

As already mentioned the failures may be quantified by indicating expected frequencies for the occurrence of the different failure modes and the severity of the associated consequences. We then speak of failure mode, effect, and criticality analysis (FMECA).

It is a characteristic of the method that all components of a system are covered and that the consequences of the failure of an individual component are treated. Hence, it is suited to check the compliance with the so-called single failure criterion. This criterion implies that the failure of a single component must not lead to a hazardous state of the system.

On the other hand the method is not well suited to discover hazards which result from the simultaneous failure of several components. Hence, it is often used to prepare the application of other methods of safety analysis, for example event tree and fault tree analyses (cf. Sects. 9.1.2 and 9.1.2.7). It then serves primarily to identify accident initiating events, i.e. such events which would lead to an accident, should the safety equipment of a system fail.

Example 9.5 Failure mode and effect analysis for a storage tank (after [17])

Figure 9.6 shows an open tank for storing a liquid feed for a production process. The required supply of this feed varies with time. Consequently the liquid level in the tank varies. The filling of the tank is controlled automatically and is described as follows. Whenever the liquid level is low, the level switch LSHL (“level switch high low”) gives a signal for the valve V1 to be opened: filling starts. When a certain filling level is reached “nominal level”, the level switch is activated once again; it then gives a signal for closing valve V1. Thus, the liquid supply to the tank ends. Should this mechanism fail and the filling level therefore rise to an “abnormally high level”, level switch LSHH (“level switch high high”) is activated. It then sends a closing signal to valve V2 and the filling of the tank ends. At

the same time an opening signal is sent to valve V3. The tank is emptied. The outlet is dimensioned such that the mass flow rate out of the tank is larger than the filling mass flow rate.

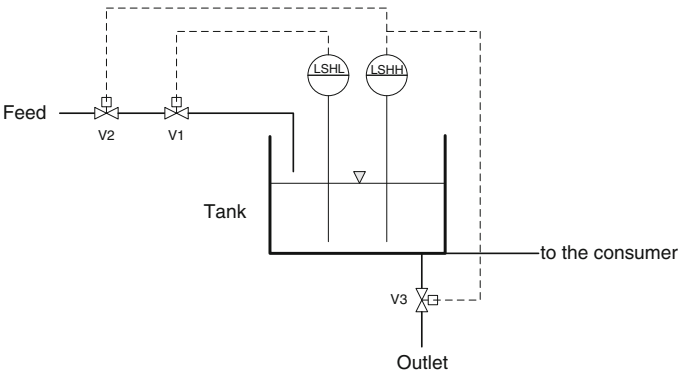


Fig. 9.6 Storage tank for a fluid (after [17])

The undesired (unwanted) event is a liquid spill to the surroundings of the tank. The result of the failure mode and effect analysis is summarized in Table 9.13.

Table 9.13 Failure mode and effect analysis for the storage tank of Fig. 9.6 (failure of LSHL not opening on low level is not contemplated because it is not safety-relevant)

Item	Function/operational state	Failure or error mode	Effects on other components of the system	Effects on the whole system
LSHL	Switch which provides V1 with a closing signal at high level and an opening signal at low level	No signal at high level	V1 does not close	Abnormal rise of the filling level
		Signal although level not high (false alarm)	V1 closes unintentionally	Filling ends
LSHH	Switch which provides V2 with a closing signal and V3 with an opening signal at a very high level (high-high)	No signal at high level	V2 does not close, V3 does not open	Overfilling of tank, if V1 does not close, liquid spill into the surroundings of the tank
		Signal although level not high (false alarm)	V1 closes unintentionally, V2 opens unintentionally	Tank is emptied

(continued)

Table 9.13 (continued)

Item	Function/operational state	Failure or error mode	Effects on other components of the system	Effects on the whole system
V1	Stops the liquid feed if level is high; Normal position: open/closed	Does not close despite signal		Abnormal rise of filling level
		Closes unintentionally		Filling ends
		Major leakage to the outside		Filling ends, liquid spill into the surroundings
V2	Stops the liquid feed if level is high; Normal position: open	Does not close despite signal		Abnormal rise of filling level, liquid spill into the surroundings, if V3 does not open and V1 not closed
		Closes unintentionally		Tank is emptied, if V3 opens
		Major leakage to the outside		Filling ends, liquid spill into the surroundings
V3	Discharges liquid at very high filling level; normal position: closed	Does not open despite signal		Discharge fails
		Opens unintentionally		Unintentional discharge
		Major leakage to the outside		Liquid spill into the surroundings

□

9.1.2.5 Event Tree Analysis

Event tree or event sequence analysis (ETA) is an inductive method. In the first place it is qualitative. Yet, it is well suited for quantification and is therefore mostly used quantitatively. Starting from a defined initiating event (e.g. pipe rupture, failure of energy supply) and depending on the functional success or failure of the operating and safety systems (barriers) required for coping with it, the different possible consequences of the initiating event are determined [18]. In doing this it is useful to distinguish between plant internal and plant external events:

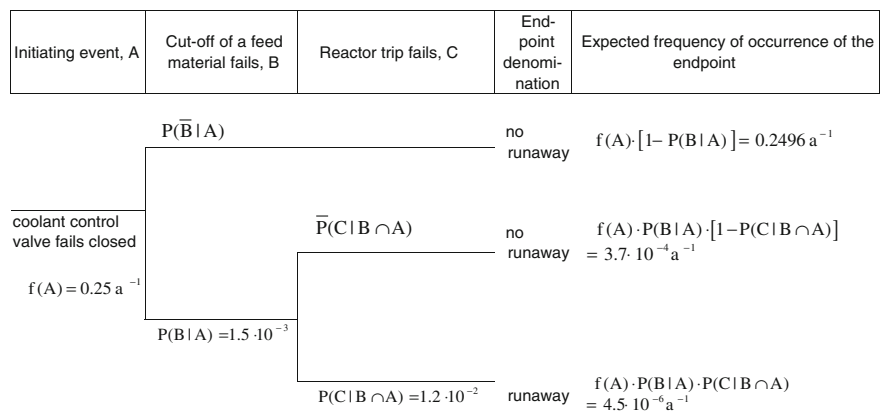


Fig. 9.7 Example of an event tree—scenarios for the potential consequences of the failure of the coolant control valve of a reactor for an exothermic reaction with quantification (after [15])

- Plant internal events are, for example:
 - mechanical failures of active components (e.g. pumps) and of passive components (e.g. pipes and tank),
 - malfunctions or failures of process control equipment,
 - failure of the supply of electricity or other media to the equipment,
 - human error.
- Plant external events are, for example:
 - natural events such as lightning, earthquakes, and flooding,
 - impacts from other hazardous installations in the neighbourhood (e.g. industrial plants),
 - impacts from transportation media (e.g. aircraft crash or explosion of a passing tank car or lorry).

Since it is impossible to treat all conceivable initiating events, it suffices to deal with the important ones, i.e. those which dominate with respect to frequency of occurrence of the endpoints (vid. Fig. 9.7) and/or the associated consequences.

The expected frequencies of the initiating events are in general derived from observation. Either estimates are directly obtained from operating experience (e.g. for the occurrence of pipe leaks) or the initiating event is decomposed into such sub-events for which operational experience is available. The frequency of occurrence is then assessed using fault tree analysis (vid. Sect. 9.1.2.7). Additionally, there are cases where one has to have recourse to expert judgment.

Depending on the countermeasures required and the operating and safety systems available for these measures the functioning or failure of these systems results in bifurcations leading to different possible event sequences. These are represented by the event tree (vid. Fig. 9.7). Every path through such a tree represents a scenario, i.e. a possible development of the future triggered by the initiating event.

Which of the systems have to maintain their function and which ones are demanded is assessed by simulating the dynamic behaviour of the process. The simulation is based on mathematical models for physical or chemical processes. Each branch of the event tree is the static description of an event proceeding in time. The process is represented by a few bifurcations where, depending on the failure (downward branch) or functioning (upward branch) of the required system, the further course of the process is determined.

In order to determine the minimum requirements for fulfilling a success criterion (e.g. 75 % of pump flow must be available for sufficient cooling) frequently information from accident simulations is used, which have been carried out in other contexts, e.g. the licensing procedure. The event tree analysis for the technical systems of a plant may be divided into two tasks:

- the analyses dealing with the event sequence, as far as it is determined by the intervention of the operating and safety systems, and
- the analyses which deal with the event sequences resulting from the assumption that the operating and safety systems fail; these concern events within the plant up to the release of hazardous substances and energy.

The first task includes all the bifurcations in the event sequences which prove important in plant dynamic analyses and because of the demands on operating and safety systems. The second task implies plant dynamic analyses with modified boundary conditions which reflect the preceding failures of operating and safety systems. In practice, these calculations or at least part of them are often replaced by engineering judgment.

Event trees are based on binary logic, i.e. components and systems either function fully or fail completely. Possible intermediate states are assigned to one of the two, normally the failed state. The material bases for the logic structure result from plant dynamic calculations, experiments as well as engineering judgment.

In performing an event tree analysis the following aspects have to be observed:

- Mutual dependencies can exist. The reason may be that the measures to counter the initiating event are often realized by systems which are not independent from one another. The demands on the system function depend on the event sequence and initiating event under investigation.
- Secondary failures may occur, i.e. for any event of a sequence possible impacts from preceding events must be considered. If, for example, a fluid flowing from a leak impacted a sensor of a protective system, the potential increase of its failure probability and other possible consequences must be accounted for.

Hence, all probabilities assigned to events are conditional probabilities depending on the outcome of events prior (exit of preceding bifurcations) to the one under consideration. Independent probabilities may be used if the influence of dependencies is negligible (for example, if the above mentioned sensor is liquid-proof).

The following steps have to be performed in an event tree analysis (based on [19])

Qualitative analysis

1. Identify (and define) a relevant accidental (initiating) event that may give rise to unwanted consequences.
2. Identify the barriers that are designed to deal with each particular accidental event.
3. Construct the event tree.
4. Describe the (potentially) resulting accident sequences.

Quantification

5. Determine the expected frequency of the accidental event and the (conditional) probabilities of the branches in the event tree.
6. Calculate the probabilities/frequencies for the identified consequences (endpoints).
7. Compile and present the results of the analysis.

The above steps are repeated for every relevant initiating event.

The description of event tree analysis given here is based on the analysis of plant internal sequences. It must be emphasized, however, that event trees are fundamental for describing accident consequences, e.g. events following the release of a flammable substance like fires or explosions. This is dealt with in detail in Chap. 10.

9.1.2.6 Layer of Protection Analysis

A more recent development in the sector of risk analysis for process plants is the Layer of Protection Analysis (LOPA) [20]. It uses the underlying idea of event tree analysis usually selecting the graver scenarios for analysis. Generic failure rates chosen from ranges (categories) indicated in [20] are attached to the initiating events, for example the failure of a coolant pump. Likewise this is true for the unavailabilities of protective barriers which are meant to control the initiating event (e.g. monitoring or safety systems). The severity of accident consequences is described by categories. In choosing a value the analyst may show a tendency to prefer the lower bound of the range (optimistic) or its upper bound (pessimistic). The barriers of protection have to be independent from one another. This means, for example, that the same component may not contribute to several barriers or that several barriers share the same electricity or compressed air supply. If the barriers are not independent the result of the analysis is not conservative.

In order to obtain an estimate for the risk the expected frequencies of undesired events such as the release of hazardous materials, which occur after the barriers have failed, are combined with categorized accident consequences. The effort required for carrying out a LOPA is much less than that for a detailed risk study. LOPA provides an order of magnitude estimate of risk and shall not replace a detailed analysis. The procedure is suited to identify those plants (or parts of them)

which require a more detailed analysis, i.e. it is a screening analysis. For identifying potential hazardous states in the plant under analysis a HAZOP study is often performed prior to the LOPA.

The result of a LOPA is presented in a worksheet, as shown below.

Case study 9.1 LOPA for a cooling control failure of an exothermic reaction

The nitrator shown in Fig. 4.10 and discussed in case studies 4.2 and 9.4 is investigated. A LOPA is to be used to analyze the failure of the cooling of the reactor, which would lead to a temperature rise, a runaway reaction and the explosion of about 101 kg of the explosive hexogen.

If the temperature rises an emergency trip is carried out by dumping the reactor contents into the receiving emergency vessel located below it.

The dumping of the reactor contents into the receiving emergency vessel is triggered by an electric measuring chain. This chain is independent of plant operation and buffered by batteries, which are constantly charged from the grid. In this way the electric supply is ensured with high probability even in case of grid failure. The measuring chain consists of resistance thermometer TE2, temperature switch TSH2, which cuts off the hexamine supply if its setpoint is exceeded, and the temperature switch TSHH2, which activates the dumping. Additionally, the instrument TI2 indicates the reaction temperature in the control room. Solenoid valve SV1 is opened which in turn opens the discharge valve HV1 when the reactor content is dumped. At the same time the stirrer in the emergency receiving vessel is turned on.

In case of an explosion it may safely be assumed that a person in the vicinity of the reactor is killed with probability 1.

The safety objective considered here is the protection of the employees in the surroundings of the reactor. The protection goal (taking into consideration further potential accident scenarios) is assumed to be $0.5 \times 10^{-4} \text{ a}^{-1}$.

The expected frequency for the failure of duty components (required for process operation, e.g. basic control system) and of the demands of the safety system resulting therefrom is 1.2 a^{-1} .

The result is summarized in Table 9.14. The calculations underlying Table 9.14 were carried out as follows:

- Frequency of the unmitigated accident consequences: Frequency of the initiating events (1.2 a^{-1}) · probability that staff in the surroundings is affected (0.3) = 0.36 a^{-1}
- Probability of failure of the independent protection barriers (total probability of failure on demand): emergency trip system (0.01) · not yet installed additional safety function (0.01) = 0.0001
- Frequency of the mitigated accident consequences: $0.36 \text{ a}^{-1} \times 0.0001 = 0.36 \times 10^{-4} \text{ a}^{-1}$.

Table 9.14 LOPA for the failure of cooling control of an exothermic reaction

Scenario number 1		Equipment number	Scenario title: Cooling control failure and failure of the emergency trip system	
Date		Description	Probability	Frequency in a^{-1}
Consequence description		Reactor temperature rises, runaway and an explosion occur		
Risk tolerance criterion (category or frequency)				0.5×10^{-4}
Initiating event (typically a frequency)		Failure of the measuring chain for the control valve or of the control valve itself		1.2
Enabling event or condition for the initiating event		–		
Conditional modifiers, if applicable				
		Conditional probability of explosion	1	
		Probability that staff is present in the surroundings of the reactor	0.3	
		Conditional probability for fatal injury	1	
		Others		
Frequency of the unmitigated consequence				
		Independent protection layers		0.36
		Emergency trip system	0.01	
		Required additional safety function (not yet installed)	0.01	
		<i>Safety functions (no independent layers of protection)</i>		
		Trip by operator after alarm from TAH1		
		Cut-off of hexamine feed by TSH2		

(continued)

Table 9.14 (continued)

Scenario number 1	Equipment number	Scenario title: Cooling control failure and failure of the emergency trip system
	Human intervention after alarm	
Total probability of failure on demand		
Frequency of the mitigated accident consequence		0.0001
Risk tolerance criterion met (yes/no): yes		0.36×10^{-4}
Actions required to meet risk tolerance criterion (yes/no): yes		
Installing an additional independent protection layer with a probability of failure on demand $u = 0.01$		
Notes		
References (e.g. original hazard review (e.g. HAZOP), probability of failure on demand, P&I diagram etc.)		
LOPA analyst (and team members, if applicable)		



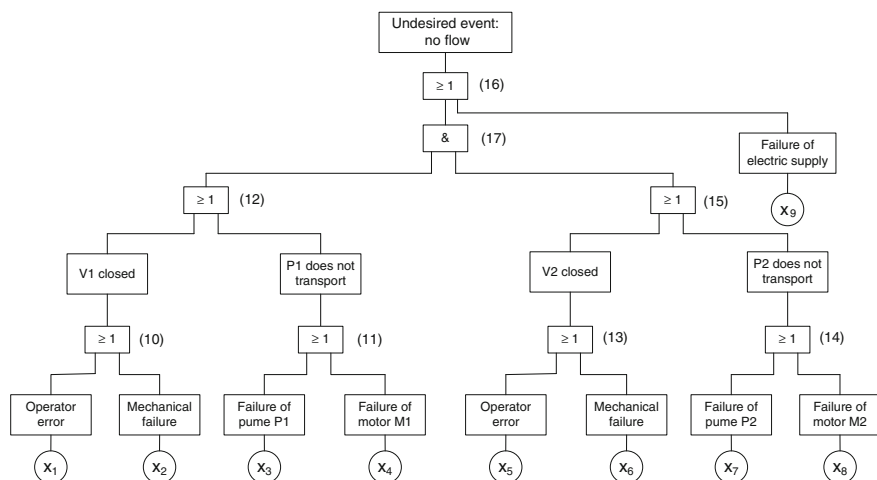


Fig. 9.8 Fault tree example for the system for transporting a fluid of Fig. 9.4 (without pipe rupture and impurities)

9.1.2.7 Fault Tree Analysis

Fault tree analysis (FTA) is a deductive method, which usually serves for quantification. Just like any method of systems analysis it requires in the first place a qualitative investigation of the system under analysis. After system failure or more generally the undesired or unwanted event (e.g. toxic release)² has been defined, logic relationships with the so-called primary or basic events² are identified and represented by a fault tree (vid. Fig. 9.8). The primary event may represent the failure of a technical component, an operator error or an impact from outside the plant like flooding or the spreading of a fire from neighbouring installations.

The fault tree represents the result of the qualitative part of the analysis. This is based on questions such as “How can this happen?”. These questions enable one to firstly relate the undesired event (also called TOP event) with the failure of subsystem functions such as cooling or energy supply. Successively these failures are broken down into the failures of sub-subsystems etc. until the level of the primary events is reached. Hence only portions of the plant of a size which can be handled by the human intellect at any one time are analyzed. These portions are then logically connected with analyses of other parts of the plant in order to eventually provide a model of the entire plant.

In general, a variety of failure combinations of various components or events such as human error are obtained which make subsystems fail. The failure of a subsystem may either directly cause the undesired event or do so in combination with failures of other subsystems, components or human error. The combinations

² In [3] the word primary failure is used. However, since one does not always refer to a failure, the more general term “primary event” is used here. Often the term “component failure” is applied.

are described by logical “AND” and “OR” gates. The output of an “OR” gate is true if any one, several or all of its inputs are true (inclusive “or”). The “AND” gate requires all of its inputs to be true in order for its output being true. Occasionally the “NOT” gate is used which converts its input into its contrary. The corresponding symbols for the fault tree are shown in Fig. 9.9.

The procedure may well be explained using the fault tree of Fig. 9.8, which is based on Example 9.3. It deals with the analysis of a system which consists of two electrical pumps, each of which can be blocked on the pressure side by a valve. The task of the system is to transport a fluid. It suffices if one of the two pumps can work without obstruction (system design: $2 \times 100\%$, 1oo2, one-out-of-two redundancy). This is the success criterion.

Obviously the undesired event in this case is the interruption of the fluid transport. This can occur in several different ways. For example, the electricity supply can fail (primary event x_9). Both pumps would stop then. Furthermore, disturbances may occur which affect both trains. Hence, gate (16) is an “OR”-gate. Its output is true if any one or both of its inputs are true (failure of the electricity supply or failure of both trains). Since both trains are of identical design it suffices to explain, how the failure of one of the trains comes about. Analogous arguments then apply to the other train.

Fluid flow is interrupted if the valve V1 fails closed or the pump does not work or if both events occur simultaneously. In the fault tree these two events are therefore connected by the “OR”-gate (12). If we ask ourselves why valve V1 can fail, the answer can be: “it failed mechanically in closed position (primary event x_2) or the operator closed it erroneously (primary event x_1)”. Both events are again connected by an “OR”-gate. Its number is (10).

Pump P1 can fail because its driving motor M1 stops (primary event x_4) or the pumping part itself fails (primary event x_3). The “OR”-gate (11) connects both events. Since both trains have to fail to make the system fail their partial fault trees are connected by the “AND”-gate (17). Its output is true only if all of its inputs are true, in the present case both trains must have failed. The “AND” gate signals a redundancy.

A more profound insight into the procedure is gained if one imagines how a modified success criterion affects the fault tree. For example, a thermohydraulic calculation might show that both trains have to operate in order for the task of the system (the system function) to be fulfilled. In such a case the “AND”-gate (17) would have to be replaced by an “OR”-gate. The system is no longer redundant, but has become a 2 times 50 % configuration.

The primary events of the fault tree may be further decomposed. For example, the failure of the pump motor M1 might be caused by a failure of its stator or rotor windings, cables or such like. This would make sense if the motor itself were the object of the fault tree analysis. In practice the degree of decomposition (degree of detail) is determined by the boundaries (delimitation) of the reliability data for describing component behaviour, which are needed for quantifying a fault tree.

As mentioned already, the fault tree represents a simplified model of the system with regard to the undesired event. Its advantage is that the influence of components on one another and the consequences of their failure, of human error, and of

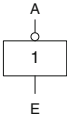
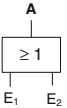
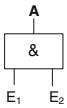
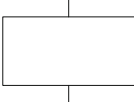
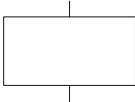
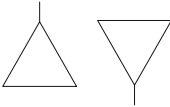
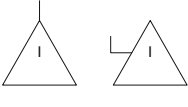
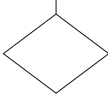
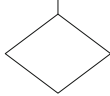
Meaning	Symbol according to DIN 25424-1	Symbol according to IEEE Std. 352-1975
Standard input for a primary or basic event		
Logcal NOT gate. If E is true, A is not true and vice versa		
OR gate. A is true,if either E ₁ or E ₂ or both are true (logical union)		
AND gate. A is only true if both E ₁ and E ₂ are true at the same time (logic intersection)		
Comment		
Transfer symbols. The symbols are used if a fault is interrupted in one place and continued in another.	Transfer-in  Transfer-out	Transfer-in  Transfer-out
Secondary event (failure as a consequence of a preceding faillure)		

Fig. 9.9 Frequently used fault tree symbols

impact from external events on the system may be accounted for. To model an entire system accounting for all the process parameters (e.g. pressure, temperature, concentration, mass flow etc.) and their evolution with time after the occurrence of an initiating event usually results too difficult. Nevertheless the knowledge of the time-dependent behaviour of the physical, chemical or other relevant process parameters (e.g. biological) following the occurrence of an initiating event is necessary. This knowledge is reflected by the logical structure of the fault tree, i.e. the choice of “AND” or “OR”-gates. The latter is supported, for example, by decisions on whether temperatures or pressures occur during the accident event sequence which exceed material limits or not. The knowledge on system behaviour in general stems from dynamic calculations of material loads, experiments or engineering judgment. The latter should be exerted with conservatism, i.e. an unfavourable result for the system should be used.

When performing a fault tree analysis it is generally assumed that all components are designed, built and installed such that they fulfil their function if they work properly. For example, one supposes that a relief valve has a cross section which allows a sufficient mass flow rate to maintain the pressures inside the equipment to be protected within permissible limits (this might not be the case, if instead of a liquid -as assumed in the design- two phases occur in the discharge). The assumption of correct functioning has to be checked in the context of the analysis, especially if failure combinations are considered which may lead to loads beyond the design limits of the components. In such a case correct functioning may not be assumed. An example may be a pressure switch exposed to temperatures and air humidities for which it is not designed after the rupture of a steam pipe.

Fault tree analysis may be used during the design phase of a plant thus influencing its final configuration. It may be applied as well to assess existing designs. In the latter case knowledge is gained on the efficiency of the existing design and procedures and their potential improvements. Fault tree analysis should especially be used if there is little operating experience with a type of a plant. In such a case the probability of plant failure may not be derived from records on operation (actuarial approach) but has to be assessed starting from probabilities for the occurrence of the primary events. In any case the expression of the undesired event in terms of primary events reveals possibly existing design weaknesses which cannot be discovered if the actuarial approach is used.

When determining the failure probabilities of components use is made of the circumstance that many items of the same type of component are used and that several plants use the same type of component. Additionally, components usually fail more frequently than the systems in which they are installed. Thus, sufficient operating experience (number of component failures and operating time) can be collected in relatively short periods of time. Although the possibility exists to assess the failure probability of a plant directly if the number of a plant type and the operating experience is sufficiently large fault tree analysis does not lose its value. It provides insight into system structure, enables one to identify design weaknesses and to judge the effectiveness of planned remedial actions. Such knowledge cannot usually be obtained from records on a specific type of plant. In general it may be

stated that fault tree analysis searches for the conditions of plant failure and therefore may be regarded as the antithesis of the design process, which aims at identifying the conditions for functioning. Hence, it proves useful for identifying design weaknesses in both its qualitative and quantitative parts. Eventually, the synthesis of design and safety analysis leads to a better and safer plant.

The steps listed below are needed for carrying out a fault tree analysis. The first step is largely a matter of organization. It is not dealt with here; a detailed treatment is found in [21]. In what follows the remaining steps are discussed in detail and illustrated by a number of examples and case studies.

1. Familiarization with the process and plant using the corresponding descriptions, P&I diagrams, information from the plant designer and operator etc.
2. Determination of the undesired and initiating event(s) using checklists, information on material properties, reports on events and near misses (events which almost had a negative outcome) as well as studies of similar plants.
3. Development of the fault tree or trees.
4. Preparation of probabilities for the failure of technical components, human error, and impacts from external events.
5. Numerical evaluation of the fault tree or trees.
6. Valuation of the results, proposals for improvements, if necessary, and renewed evaluation of the fault tree(s) after having introduced the improvements in them in order to check whether the proposed improvement is real or not.

A technical system normally has a number of standby components (components which become active only after demand). Components of the monitoring and safety systems belong to this category. These systems are devised to cope with accident initiating events. They form the barriers between the initiating and the undesired event. The latter only occurs if all barriers fail. The situation is shown schematically in Fig. 9.10. Obviously in the same system initiating events can occur for whose control various barriers may become effective, and initiating events which directly lead to the undesired event, for example the spontaneous failure of a chlorine pipe.

The number of barriers depends on the number of redundant standby components in the monitoring and safety systems, which can become effective in case of the initiating event under investigation. If components from barriers have to fail before the undesired event occurs, their failure is connected with the initiating event by an “AND”-gate.

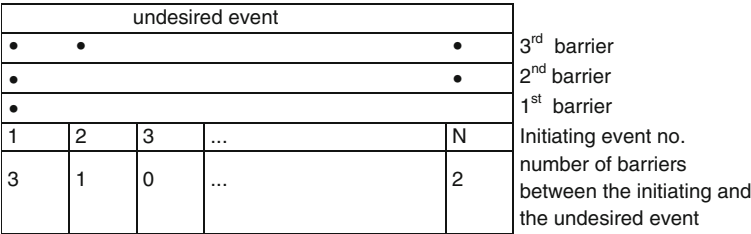


Fig. 9.10 Barriers against the occurrence of undesired events (after [22])

If there are several such combinations these are input into an “OR”-gate just as the contributions of several initiating events to the undesired event. The components which figure together with the initiating event are called redundant. Their number indicates the degree of redundancy. Fault trees are elaborated according to the outlined principles.

9.1.2.8 Determination of Undesired and Initiating Events

The determination of the undesired and initiating events depends on the area, to which a plant belongs, on the object and the objective of the analysis. It belongs to the qualitative part of the analysis and may be supported by checklists (vid. Sect. 9.1.2.1) or systematic methods like FMEA (vid. Sect. 9.1.2.4) or HAZOP (vid. Sect. 9.1.2.3).

Undesired events

The identification of undesired events is best explained giving a few examples.

If an emergency power system is to be analyzed the undesired event is that it fails to enter into operation when demanded, i.e. that it is not available, or in case it starts it does not maintain its function until the supply from the grid is re-established, i.e. it fails before its mission ends.

If a nuclear power station is analyzed the undesired event is core melt or in a further step a release of radioactive material from the containment, depending on the scope of analysis.

In case of the storage of ammonia its release into the environment is undesired because of its toxicity and the possibility of an explosion or fire.

Initiating events

If a system is designed correctly operation disturbances can only occur if there are deviations from the nominal operating conditions. These can be the consequence of component failures which may lead to a loss of their function (e.g. stuck valve) or a loss of their integrity (e.g. pipe leak), of a human error in handling the system or an impact from an external event.

Systems are generally made up of components which must be operating in order for the system to fulfil its mission (continuous and intermittent duty components), standby components which take over the function of the operating component if it should fail and the components of the monitoring and safety systems. The latter only have to function on demand. Therefore they also belong to the class of standby components.

Since only failures of components required for the system operation influence the system behaviour these usually constitute the initiating events (however not any failure must be safety-relevant, they may instead lead to bad product quality or standstill). Furthermore, the loss of integrity of containment must be contemplated, if resulting releases produce the undesired event. Additionally, operator errors, which can cause disturbances, must be considered as well.

If process plants are analyzed it must be remembered that there are materials which are capable of spontaneous reactions like decomposition or polymerization (vid. Sect. 2.2). Such events must be added to the list of initiating events.

Furthermore the impact of external events such as earthquakes, aircraft crash, tornado, flooding or pressure waves (possibly resulting from events in neighbouring plants or transportation routes) have to be accounted for as initiating events or events triggering initiating events.

By way of example several potential initiating events in a stirred reactor for an exothermic reaction are listed below (vid. Sect. 4.2.5):

- cooling system failure,
- stirrer failure,
- dosing malfunction,
- external hazards (flooding, aircraft crash,...).

Of course, it has to be ensured that all relevant events have been considered in the analysis. Not relevant are initiating events whose expected frequency of occurrence and/or consequences are one or several orders of magnitude smaller than that of the considered ones, e.g. below the limiting values of Chap. 8. This argument may be applied as well to events which have not been observed until the time of analysis. The expected frequency of such events is assessed in what follows.

We assume that plants of a certain type may be considered as a homogeneous group (a far reaching assumption but there is no better one) and that events in this group are registered over a certain period of time as in [23]. We can then make statements about the expected frequency of occurrence for an event which has not occurred during the period of time of registration. For the upper bound of the 95 % confidence interval, h_{95} , we find from frequentist statistics (cf. Appendix C)

$$h_{95} = \frac{\chi^2_{2;0.95}}{2T} \quad (9.12)$$

In Eq. (9.12) $\chi^2(2; 0.95)$ is the χ^2 -distribution with a degree of freedom of 2 and a level of confidence of 95 % (cf. [24]) and $T = \sum_{i=1}^I T_i$ is the accumulated time observation, where T_i is the operating period of plant i , ($i = 1, \dots, I$) and I the total number of observed plants. The expected (mean) value can be obtained using Bayesian statistics (vid. [25], Sect. 9.3.3 and Appendix C), which gives

$$h = \frac{1}{2T} \quad (9.13)$$

The identification of initiating events for process plants is difficult because of their great variety. As pointed out before chemical processes involve both physical and chemical hazards. Physical hazards derive from operating conditions which may be extreme, such as very low or very high temperatures and pressures. Chemical hazards are those associated with the materials present in the process, which may be toxic, flammable or explosible, or exhibit several of these properties at the same time. A further complication stems from the fact that some of these

properties may vary with changes of process parameters such as temperatures, pressures, or concentrations or that these changes may give rise to unwanted side reactions or spontaneous reactions such as heating, decomposition and polymerization. In addition, dangerous properties, if not present under normal process conditions, may evolve upon contact of process media with auxiliary media such as coolants, lubricants or impurities. The latter can be introduced with process streams or be washed out from the structural materials of the plant. After release, reactions with substances present in the environment, e.g. the humidity of the air, may give rise to dangerous properties. This enumeration, which is by no means complete, illustrates the difficulties in identifying initiating events in process plants as compared, for instance, with nuclear power stations.

Example 9.6 Assessment of the expected frequency of an event which has not been observed during a certain period of time

During a period of observation of ten years no accident with a fatality outside the plant was registered in [23] in any of the approximately 7,800 plants subject to the Major Accident Ordinance (German implementation of the Seveso Directive).

Calculate the expected frequency for a fatality outside the plant using Bayesian statistics and the 95 % confidence bound of a frequentist calculation.

Solution

With the (certainly far reaching assumption) that the “Seveso” plants represent a homogeneous population the Bayesian zero-event statistic according to Eq. (9.13) gives

$$h = \frac{1}{2T} = \frac{1}{2 \times 7,800 \times 10 \text{ a}} = 6.4 \times 10^{-6} \text{ a}^{-1}$$

The calculation of the corresponding distribution percentiles is shown in Sect. 9.3.3.

The 95 % upper confidence bound of the frequentist treatment is obtained from Eq. (9.12)

$$h_{95} = \frac{\chi^2(2; 0.95)}{2T} = \frac{5.991}{2 \times 7,800 \times 10 \text{ year}} = 3.84 \times 10^{-5} \text{ a}^{-1}$$

□

Example 9.7 Elaboration of a fault tree for the cooling system of a plant for producing hexogen [15]

Figure 9.11 shows the fault tree for the failure of the cooling of the plant producing hexogen from Example 9.4. It is explained below.

The undesired event “cooling system failure” only occurs if

- the cold part of the coolant tank loses its contents undetectedly or
- the coolant supply to the process fails undetectedly or
- recooling fails without countermeasure.

The cold part of the coolant tank loses its contents undetectedly, if

- the leak is not detected (x_{10}) and
 - the coolant level drops because of a leak (initiating event x_9) or
 - the continuous duty pump P1A fails (initiating event x_1) and
 - (a) the alarm via FAL01 fails (x_2) or
 - (b) no attention is paid to the alarm (x_3) or
 - (c) the reserve pump P1B is not switched on (x_4) or
 - (d) the check valve behind P1B does not open (x_8) or
 - (1) the manual valve in front of P1A is not closed (x_6) and
 - (2) the check valve behind P1A does not close (x_7).

[Note: The event x_1 (P1A fails) figures twice in the fault tree. However, it is counted only once because of the idempotent property of the binary variables x according to Eq. (9.60)]

The coolant supply to the process fails undetectedly if

- an undetected leak occurs behind the pressure switch (initiating event x_{11}) or
- the continuous duty pump P2A fails (initiating event x_{12}) and
 - pressure alarm PAL 06 fails (x_{13}) or
 - reserve pump P2B is not switched on (x_{14}) or
 - no attention is paid to the pressure alarm PAL 06 (x_{15}) or
 - the reserve pump P2B does not start (x_{16}) or
 - (1) the check valve behind P2A does not close (x_{18}) and
 - (2) the manual valve in front of P2A is not closed (x_{19})

The recooling apparatus fails without countermeasure, if

- the refrigerating unit R1 fails (initiating event x_{20}) or
- the thermostat of R1 fails (initiating event x_{21})

and

- the temperature alarm TAH04 fails (x_{22}) or
- no countermeasure is taken following alarm from TAH04 (x_{23}).

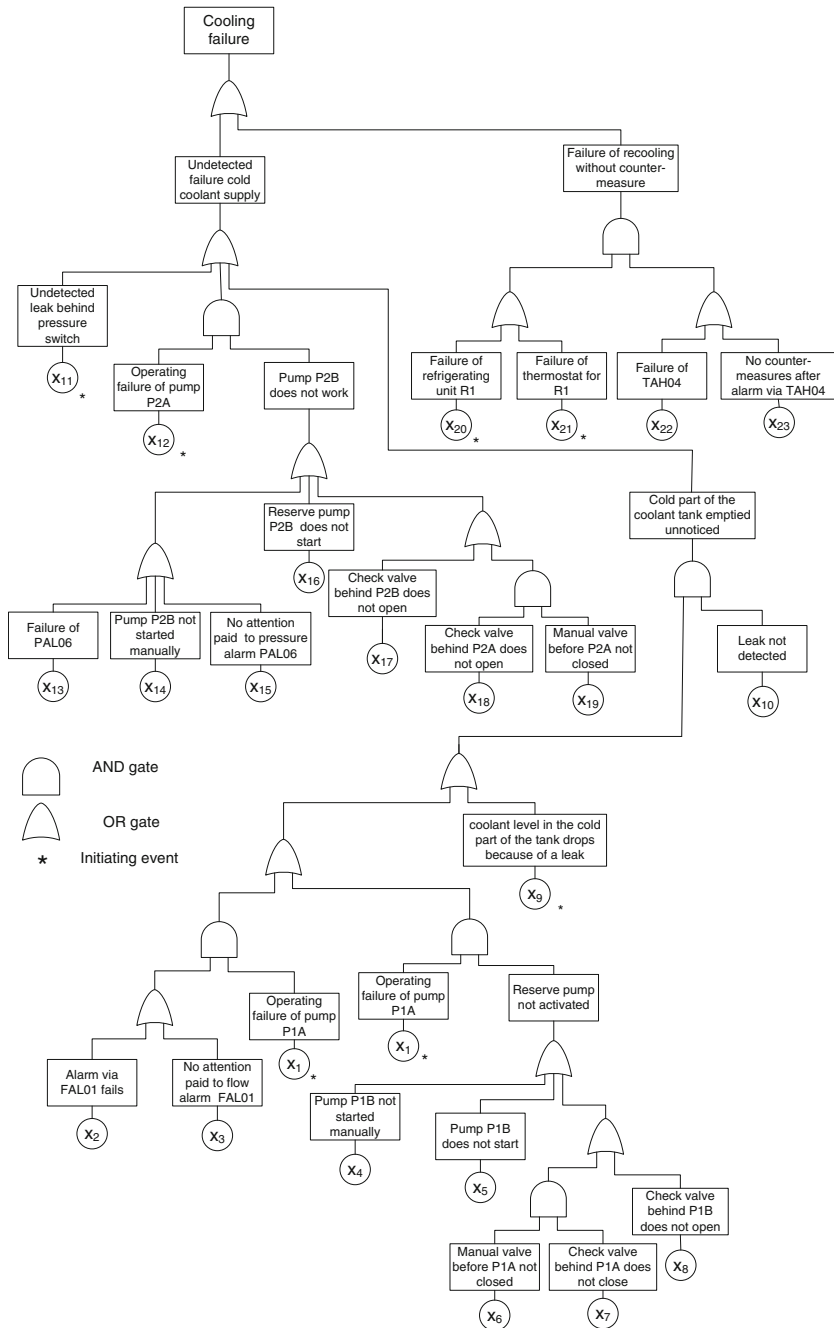


Fig. 9.11 Fault tree for the failure of the cooling system of Fig. 9.5 (* initiating event; (x_i , $i = 1, \dots, 22$ are binary indicator variables describing the state of the component, i.e. $x_i = 1$ failed, $x_i = 0$ working, cf. Sect. 9.4) □

9.2 Mathematical Description of the Components of Technical Systems

Technical systems are made up of components such as valves, pumps, pipes, measuring devices, control loops etc. These have to fulfil certain tasks within the system. If they do not comply with these tasks because their technical properties have changed in such a way that they lie outside the permissible regions of tolerance of the system, they have failed. There are many reasons for component failures, e.g. manufacturing flaws, corrosion, overload, unfavourable environment or wear to name just a few. It is known that components fail after a certain period of time, but it is impossible to predict the point in time of failure. Yet, models describing the operating behaviour can be developed. They are based on the observation of large numbers of components and they are statistical in nature.

If the operation of a number of components starts at the same time and their behaviour is observed, the points in time of their failure can be recorded. Thus, their corresponding lifetimes, i.e. the time intervals between start and failure can be determined. In order to treat this with a probability model the random variable τ is introduced for the component lifetime. The corresponding probability distribution function is

$$F(t) = P\{\tau \leq t\} \quad t > 0 \quad (9.14)$$

$F(t)$ is the probability that a component which has functioned at point in time $t = 0$ fails before or in point in time t . This probability is called failure probability or unreliability. It amounts to 0 at point in time $t = 0$ and tends to 1 for $t \rightarrow \infty$.

Frequently a component is characterized by the complementary value of Eq. (9.14), the probability that the component works within the time interval $[0, t]$ without failure

$$\bar{F}(t) = 1 - F(t) = P\{\tau > t\} \quad (9.15)$$

$\bar{F}(t)$ is called survival probability or reliability.

In general $F(t)$ is differentiable so that the corresponding probability density function (pdf) can be formed

$$f(t) = \frac{dF(t)}{dt} = F'(t) = -\bar{F}'(t) \quad (9.16)$$

The quantity $f(t)\Delta t$ then is the probability that the lifetime τ lies in the interval $[t, t + \Delta t]$. This is equivalent to a component failure within this interval.

The mean lifetime of the component, T , is the expected value of τ , i.e.

$$E[\tau] = T = \int_0^{\infty} t \cdot f(t) dt = -[\bar{F}(t) \cdot t]_0^{\infty} + \int_0^{\infty} \bar{F}(t) dt = \int_0^{\infty} [1 - F(t)] dt \quad (9.17)$$

The expression in square brackets in Eq. (9.17) is equal to 0, since $\bar{F}(0) \cdot 0 = 0$ and $\lim_{t \rightarrow \infty} \bar{F}(t) = 0$. The mean lifetime is also denominated by **Mean Time To Failure (MTTF)**. It is often important to determine the probability that a component fails in the time interval $[t, t + \Delta t]$ if it has functioned during $[0, t]$. To answer this, in the first place the probability for a component which has worked during $[0, t]$ and continues to do so during $[t, t + \Delta t]$ is established. Its complementary value then is the probability to be determined.

Let A denote the event that a component functions until point in time t and B that it continues to work during $[t, t + \Delta t]$ under the condition of having functioned during $[0, t]$. We then have [cf. Eq. (C.7)]

$$P(B|A) = \frac{P(A \cap B)}{P(A)} = P(t, t + \Delta t) \quad (9.18)$$

Using Eq. (9.16) in Eq. (9.18) we obtain

$$P(B|A) = \frac{\bar{F}(t + \Delta t)}{\bar{F}(t)} = P(t, t + \Delta t) \quad (9.19)$$

The complement of $P(t, t + \Delta t)$, namely the probability that a component which has functioned in $[0, t]$, fails during $[t, t + \Delta t]$, is

$$q(t, t + \Delta t) = 1 - \frac{\bar{F}(t + \Delta t)}{\bar{F}(t)} = \frac{\bar{F}(t) - \bar{F}(t + \Delta t)}{\bar{F}(t)} \quad (9.20)$$

If $\bar{F}(t + \Delta t)$ is expanded in a Taylor series which is truncated with its second term, since $\Delta t \ll 1$, Eq. (9.20) becomes

$$q(t, t + \Delta t) = -\frac{\bar{F}'(t)}{\bar{F}(t)} \cdot \Delta t = -\frac{\bar{F}'(t)}{1 - F(t)} \cdot \Delta t = \lambda(t) \cdot \Delta t \quad (9.21)$$

where $\lambda(t)$ given by

$$\lambda(t) = -\frac{\bar{F}'(t)}{\bar{F}(t)} = -\frac{\bar{F}'(t)}{1 - F(t)} = -\frac{d}{dt} \ln[\bar{F}(t)] \quad (9.22)$$

is a positive parameter. It is called failure rate and has the dimension $(\text{time})^{-1}$.

After integrating Eq. (9.22) becomes

$$\bar{F}(t) = \bar{F}(t = 0) \exp\left(-\int_0^t \lambda(t') dt'\right) = \exp\left(-\int_0^t \lambda(t') dt'\right) \quad (9.23)$$

Table 9.15 Interrelationships between the different reliability parameters

Parameter	$F(t)$	$\bar{F}(t)$	$f(t)$	$\lambda(t)$
$F(t)$	–	$1 - F(t)$	$\frac{dF(t)}{dt}$	$\frac{F'(t)}{1 - F(t)}$
$\bar{F}(t)$	$1 - \bar{F}(t)$	–	$-\frac{d\bar{F}(t)}{dt}$	$-\frac{\bar{F}'(t)}{\bar{F}(t)}$
$f(t)$	$\int_0^t f(t')dt'$	$\int_t^\infty f(t')dt'$	–	$\frac{f(t)}{\int_t^\infty f(t')dt'}$
$\lambda(t)$	$1 - \exp(-\int_0^t \lambda(t')dt')$	$\exp(-\int_0^t \lambda(t')dt')$	$\lambda(t) \exp(-\int_0^t \lambda(t')dt')$	–

In Eq. (9.23) $\bar{F}(t = 0) = 1$, since we assume that the component functioned at the beginning of its lifetime, i.e. for $t = 0$.

After presenting the main parameters for describing the behaviour of components of technical systems, their interrelationships are summarized in Table 9.15.

As can be seen in Eq. (9.23) the survival probability of a component is completely determined by its failure rate $\lambda(t)$. Its general shape is known as the “bathtub curve”, which is similar to the curve of human mortality. The bathtub curve is shown in Fig. 9.12.

The distribution of the component lifetimes from the beginning of use until failure may be split up into distributions describing different failure causes [26]. These then represent the periods “early failures”, “random failures” and “wear-out failures”. By superposing the distributions periods result during which component behaviour is dominated by individual causes. These are characterized as follows:

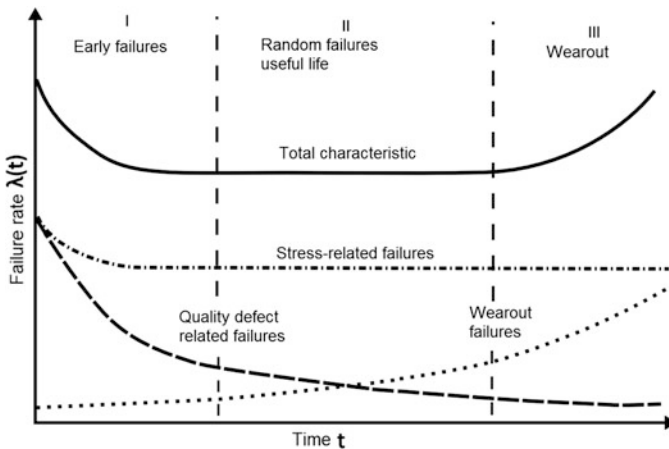


Fig. 9.12 Plot of the failure rate $\lambda(t)$ over time and contributions to component failures (after [26])

Period I: Early failures

The higher failure rate during this period is due to hidden design, quality, manufacturing or material defects or to damage during installation in the plant. It is also called the period of infant mortality. In order to keep the failure rate during this period as low as possible and to make its duration short or even eliminate it completely before component use, components are amply tested during their development process. Furthermore they are subjected to burn-in tests and controls during the manufacturing process. Hidden design flaws are mostly detected in the development phase of a component, quality and manufacturing flaws by controls of the manufacturing process. Remaining flaws are discovered by observing the operating behaviour of components. Hence, it may generally be assumed that in a plant, made up of well-engineered standard components, components are used whose failure behaviour is inscribed in period II.

Period II: Random failures

This period with its constant failure rate represents random failures of such nature that future failures do not depend on past operation. These random failures are caused mainly by random fluctuations of operating and environmental conditions which cause loads exceeding design strength. In addition failures may occur due to unprofessional maintenance and hidden design and manufacturing flaws which have remained despite the measures mentioned above.

Period III: Wearout failures

During this period the failure rate increases. This is due to physical and chemical changes during the use of the component, which reduce its strength. In general, maintenance strategies provide for replacement before wearout (aging) becomes manifest. However, it should be noted that an exact prediction of the beginning of wearout is not possible and replacement relies on engineering judgment. It is also possible that the period of wearout begins earlier than expected from experience, if circumstances like unforeseen excessive loads, hidden design flaws, insufficient safety distances (between load and resistance) or unexpected environmental impacts occur.

As already mentioned, the use of components in plants usually begins after the period of early failures and is usually terminated before aging effects become manifest. Hence, there is good reason to assume that components in operation are inscribed in period II and therefore characterized by a constant failure rate ($\lambda(t) = \lambda = \text{const.}$). This then leads to exponentially distributed lifetimes which are treated below. They are generally used in safety and risk studies (cf. [27–29]).

It should be noted that the curve of Fig. 9.12 also applies to piece parts. Therefore one or several piece parts may have reached period III whilst the remainder is still in period II. Replacement of these piece parts would then make the component “as good as new”.

9.2.1 Exponential Distribution

If in Eq. (9.23) λ is taken to be a constant, we obtain the survival probability

$$\bar{F}(t) = \exp(-\lambda t) \approx 1 - \lambda t \quad t \geq 0 \quad (9.24)$$

This leads to the failure probability

$$F(t) = 1 - \exp(-\lambda t) \approx \lambda t \quad t \geq 0 \quad (9.25)$$

The approximations in Eqs. (9.24) and (9.25) result from expanding the exponential function in a Taylor series and truncating it with the second term. This may be done, if $\lambda t \ll 1$ holds.

The corresponding pdf is obtained by differentiating Eq. (9.25) with respect to t

$$f(t) = \lambda \cdot \exp(-\lambda t) \quad t \geq 0 \quad (9.26)$$

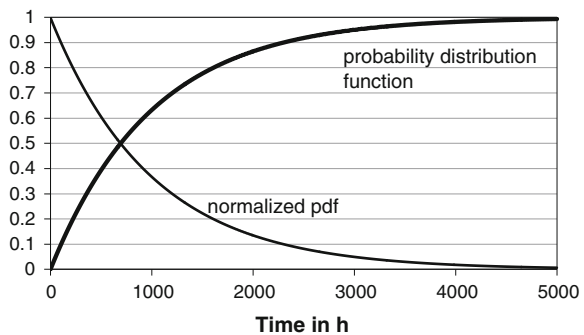
Figure 9.13 shows an example for the time-dependence of failure probability and pdf.

The mean or average lifetime follows from Eq. (9.17) as

$$E[\tau] = T = \int_0^{\infty} \exp(-\lambda t) dt = -\left[\frac{1}{\lambda} \cdot \exp(-\lambda t)\right]_0^{\infty} = \frac{1}{\lambda} \quad (9.27)$$

Hence, the average lifetime is equal to the inverse of its failure rate in case the failure rate is constant. The important property of the exponential distribution is that the probability of the failure of a component in the time interval $[t, t + \Delta t]$ does not depend on its preceding operating time but only on the value of its failure rate λ and the duration of the time interval Δt . This is shown by inserting Eq. (9.24) in Eq. (9.25). Furthermore, it can be proved that the exponential distribution is the only one with a constant failure rate [30].

Fig. 9.13 Variation with time of an exponential distribution with $\lambda = 1,000 \times 10^{-6} \text{ h}^{-1}$ and the corresponding probability density function (pdf) normalized to 1



Example 9.8 Failure behaviour of a valve

A manual valve fails closed (unwantedly in closed position). The applicable failure rate is $\lambda = 0.3 \times 10^{-6} \text{ a}^{-1}$. Calculate:

- its average lifetime,
- its failure probability for $t = 10,000 \text{ h}$,
- the failure rate of a higher quality valve characterized by a failure probability of half its original value for $t = 10,000 \text{ h}$.

Solution

According to Eq. (9.27) we have

$$T = 1/\lambda = 3.34 \times 10^6 \text{ h}$$

The failure probability is obtained from Eq. (9.25) as

$$F(t = 10,000 \text{ h}) = 3.0 \times 10^{-3}$$

The valve with a better design is to have a failure probability of $F(t = 10,000 \text{ h}) = 1.5 \times 10^{-3}$. Using Eq. (9.25) this gives

$$\lambda = \frac{-\ln(1.0 - 1.5 \times 10^{-3})}{10,000 \text{ h}} = 0.15 \times 10^{-6} \text{ h}^{-1}$$

□

9.2.2 Other Distribution Types

If the assumptions underlying the use of the exponential distribution do not apply, for example because early failures and aging have to be treated, a number of other probability distributions are in use. Further details may be taken from the literature, e.g. [30–33] and from the Appendix C.

9.2.3 Constant Failure Probabilities

Sometimes components are to be treated which have to fulfil their task at a certain moment in time. For example, an emergency power generator has to enter into operation when the supply from the grid fails. Occasionally components have to be modelled which only function during certain periods of time, for example during charging and discharging operations. This can be handled with the following model.

The probability of a component to function when required at a certain instant in time is called probability to function on demand or simply availability, p ,

$$p = \text{const.} \quad (0 \leq p \leq 1) \quad (9.28)$$

Its complement, i.e. the probability that a component fails at a certain instant in time or has failed before and not been repaired is called unavailability or probability of failure on demand, i.e.

$$u = 1 - p = \text{const.} \quad (0 \leq u \leq 1) \quad (9.29)$$

When modelling components which have to fulfil their function on demand it is supposed that their failure is caused by the demand itself, for example by overload or wrong handling.

If, on the other hand, component behaviour is described by a failure rate the assumption is that corrosion, dirty environment etc. are at the root of failure. Such influences are also present during standby of components (e.g. those of safety systems). If they then cause a failure it manifests itself only on demand. Therefore frequently failure rates are also used to describe standby components. However, the numerical values may differ from those applicable to their operating phases.

Example 9.9 Failure probability of a Diesel generator

A Diesel generator is started 1,000 times. In 25 cases the start did not succeed. What is its probability of failure on demand?

Solution

$$u = \frac{25}{1,000} = 0.025$$

□

Example 9.10 Emergency power supply in a hospital

The electricity supply of a hospital fails. It is restored 2 h later. What is the probability, P_S , for an operation to be carried out, if this requires electricity which has to be supplied by the emergency power generator?

Data: One failure in 1,000 starting attempts was observed. The failure rate for a failure during operation is $\lambda = 111 \times 10^{-6} \text{ h}^{-1}$

Solution

Using the procedure of Example 9.9 and Eq. (9.25) one obtains

$$\begin{aligned} P_S &= 1 - u - (1 - u) \cdot \left(1 - e^{-2 \times 111 \times 10^{-6}}\right) = 1 - 0.001 - 0.999 \times 2.22 \times 10^{-4} \\ &= 0.9988 \end{aligned}$$

□

9.3 Determination of Reliability Data for Technical Components

The applications of the mathematical relations of the preceding section, which describe the behaviour of technical components, require reliability data, i.e. λ or u , to be determined. The following three methods offer themselves for this purpose:

1. Expert judgment,
2. Experiments in laboratories,
3. Observations during plant operation (field studies).

Reliability data obtained from observations during plant operation naturally are the most appropriate to ensure that analyses based on them provide realistic results. Furthermore, such data may be used as a yardstick for data obtained in other ways. They reflect component properties, their working and environmental conditions as well as the quality of their maintenance. Since in the meantime reliability data are evaluated in several areas, for example for nuclear power stations [34–38], for offshore installations [39] and for process plants [33, 40], the procedures under (1) and (2) have lost importance and are therefore not dealt with here.

9.3.1 Models

9.3.1.1 Determination of Failure Rates

A model is needed to describe the observed operating behaviour mathematically. This is provided by renewal theory (cf. [41]). For its application in the present context the following assumptions are made:

- the probability for a component failure to occur in an arbitrary interval of time $[t, t + \Delta t]$ does not depend on the number of prior failures during $[0, t]$;
- the probability of a failure to occur is proportional to the length of the time interval $[0, t]$;
- the component is repaired immediately after a failure and the time required for repair may be neglected compared with its operating time and therefore be set equal to zero;
- after repair the component is “as good as new”; it is either replaced or repaired in such a way that its new state is restored; mathematically this means that the same lifetime distribution as before applies after repair.

The probability for k failures to occur from time 0 up to the point in time t and hence k repairs is then given by

$$P\{N(t) = k\} = \frac{(\lambda t)^k}{k!} \cdot \exp(-\lambda t) \quad (\lambda, t \geq 0; k = 0, 1, \dots) \quad (9.30)$$

Equation (9.30) is a Poisson-distribution (cf. [31]) and the underlying process a Poisson process of intensity λ . In particular we have for the probability that no failure occurs up to t

$$P\{N(t) = 0\} = 1 - F(t) = \exp(-\lambda t) \quad (\lambda, t \geq 0) \quad (9.31)$$

the complementary exponential distribution of Eq. (9.24).

If several units, which can be considered as statistically identical, for example m similar valves under comparable working conditions, are observed, their failure behaviour is described by a Poisson distribution of intensity $m \cdot \lambda$. We then have

$$P\{N(t) = k\} = \frac{(m \cdot \lambda t)^k}{k!} \cdot \exp(-m\lambda t) \quad (\lambda, t \geq 0; k = 0, 1, \dots) \quad (9.32)$$

Using the number of observed failures and the corresponding period of observation the failure rate λ required for using Eq. (9.31) is obtained from Eq. (9.32). This is done by applying the maximum likelihood estimation (MLE) for λ (cf. [31]), which results from determining the maximum of Eq. (9.32). Thus we have

$$\frac{dP}{d\lambda} = \frac{k \cdot t \cdot m \cdot (m\lambda t)^{k-1}}{k!} \cdot \exp(-m\lambda t) - m t \cdot \frac{(m\lambda t)^k}{k!} \cdot \exp(-m\lambda t) = 0 \quad (9.33)$$

Isolating λ in Eq. (9.33) we obtain

$$\hat{\lambda} = \frac{k}{m \cdot t} \quad (9.34)$$

the maximum likelihood estimator for the failure rate λ . It is denoted by a hat over λ , as is usual for empirical statistical estimators (the empirical estimator replaces in practical applications the unknown true parameter, in the present case $\hat{\lambda}$ replaces λ). The failure rate is equal to the number of failures divided by the accumulated time of observation (number of components considered as statistically equivalent, m , each of them multiplied by its respective observation time; the number m is sometimes called “components at risk”).

The practical application of Eq. (9.34) requires engineering judgments which are briefly discussed below.

In order to carry out a good quality estimate a sufficient number of failures have to be observed. This is the reason why in general several components of the same type are grouped together. Yet, as a rule several components exposed to identical working and environmental conditions are not encountered in a plant. For this reason one must decide which components can be considered as statistically identical. This is done using criteria such as building type, diameter, working medium, operating pressure and temperature as well as location inside the plant. It must then be decided within which ranges similarity may be assumed. This is the

real world approximation to the statistician's requirement of identical components working under identical conditions.

Further judgments concern the time of observation. Possible choices are:

- calendar time: $t = T_K$, time during which the items were observed,
- plant operation time: $t = T_A$, time during which the plant was in operation,
- component operating time: $t = T_B$, time during which the item was in operation.

The relevant time of observation reflects the time during which the conditions determining the failure rate prevail. It should be noted that this does not imply that failures cease to be random. For example, a component exposed to a corrosive environment would be expected to exhibit a larger failure rate than an identical one working under non-corrosive conditions. Nevertheless, the moment of component failure cannot be predicted.

Calendar time [$t = T_K$ in Eq. (9.34)] is used if the exposure to the relevant loads is permanent, for example strong temperature variations for outdoor components.

Plant operating time [$t = T_A$ in Eq. (9.34)] should be used if the relevant loads for the component stem from plant operation. Examples are vibrations caused by the plant, which would impact a component even if it is not operating itself.

The choice of the component operating time [$t = T_B$ in Eq. (9.34)] is appropriate if the relevant loads are caused by the operation of the component itself or prevail while it is operating (e.g. processing of corrosive materials).

Finally engineering judgment has to be exercised for categorizing observed component damage, which has an influence on the value of k in Eq. (9.34). For example a failure shortly after a repair points to unprofessional maintenance rather than to renewed failure.

In summary it must be borne in mind that the necessary judgments introduce a subjective element into the determination of reliability data. However, this is unavoidable. Therefore, it is essential that the judgments are exercised with a background of profound knowledge of plants, processes and components.

Example 9.11 Failure rate of multiport valves

Lifetimes of components were observed in a process plant during a time period of two and a half years. Among the observed components there are $m = 35$ multiport valves, which were operating during 37.8 % of the time period; $k = 7$ failures were observed. What is the failure rate of this component type?

Solution

The basis for calculation is Eq. (9.34). The plant operating time to be used there is $t = 0.378 \times 2.5 \times 8,700 \text{ h} = 8278.2 \text{ h}$.

Hence we have a failure rate of

$$\hat{\lambda} = \frac{7}{37 \times 8,278.2 \text{ h}} = 22.9 \times 10^{-6} \text{ h}^{-1}$$

□

9.3.1.2 Determination of Unavailabilities

If loads on components primarily arise because of their demand as, for example, in case of electric power switches, the unavailability or probability of failure on demand proves apt for describing component behaviour. Observed failures are then evaluated using the binomial distribution (cf. [24]). Its use in the present context requires the following assumptions to be fulfilled:

- The component is repaired after failure before the next demand.
- After repair the component is “as good as new”. It is either replaced or repaired in such a way that its new state is restored. In mathematical terms this implies that after repair the same unavailability applies as before.
- The observed sample is homogeneous, i.e. all components lumped together in a group have the same unavailability.

The probability that x failures are observed during n demands (n is the total number of demands on a group of m components, which are considered as equivalent) is given by

$$w_n(x/u) = \binom{n}{x} \cdot u^x \cdot (1-u)^{n-x} \quad (9.35)$$

In Eq. (9.35) u is the unavailability of the component. It is derived from the number of observed demands and the number of failures which occurred following these demands. The maximum-likelihood estimator for u is derived from the requirement that

$$\frac{dw_n}{du} = \binom{n}{x} \cdot x \cdot u^{x-1} (1-u)^{n-x} - u^x \cdot (n-x) \cdot (1-u)^{n-x-1} = 0 \quad (9.36)$$

Isolating u in Eq. (9.36) we obtain

$$\hat{u} = \frac{x}{n} \quad (9.37)$$

Equation (9.37) shows that the estimator for the unavailability is the quotient of the number of failures divided by the number of demands on a group of components deemed to be equivalent.

The remarks in the previous section on the applicability of Eq. (9.34) apply *mutatis mutandis* to Eq. (9.37) as well.

Example 9.12 Failure probability on demand

8 centrifugal pumps for transporting cooling water were observed during nine and a half years. During this period of time every pump was started 200 times. A total of 10 starting failures were observed. What is their failure probability on demand?

Solution

Based on Eq. (9.37) we obtain with $n = 8 \times 200 = 1,600$ and $x = 10$

$$\hat{u} = \frac{10}{1,600} = 6.3 \times 10^{-3}$$

□

9.3.2 Confidence Intervals

The distribution parameters are estimated according to Eqs. (9.34) and (9.37) on the basis of samples. These are considered to be representative of the underlying population, for example all valves of a certain type which operate under certain well-defined conditions. If the entire population were known and the period of observation infinitely long, the exact values of the distribution parameters could be determined. However, this is not the case. This is why a so-called confidence interval is calculated based on the information from the sample. The exact value of the parameter lies within this interval with a predetermined level of confidence, γ . This confidence interval is all the smaller the larger the sample and thus the accumulated time of observation and the lower the required level of confidence. In an extreme case we might ask for an interval, in which the parameter would be encountered with a level of confidence of one. However, such an interval comprises the entire domain of values of the parameter in question ($[0, \infty]$ in case of λ and $[0, 1]$ for u); it is of no use. That is why normally confidence intervals for confidence levels of 90 or 95 % are calculated.

9.3.2.1 Failure Rates

In order to fix the endpoints of the confidence interval for a confidence level γ we search for the value of λ , for which fewer than the actually observed k failures would have occurred with a probability of $(1 - \gamma)/2$. This gives the lower endpoint, which is denoted here by $\underline{\lambda}$. Analogously, the upper endpoint is that value of λ for which more than the actually observed failures would have occurred with a probability of $(1 + \gamma)/2$. This value is denoted by $\bar{\lambda}$. The calculation of the endpoints leads to sums over the Poisson distribution of Eq. (9.30). These sums may be expressed in terms of the χ^2 distribution [24].

The lower endpoint is then given by

$$\underline{\lambda} = \frac{\chi_{2k; (1-\gamma)/2}^2}{2 \cdot m \cdot t} \quad (9.38)$$

and the upper endpoint by

$$\bar{\lambda} = \frac{\chi_{2(k+1); (1+\gamma)/2}^2}{2 \cdot m \cdot t} \quad (9.39)$$

so that with a confidence level of γ the true value of λ is encountered within the interval $[\underline{\lambda}, \bar{\lambda}]$.

Example 9.13 Determination of confidence interval endpoints for failure rates

The lower and the upper endpoints of the confidence interval for a confidence level of 90 % are to be determined for the multiport valves of Example 9.11. How would these endpoints change, if twice the number of failures were observed after doubling the period of observation with all other conditions remaining unchanged?

Solution

The calculations are based on Eqs. (9.38) and (9.39). We obtain for $\gamma = 0.9 \triangleq 90\%$

$$\underline{\lambda} = \frac{\chi_{14;0.05}^2}{2 \times 37 \times 8,278.2 \text{ h}} = \frac{6.571}{612,586.8 \text{ h}} = 10.7 \times 10^{-6} \text{ h}^{-1}$$

and

$$\bar{\lambda} = \frac{\chi_{16;0.95}^2}{2 \times 37 \times 8,278.2 \text{ h}} = \frac{26.296}{612,586.8 \text{ h}} = 42.9 \times 10^{-6} \text{ h}^{-1}$$

After doubling the time of observation the following result is obtained

$$\underline{\lambda} = 13.8 \times 10^{-6} \text{ h}^{-1} \quad \text{and} \quad \bar{\lambda} = 35.7 \times 10^{-6} \text{ h}^{-1}$$

The confidence interval becomes narrower with the expected value remaining unchanged. The reason is the more reliable sample size for the longer observation. $\square$

9.3.2.2 Unavailabilities

The arguments leading to the determination of the lower and upper endpoints of the confidence interval are analogous to those of the preceding section. Instead of summing over a Poisson distribution this has to be done over a binomial distribution according to Eq. (9.35) for a number failures which are smaller, respectively larger than the observed number x . If the relationship between sums over binomial distributions and Fisher's F-distribution is used [24], we obtain for the lower endpoint with a level of confidence of γ

$$\underline{u} = \frac{x}{x + (n - x + 1) \cdot F_{(1+\gamma)/2}[2(n - x + 1), 2x]} \quad (9.40)$$

and for the upper endpoint

$$\bar{u} = \frac{(x + 1) \cdot F_{(1+\gamma)/2}[2(x + 1), 2(n - x)]}{(n - x) + (x + 1) \cdot F_{(1+\gamma)/2}[2(x + 1), 2(n - x)]} \quad (9.41)$$

Hence, u is expected to lie within the interval $[\underline{u}, \bar{u}]$ with a confidence level of γ .

Example 9.14 Calculation of the confidence interval for probabilities of failure on demand

The confidence interval for the starting failures of pumps dealt with in Example 9.12 is to be calculated. How would the endpoints of the confidence interval change, if twice the number of failures were observed after doubling the period of observation with all other conditions remaining unchanged?

Solution

The calculation is based on Eqs. (9.40) and (9.41). These give

$$\underline{u} = 3.4 \times 10^{-3} \quad \text{and} \quad \bar{u} = 1.1 \times 10^{-2}$$

After doubling the period of observation the confidence interval narrows, i.e. the result becomes more precise. We then have

$$\underline{u} = 4.1 \times 10^{-3} \quad \text{and} \quad \bar{u} = 9.1 \times 10^{-3}$$

where

$$F_{0.95}[3182, 20] = 1.843 \quad \text{and} \quad F_{0.95}[22, 3180] = 1.544$$

□

9.3.3 Bayesian Evaluation of Reliability Data

In the preceding sections the so-called “classical” methods for estimating reliability data from observed lifetimes and failure frequencies were treated. It was shown as well how the corresponding confidence intervals are determined. All procedures were based on the frequentist concept of statistics. Its underlying idea is the probability expressed as the limit of a relative frequency, i.e.

$$u = \lim_{n \rightarrow \infty} \frac{n_E}{n} \quad (9.42)$$

Equation (9.42) has the following meaning:

If an experiment, in which the event denoted by E (e.g. the failure on demand of an electric shunt) can occur, is carried out n times with n tending towards infinity, the observed relative frequency for the occurrence of the event n_E/n tends towards the unknown constant value u . This value is called probability of E (cf. Appendix C).

The definition of probability as relative frequency implies that the event under investigation—here the failure of a component—must have occurred several times lest the confidence intervals be too large. If a component has rarely failed an evaluation using Bayes’ theorem is appropriate [25]. It is based on the so-called subjective notion of probability.

In evaluating reliability data, as treated in detail in [25], Bayes' theorem serves to combine lifetime observations for technical components coherently with the knowledge on the lifetime of this component type that existed prior to the lifetime observations. The formula is³

$$f(\lambda/E) = \frac{f(\lambda) \cdot L(E/\lambda)}{\int_0^{\infty} f(\lambda) \cdot L(E/\lambda) d\lambda} \quad (9.43)$$

In Eq. (9.43) $f(\lambda)$ is the prior probability density function. It reflects the—subjective—assessment of component behaviour which the analyst had before the lifetime observations were carried out. $L(E/\lambda)$ is the likelihood function. It is the conditional probability describing the observed failures under the condition that $f(\lambda)$ applies to the component under analysis. For failure rates $L(E/\lambda)$ is usually represented by a Poisson distribution of Eq. (9.30) and for unavailabilities by the binomial distribution of Eq. (9.35). The denominator in Eq. (9.43) serves for normalizing so that the result lies in the domain of probabilities [0, 1]; $f(\lambda/E)$ finally is the new probability density function, which is called posterior probability density function. It represents a synthesis of the notion of component failure behaviour before the observation and the observation itself. Thus it is the mathematical expression of a learning process.

It can be shown that the results of Eq. (9.43) approach those obtained with the maximum likelihood estimation in case of a large number of observed events. The latter is a procedure of classical statistics. It may be stated that the choice of the prior pdf influences the posterior pdf all the less the larger the number of observed failures.

The use of the methods of subjective statistics has often been regarded as opposed to the “objective” frequentist statistics. In reality there is not such a great difference. The extent, to which the evaluation with frequentist statistics requires engineering judgment, as explained above, must be borne in mind.

In evaluating reliability data the logarithmic normal (log-normal) distribution (vid. Sect. 9.3.4) is often used as prior pdf. It may, for example, be obtained by describing reliability data which were observed in other similar plants. If a log-normal pdf as prior pdf is combined with a Poisson likelihood, the denominator of Eq. (9.43) must be evaluated numerically. Several combinations of other distributions lead to denominators which are amenable to analytical evaluation. Details are found in [25].

A further important difference between the two notions of statistics must be mentioned. In frequentist statistics a fixed but unknown parameter, for example the failure rate λ , is estimated from component lifetime observations. The result is not exact but only obtained with a certain level of confidence. This level indicates how often the result would lie within the confidence interval, if the measurement were repeated many times. For example, if the measurement is repeated 100 times it

³ The following derivations are carried out for failure rates and apply analogously to unavailabilities as well.

would lie 90 times between the 5 and 95 % endpoints of the confidence interval (cf. Sect. 9.3.2). For the operations like addition and multiplication, which are required for evaluating fault trees, there are no mathematical rules. On the other hand such rules are needed in order to determine the influence of data uncertainties on the final result of a fault tree analysis.

In the Bayesian procedure the failure rate λ is considered as a random variable, which is described by a probability distribution. The calculation of sums and products of random variables are well-defined operations. Thus the propagation of uncertainties through the fault tree represents no difficulty. For this reason the formula of Bayes is applied as well to cases where no appropriate prior information is available, no matter how many failures were observed. In such a case the non-informative pdf is used in order to arrive at a probability distribution for the result.

In what follows the procedure is shown only for the use of a non-informative prior pdf. Details on the use of other prior pdfs are found in [25, 33].

In case of a Poisson likelihood function the non-informative prior pdf is proportional to $\lambda^{-1/2}$ [25], i.e.

$$f(\lambda) \propto \lambda^{-\frac{1}{2}} \quad (9.44)$$

Inserting Eq. (9.44) in Eq. (9.43) gives

$$f(\lambda/E) = \frac{\lambda^{k-1/2} \cdot \exp(-\lambda t)}{\int_0^\infty \lambda^{k-1/2} \cdot \exp(-\lambda t) \cdot d\lambda} \quad (9.45)$$

After integrating Eq. (9.45) we obtain

$$F(\lambda/E) = \frac{\Gamma(k + \frac{1}{2}, \lambda t)}{\Gamma(k + \frac{1}{2})} \quad (9.46)$$

In Eq. (9.46) $\Gamma(k + 1/2, \lambda t)$ is the incomplete gamma function [42]. The expected value of the posterior distribution is

$$E = \frac{2 \cdot k + 1}{2 \cdot t} \quad (9.47)$$

The percentiles of the posterior distribution are determined using the relationship between the incomplete gamma function and the χ^2 -distribution [42]. We then obtain

$$\bar{\lambda} = \frac{\chi_{2k+1; (1+\gamma)/2}^2}{2 \cdot t} \quad (9.48)$$

and

$$\underline{\lambda} = \frac{\chi_{2k+1; (1-\gamma)/2}^2}{2 \cdot t} \quad (9.49)$$

The results for the posterior distribution are often approximated by a log-normal distribution (vid. Sect. 9.3.4).

Example 9.15 Failure rate for a rotary kiln using Bayes' rule with a non-informative prior pdf

In a lifetime observation of a rotary kiln 4 failures are observed during a component operating time of $t = T_B = 9399$ h. Calculate the 5th, 50th, and 95th percentiles of the resulting distribution as well as its expected value.

Note: For calculating the median (50th percentile) γ must be set equal to 0 in Eq. (9.48) or in Eq. (9.49).

Solution

The solution is based on Eqs. (9.47) to (9.49)

The expected value results from Eq. (9.47)

$$E = 478.8 \times 10^{-6} \text{ h}^{-1}$$

The corresponding percentiles are

$$\lambda_{95} = \frac{\chi_{2k+1;0.95}^2}{2 \cdot t} = \frac{16.92}{2 \times 9,399 \text{ h}} = 900.0 \times 10^{-6} \text{ h}^{-1}$$

$$\lambda_{50} = \frac{\chi_{2k+1;0.5}^2}{2 \cdot t} = \frac{8.343}{2 \times 9,399 \text{ h}} = 443.8 \times 10^{-6} \text{ h}^{-1}$$

$$\lambda_{05} = \frac{\chi_{2k+1;0.05}^2}{2 \cdot t} = \frac{3.325}{2 \times 9,399 \text{ h}} = 176.9 \times 10^{-6} \text{ h}^{-1}$$

□

Example 9.16 Calculation of the failure for refrigerating units using Bayes' rule with a non-informative prior pdf

The observation of the lifetimes of refrigerating units resulted in 2 failures during an accumulated time of observation of 50,843 h. Calculate the 5th, 50th, and 95th percentiles of the resulting distribution as well as its expected value.

Solution

Equation (9.47) gives for the expected value

$$E = \frac{2 \times 2 + 1}{2 \times 50843} = 49.2 \times 10^{-6} \text{ h}^{-1}$$

The percentiles are obtained from Eqs. (9.48) and (9.49); the median is calculated as in Example 9.15. We obtain

$$\lambda_{95} = \frac{\chi_{5;0.95}^2}{2 \times 50,843 \text{ h}} = \frac{11.07}{100,966 \text{ h}} = 109.6 \times 10^{-6} \text{ h}^{-1}$$

$$\lambda_{50} = \frac{\chi_{5;0.5}^2}{2 \times 50,843 \text{ h}} = \frac{4.351}{100,966 \text{ h}} = 43.1 \times 10^{-6} \text{ h}^{-1}$$

$$\lambda_{05} = \frac{\chi_{5;0.05}^2}{2 \times 50,843 \text{ h}} = \frac{1.145}{100,966 \text{ h}} = 11.34 \times 10^{-6} \text{ h}^{-1}$$

□

9.3.4 Treatment of Uncertainties

Uncertainties of reliability data are often represented by means of the log-normal distribution (vid. Eq. (C.27) in Appendix C and [24]). This distribution is generated by applying a normal distribution to the logarithms of the original values. Thereby a distribution results which is skewed to the right and defined on the positive half axis. Its pdf is

$$f(\lambda) = \frac{1}{\sqrt{2\pi} \cdot s \cdot \lambda} \cdot e^{-\frac{(\ln \lambda - \mu)^2}{2s^2}} \quad \lambda, s > 0 \quad (9.50)$$

In Eq. (9.50) μ is the mean value of the failure rates from the literature or other sources and s^2 the corresponding variance. They are obtained as follows:

$$\mu = \sum_{n=1}^N \ln \lambda_n \quad (9.51)$$

$$s^2 = \frac{1}{N-1} \cdot \sum_{n=1}^N (\ln \lambda_n - \mu)^2$$

The following relation exists between μ and the median of the distribution, λ_{50} ,

$$\lambda_{50} = e^{\mu} \quad (9.52)$$

The expected value is given by

$$\lambda = \exp\left(\mu + \frac{s^2}{2}\right) \quad (9.53)$$

The log-normal distribution is usually characterized by indicating the factor of dispersion, also called uncertainty or error factor (EF). It has the following relationship with the standard deviation of the logarithms

$$K_{95} = \exp(1.6449 \times s) \quad (9.54)$$

The factor 1.6449 represents the 95th percentile of the standard normal distribution. The 5th and 95th percentiles, i.e. the values below which 5 % respectively 95 % of the failure rates lie, are obtained by using the factor K_{95}

$$\begin{aligned} \lambda_{05} &= \frac{\lambda_{50}}{K_{95}} \\ \lambda_{95} &= \lambda_{50} \cdot K_{95} \end{aligned} \quad (9.55)$$

Frequently other distribution types are represented by log-normal distributions. This is done, for example, by requiring that the median and the 5th percentile of the original distribution correspond to those of the log-normal distribution. The two resulting equations enable one to determine the parameters μ and s of the log-normal distribution (vid. Example 10.1).

9.3.5 Transferability of Reliability Data

In the strict statistical sense reliability data may only be used if the component to be assessed belongs to the population, whose observation served to determine the data. This is only true if plant-specific reliability data is used. Yet, this requirement is, as a rule, sufficiently satisfied if the reliability data does not stem from the plant under investigation, but

- all the features recorded to characterize the population apply to the component at hand or
- the analysis of possible dependencies has shown that variations of one or several of the recorded features do not affect the reliability datum and the remaining features apply.

In deciding on this matter it has to be borne in mind that it cannot be demonstrated that all features required to characterize the population have been recorded.

If the above situations do not apply case-by-case decisions have to be taken. For example, if there are differences in the structure between the component to be assessed and the observed one often recourse can be had to the individual sub-components (piece parts of components, e.g. the component “pump” consists of motor, power transmission, the pump itself, local controls and connected wiring). They enable one to compose reliability data for components made up of different numbers of sub-components or of sub-components with a different design and

different working conditions. This implies, of course, that all sub-components required for the composition have been observed.

If there are differences in the working conditions between the component to be assessed and the one which has been observed it has to be examined to what extent these working conditions are encountered in any of the observed plants. An analysis of dependencies is helpful in this context. For example, generally reliability data of components exposed to aggressive media are worse than those to be expected in case of exposure to water. They then may serve as conservative estimates. The same is true for cases of strong mechanical loads like, for instance, strong vibrations. Values obtained for such cases may also serve as conservative assessments for components under normal loads.

In probabilistic analyses the influence of uncertainties of input data on the result is usually accounted for. In order to do this the reliability of components is represented by probability distributions instead of point values (usually expected values). Often log-normal distributions, which were presented in the previous Section, are used. The factor K_{95} then is a measure for the uncertainty. In general K_{95} lies between 2 and 10.

If only a point value (e.g. the mean value) is available and the validity of transfer cannot be totally clarified this can be accounted for by a choice of $3 \leq K_{95} \leq 10$.

If operating experience is available for the component to be assessed the Bayesian approach described in Sect. 9.3.3 should be used for evaluating reliability data.

9.4 Boolean Variables and Their Application in Fault Tree Analysis

As already mentioned the fault tree represents the logical relations between the primary events (in what follows often denoted by ‘component failures’ for the sake of simplicity) and the undesired (unwanted or top) event (in what follows often denoted by ‘system failure’ for the sake of simplicity). The relations represented by the fault tree are deterministic. We arrive at probabilistic statements only if probabilities are assigned to the component failures.

The logical relations can advantageously be represented if Boolean or binary variables⁴ are used for describing component and system states [30], i.e.

$$a_n = \begin{cases} 1, & \text{if component } n \text{ functions} \\ 0, & \text{if component } n \text{ does not function} \end{cases} \quad (9.56)$$

In Eq. (9.56) N is the total number of components of the system. The system state is described analogously, i.e.

⁴ Boolean or binary variables and the corresponding functions only adopt two values: 0 or 1.

$$\Phi(a_1, \dots, a_N) = \begin{cases} 1, & \text{if the system functions} \\ 0, & \text{if the system does not function} \end{cases} \quad (9.57)$$

Since the a_n are Boolean variables, Φ is a Boolean function called structure or system function.⁵

In Eqs. (9.56) and (9.57) the so-called positive logic is used. In the present context it is more appropriate to apply the negative logic with the following definitions:

$$x_n = 1 - a_n = \begin{cases} 1, & \text{if the component } n \text{ does not function} \\ 0, & \text{if the component } n \text{ functions} \end{cases} \quad (9.58)$$

for components and

$$\Psi(x_1, \dots, x_N) = 1 - \Phi(a_1, \dots, a_N) = \begin{cases} 1, & \text{if the system does not function} \\ 0, & \text{if the system functions} \end{cases} \quad (9.59)$$

for the structure function.

In what follows only the definitions of Eqs. (9.58) and (9.59) are used. The results thus obtained can easily be converted into the corresponding expressions for the positive logic of Eqs. (9.56) and (9.57).

In general the structure function is monotonously non-decreasing (isotonous). This follows from the fact that a system which is in failed state does not normally begin to function again if a further component fails. Expressed in different terms: a system which functions does not fail because a failed component begins to function again.

Non-isotonous structure functions occur if negations of primary events figure in a fault tree so that it contains the event and its negation (cf. [43]). The negation requires the complementary event to be formed, i.e. x_n has the complement $\bar{x}_n = 1 - x_n$. The procedures explained in what follows apply to isotonous structure functions and to non-isotonous structure functions unless stated otherwise. Yet, approximations made are usually worse for non-isotonous structure functions than for isotonous ones. This problem can be overcome if one decomposes a non-isotonous structure function into independent isotonous ones, as shown for example in [43].

Before explaining the representation of systems by means of Boolean functions an important property of Boolean variables must be presented, that of idempotence or the idempotent operation

⁵ Only the most widely used procedure is presented here. It is restricted to two component states and two system states. In [44] an extension of the Boolean algebra is proposed which enables one to treat components and systems with more than two states (e.g. for valves: open, closed, half closed). However, there is the difficulty of determining probabilities for intermediate states of components and their impacts on the dynamic behaviour of the systems.

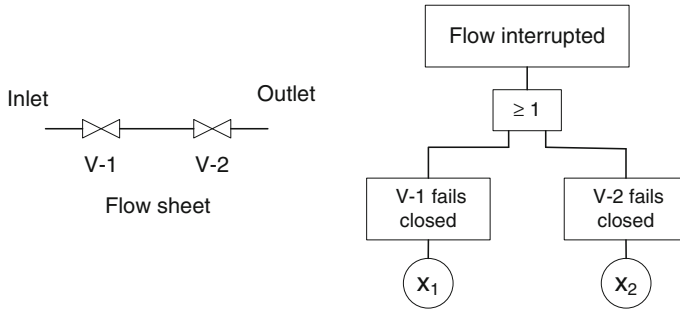


Fig. 9.14 Flow sheet and fault tree for a series configuration in the sense of reliability

$$x_n^m = x_n \quad (m \neq 0) \quad (9.60)$$

This property follows directly from the fact that Boolean variables may only adopt the two values 0 and 1.

9.4.1 Series Configuration in the Sense of Reliability

Figure 9.14 shows two valves⁶ which are arranged in series in the sense of reliability ('OR' gate; logical union). The valves are normally open. The undesired event in this case is the interruption of flow. This can occur if any one of the valves, V-1 or V-2, or both fail adopting the closed position ("fail closed").

In this case we have the following structure function [30]

$$\Psi(x_1, x_2) = \max\{x_1, x_2\} = x_1 + x_2 - x_1 \cdot x_2 = \begin{cases} 1, & \text{if } x_1 \text{ or } x_2 \text{ or both} = 1 \\ 0, & \text{if } x_1 \text{ and } x_2 = 0 \end{cases} \quad (9.61)$$

The extension of Eq. (9.61) to N components gives

$$\begin{aligned} \Psi(x_1, \dots, x_N) &= \max\{x_1, \dots, x_N\} = 1 - \prod_{n=1}^N (1 - x_n) \\ &= \sum_{n=1}^N x_n - \sum_{n=1}^{N-1} \sum_{m=n+1}^N x_n \cdot x_m + \sum_{n=1}^{N-2} \sum_{m=n+1}^{N-1} \sum_{j=m+1}^N x_n \cdot x_m \cdot x_j + \dots + (-1)^{N-1} x_1 \dots x_N \end{aligned} \quad (9.62)$$

Equation (9.62) can easily be proved by complete induction.

⁶ In what follows system structures are illustrated by means of flowing fluids and valves; it goes without saying that the statements made apply quite generally for any type of component.

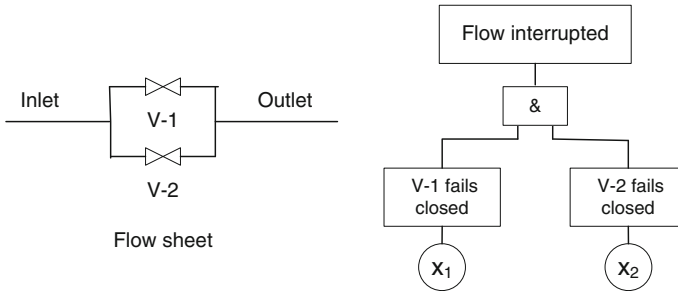


Fig. 9.15 Flow sheet and fault tree for a parallel configuration in the sense of reliability

9.4.2 Parallel Configuration in the Sense of Reliability

We consider the system of Fig. 9.15. The fluid can reach the outlet in sufficient quantity through any one of the two valves. Hence, the undesired event ‘interruption of flow’ can only occur if both valves fail adopting their closed position (‘AND’ gate, logical intersection).

For this case we have the following structure function [30]

$$\Psi(x_1, x_2) = \min\{x_1, x_2\} = x_1 \cdot x_2 = \begin{cases} 1, & \text{if } x_1 \text{ and } x_2 = 1 \\ 0, & \text{if } x_1 \text{ or } x_2 \text{ or both} = 0 \end{cases} \quad (9.63)$$

If the system consists of N components we obtain

$$\Psi(x_1, \dots, x_N) = \min\{x_1, \dots, x_N\} = 1 - \prod_{n=1}^N x_n \quad (9.64)$$

9.4.3 System with Negation

The system shown in Fig. 9.16 is designed in such a way that it functions only if one of the two valves, V-1 or V-2, is open but not both. Hence, the system neither fulfils its mission if both valves are open nor if both are closed. This success criterion leads to an exclusive ‘OR’ gate instead of the inclusive ‘OR’ gate used so far. The fault tree model is obtained by using additionally ‘NOT’ gates.

The function representing the fault tree of Fig. 9.16 is not isotonic. We have

$$\begin{aligned} \Gamma(x_1, x_2) &= x_1 \cdot x_2 + \bar{x}_1 \cdot \bar{x}_2 - x_1 \cdot x_2 \cdot \bar{x}_1 \cdot \bar{x}_2 = x_1 \cdot x_2 + \bar{x}_1 \cdot \bar{x}_2 \\ &= x_1 \cdot x_2 + (1 - x_1) \cdot (1 - x_2) = 1 - x_1 - x_2 + 2 \cdot x_1 \cdot x_2 \end{aligned} \quad (9.65)$$

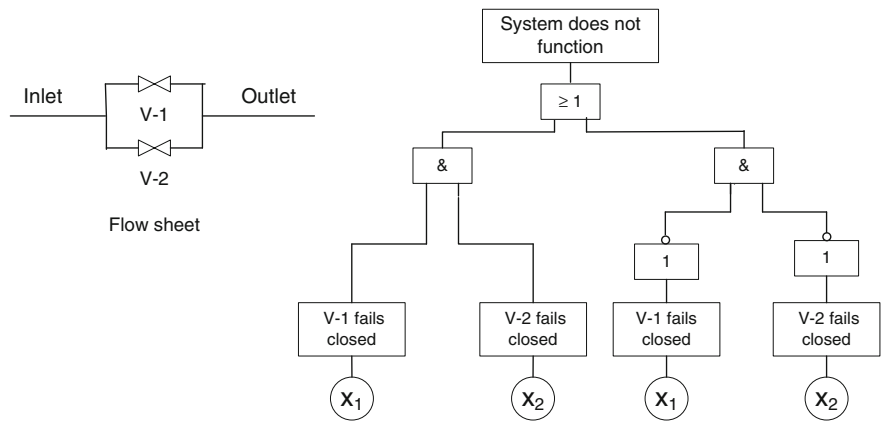


Fig. 9.16 Flow sheet and fault tree for a system with negation

Table 9.16 Possible component and system states for the fault tree of Fig. 9.16

x_1	x_2	$\Gamma(x_1, x_2)$	System state
0	0	1	Does not function
1	0	0	Functions
0	1	0	Functions
1	1	1	Does not function

The term $x_1 \cdot x_2 \cdot \bar{x}_1 \cdot \bar{x}_2$ is equal to 0 since it is logically impossible that an event and its complementary event (negation) coexist (for example, a valve cannot fail simultaneously in its open and its closed position). The possible states of the components and the system are shown in Table 9.16.

9.4.4 Voting System of the Type 2-out-of-3

Figure 9.17 shows the fault tree for a so-called 2-out-of-3 voting system, also denoted by 2oo3-voting system.

As can easily be read from Fig. 9.17 system failure occurs due the simultaneous failure of any one of several groups of components, namely $K_1 = \{1, 2\}$, $K_2 = \{1, 3\}$, $K_3 = \{2, 3\}$ and $K_4 = \{1, 2, 3\}$, with which the following binary functions are associated

$$K_1 = x_1 \cdot x_2; \quad K_2 = x_1 \cdot x_3; \quad K_3 = x_2 \cdot x_3; \quad K_4 = x_1 \cdot x_2 \cdot x_3 \tag{9.66}$$

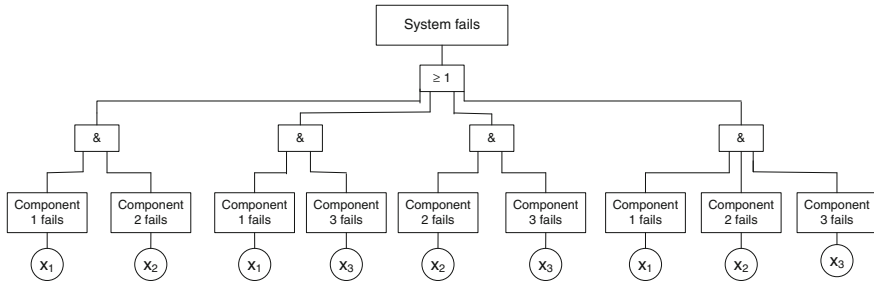


Fig. 9.17 Fault tree for a 2-out-of-3 voting system (2oo3)

In Eq. (9.66) there figure products of binary variables, since we are dealing with components arranged in parallel in the sense of reliability [cf. Eq. (9.63)]. Each of the sets K_1 to K_4 is called cut set.⁷

It is obvious that the set K_4 contains all the other sets. Since a system with an isotonus structure function, which has failed, preserves this state even if further components fail, K_4 contains no additional information. It is superfluous and hence eliminated. The remaining sets are called minimal cut sets. They contain components whose simultaneous failure is necessary and sufficient to cause system failure. Each minimal cut set represents a different mode of failure of the system. Since the minimal cut sets are compatible with one another, the structure function of the system is obtained using the relations for a series configuration [cf. Eq. (9.62)], which gives

$$\Psi = 1 - \prod_{i=1}^3 (1 - \kappa_i) \quad (9.67)$$

9.4.5 The Multilinear Form of the Structure Function and Determination of Reliability Parameters for Systems

If Eq. (9.67) is expanded we obtain

$$\begin{aligned} \Psi(x_1, x_2, x_3) &= 1 - (1 - x_1 \cdot x_2) \cdot (1 - x_1 \cdot x_3) \cdot (1 - x_2 \cdot x_3) \\ &= x_1 \cdot x_2 + x_2 \cdot x_3 + x_1 \cdot x_3 - x_1^2 \cdot x_2 \cdot x_3 \\ &\quad - x_1 \cdot x_2^2 \cdot x_3 - x_1 \cdot x_2 \cdot x_3^2 + x_1^2 \cdot x_2^2 \cdot x_3^2 \end{aligned} \quad (9.68)$$

Exploiting the idempotent property of the Boolean variables according to Eq. (9.60), Eq. (9.68) is simplified as follows:

⁷ If the analysis pursues the objective of establishing the functioning of the system the analogous sets are called path sets. The set notation is only occasionally applied; use of the associated binary functions is more common.

$$\Psi(x_1, x_2, x_3) = x_1 \cdot x_2 + x_2 \cdot x_3 + x_1 \cdot x_3 - 2 \cdot x_1 \cdot x_2 \cdot x_3 \quad (9.69)$$

Equation (9.69) is the structure function after the idempotences have been eliminated. It is called the multilinear form of the structure function and is a polynomial in which any independent variable figures to the power of 1 only.

If the primary events, which are represented by the Boolean variables, are independent from one another, they can be “replaced” by their corresponding probabilities provided the structure function is in its multilinear form (cf. [30]). Thus, the probability of failure or the unavailability of the system is obtained in accordance with the meaning of the probabilities involved.

The procedure just presented in form of a recipe is now justified. The expected value of a binary variable as defined in Eq. (9.58) is

$$E(x_n) = q_n \cdot 1 + p_n \cdot 0 = q_n \quad (9.70)$$

The properties of the expected values of random variables concerning summation and multiplication are the following [24]

$$E(x_1 + x_2 + \cdots + x_N) = E(x_1) + E(x_2) + \cdots + E(x_N) \quad (9.71)$$

If the random variables are independent from one another, their multiplication gives

$$E(x_1 \cdot x_2 \cdots x_N) = E(x_1) \cdot E(x_2) \cdots E(x_N) \quad (9.72)$$

If the properties from Eqs. (9.70) to (9.72) are applied to Eq. (9.69) we obtain the probability of failure of the 2-out-of-3 voting system. If the q_n denote the component failure probabilities the expected value of the system failure probability is

$$E[\Psi(x_1, x_2, x_3)] = q_1 \cdot q_2 + q_2 \cdot q_3 + q_1 \cdot q_3 - 2 \cdot q_1 \cdot q_2 \cdot q_3 \quad (9.73)$$

In the special case that $q = q_1 = q_2 = q_3$, Eq. (9.73) becomes

$$q_S = 3 \cdot q^2 - 2 \cdot q^3 \quad (9.74)$$

The procedure shown by means of the foregoing example holds universally. Any structure function may be brought into its multilinear form. The binary variables it contains can then be “replaced” by the pertinent probabilities. In this way the corresponding reliability parameter of the system described by the structure function is obtained. It was already pointed out that this procedure requires the primary events to be independent from one another. The treatment of dependencies is explained in Sect. 9.6.

It is evident that the fault tree is represented by ‘OR’ connections of ‘AND’ connected (and hence redundant) failure events (minimal cut sets). If the number of minimal cut sets is large the formation of the structure function leads to so large

a number of terms that they cannot be handled, as an inspection of Eq. (9.62) shows.

This problem is usually solved by neglecting small quantities of higher order which result from products of minimal cut sets. This is known as the rare event approximation, which is often applicable because failure probabilities tend to be small. The expected value of the structure function is then approximated by

$$E[\Psi(x_1, \dots, x_N)] \approx \sum_{n=1}^N E(\kappa_n) \quad (9.75)$$

In Eq. (9.75) N is the total number of minimal cut sets. The result is an upper bound of the exact result [30]. Should the assumption of small quantities not be true and therefore their products not be small either, the following recursive procedure is in place [45]

$$\begin{aligned} c_n &= E(\kappa_n) + c_{n-1} \cdot [1 - E(\kappa_n)] \quad (n = 1, \dots, N; c_0(t) = 0) \\ E[\Psi(x_1, \dots, x_N)] &\leq c_N \end{aligned} \quad (9.76)$$

Equation (9.76) gives the exact result in case of disjunct minimal cut sets and, should this not be the case, it provides an upper bound which is closer to the exact result than that of Eq. (9.75).

The determination of the structure function and the corresponding probability calculation, which can be done here by hand calculations, require the use of computer programs in case of systems with higher numbers of minimal cut sets. Such programs are not treated here. The reader is referred to Refs. [45, 46].

Example 9.17 Application of the fault tree method to a pressure relief system

A vessel is equipped with four valves, which are arranged in two trains with two valves each, as shown in Fig. 9.18. The trains serve to relieve the tank in case of overpressure.

Develop the fault tree for the undesired event “pressure relief fails” and calculate the expected frequency of vessel burst if pressure relief is required $f = 5$ times per year. Additionally, the probability of unwarranted opening is to be calculated. The vessel bursts only if both trains do not open. The failure of pressure relief entails vessel burst.

Data: $q = 8.5 \times 10^{-3}$ per demand for the failure of a valve in closed position; $p_f = 8.5 \times 10^{-3}$ for its unwanted opening (since we are dealing with different failure modes, the probabilities do not have to sum to 1, the events are not complementary).

Solution

The fault tree of Fig. 9.18 has the following minimal cut sets:

$$\kappa_1 = x_1 x_3; \quad \kappa_2 = x_1 x_4; \quad \kappa_3 = x_2 x_3; \quad \kappa_4 = x_2 x_4$$

and the corresponding structure function

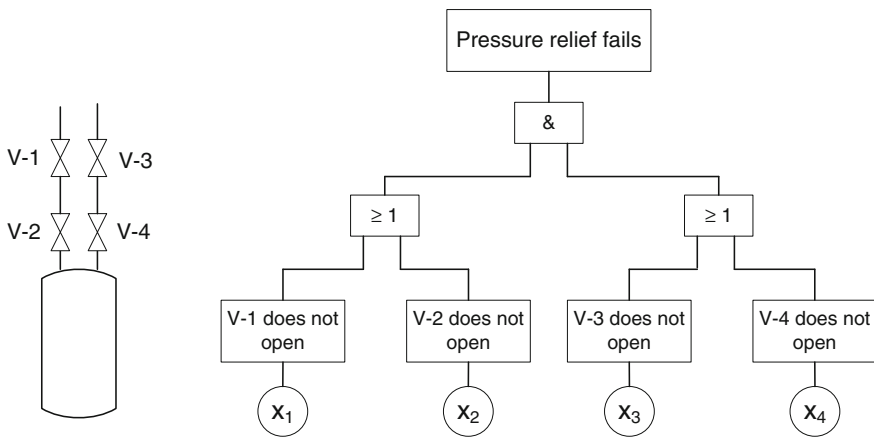


Fig. 9.18 Flow sheet and fault tree for the undesired event “pressure relief fails”

$$\begin{aligned}
 \Psi(x_1, x_2, x_3, x_4) &= x_1 \cdot x_3 + x_1 \cdot x_4 + x_2 \cdot x_3 + x_2 \cdot x_4 \\
 &\quad - x_1 \cdot x_3 \cdot x_4 - x_1 \cdot x_2 \cdot x_3 - x_1 \cdot x_2 \cdot x_3 \cdot x_4 \\
 &\quad - x_1 \cdot x_2 \cdot x_3 \cdot x_4 - x_1 \cdot x_2 \cdot x_4 - x_2 \cdot x_3 \cdot x_4 \\
 &\quad + x_1 \cdot x_2 \cdot x_3 \cdot x_4 + x_1 \cdot x_2 \cdot x_3 \cdot x_4 \\
 &\quad + x_1 \cdot x_2 \cdot x_3 \cdot x_4 + x_1 \cdot x_2 \cdot x_3 \cdot x_4 - x_1 \cdot x_2 \cdot x_3 \cdot x_4 \\
 &= x_1 \cdot x_3 + x_1 \cdot x_4 + x_2 \cdot x_3 + x_2 \cdot x_4 \\
 &\quad - x_1 \cdot x_3 \cdot x_4 - x_1 \cdot x_2 \cdot x_3 - x_1 \cdot x_2 \cdot x_4 \\
 &\quad - x_2 \cdot x_3 \cdot x_4 + x_1 \cdot x_2 \cdot x_3 \cdot x_4
 \end{aligned}$$

Hence, we obtain from Eqs. (9.70)–(9.72)

$$q_s = 4 \cdot q^2 - 4 \cdot q^3 + q^4 = 2.9 \times 10^{-4} \text{ (per demand)}$$

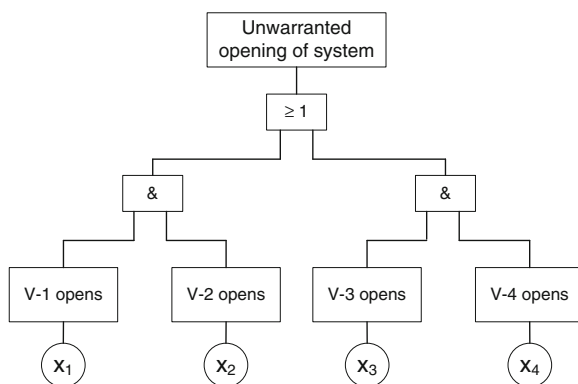
This result means that on the average the relief system is not available once in 3,448 demands. Hence, the expected frequency for vessel burst is

$$H = f \cdot q_s = 1.45 \times 10^{-3} \text{ a}^{-1}$$

Unwarranted opening

The fault tree for unwarranted opening is shown in Fig. 9.19. It results from the fault tree of Fig. 9.18 if the ‘AND’ gates there are replaced by ‘OR’ gates and the ‘OR’ gates by ‘AND’ gates. Additionally, the primary events have a different meaning here than in the fault tree of Fig. 9.18.

Fig. 9.19 Fault tree for the undesired event “unwarranted opening”



The fault tree of Fig. 9.19 has the following minimal cut sets:

$$K_1 = X_1 X_2; \quad K_2 = X_3 X_4$$

and hence the structure function

$$\Psi(X_1, X_2, X_3, X_4) = X_1 \cdot X_2 + X_3 \cdot X_4 - X_1 \cdot X_2 \cdot X_3 \cdot X_4$$

Thus one obtains

$$p_s = 2 \cdot p_f^2 - p_f^4 = 1.4 \times 10^{-4}$$

q_s and p_s are of the same order of magnitude. Therefore the system is considered as balanced safety-wise. It offers approximately the same degree of protection against the failure of pressure relief and against unwarranted opening. For unwarranted opening no expected frequency can be calculated because the demand of an ‘unwarranted opening’ is a contradiction in itself.

Example 9.18 Development of a fault tree and the corresponding structure function

A fault tree is to be developed for the flow sheet of Fig. 9.20. The undesired event is “no flow”. The corresponding structure function as well as the dual structure function is to be calculated.

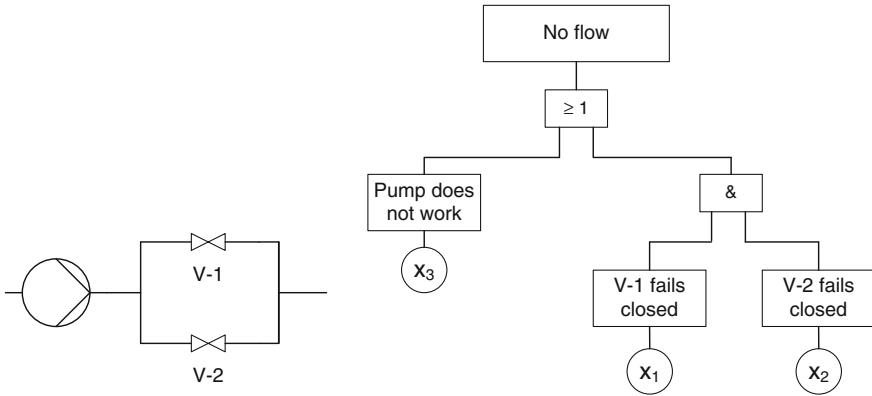


Fig. 9.20 Flow sheet and fault tree for the undesired event “no flow”

In order not to have flow either the pump has to fail or both valves, V-1 and V-2, have to be closed simultaneously. The events “pump does not work” and “closed valves” may, of course, occur simultaneously as well.

The fault tree of Fig. 9.20 has the minimal cut sets $\kappa_1 = x_3$; $\kappa_1 = x_1 x_2$ and thus the structure function

$$\Psi(x_1, x_2, x_3) = x_3 + x_1 \cdot x_2 - x_1 \cdot x_2 \cdot x_3$$

The dual structure function is as follows:

$$\begin{aligned} \Psi^d &= 1 - \Psi(1 - x_1, 1 - x_2, 1 - x_3) \\ &= 1 - (1 - x_3) - (1 - x_1) \cdot (1 - x_2) + (1 - x_1) \cdot (1 - x_2) \cdot (1 - x_3) \\ &= x_1 \cdot x_3 + x_2 \cdot x_3 - x_1 \cdot x_2 \cdot x_3 \end{aligned}$$

The fault tree of Fig. 9.21 corresponds to the dual structure function.

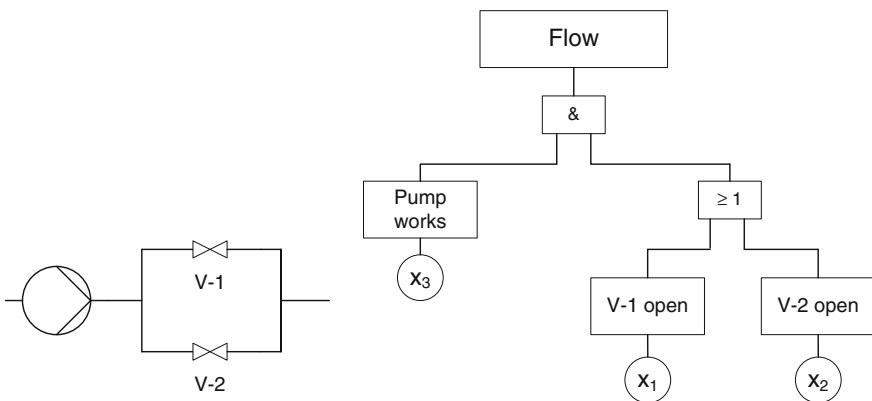


Fig. 9.21 Flow sheet and fault tree for the undesired event “flow”

If in this fault tree the x_n are replaced by the probabilities of functioning of the components, the dual structure function Ψ^d gives the probability of functioning of the system, i.e. the probability of having flow.

Since the visible configuration does not necessarily correspond to the logical one, which depends on the criterion for system failure, the addition “in the sense of reliability” made previously is always required for unambiguity. $\square$

9.5 Methods for Increasing the Survival Probability and Availability

An important objective of probabilistic safety analyses is to point out the way towards increasing the survival probability of technical systems. In what follows several possibilities for doing this are described.

The principle of redundancy was already presented. Redundancy implies that more components than strictly required for a task are available. Redundancies enable one to design a technical system in such a way that it is more reliable than the components of which it is made up.

A further measure which is frequently encountered in the process industry is the installation of reserve components. These are in stand-by and take over the function of the main component in case that should fail. They often allow plant operation to continue virtually without interruption.

Functional tests are of great importance. For example, in German nuclear power plants one of the four emergency power Diesel generators is tested every week, so that the test interval for each of them is 4 weeks. The objective of functional tests is to detect possible faults in stand-by systems and to correct them. Repairs carried out because of component failure are called corrective maintenance, inspections taking place in regular time intervals are called preventive maintenance. They are to maintain the plant in a good state over long periods of time and are especially important for redundant systems. For part of the redundant equipment may fail without impairing the function of the system in question and may therefore go unnoticed.

Finally, safety systems like the trip system or the emergency power supply have to be mentioned. These are essential for avoiding the destruction of a plant and the consequential major accident. It goes without saying that they must be highly available. If the components of these systems must function for a certain period of time in order to fulfil their mission, they must additionally have a high probability of survival.

In what follows mathematical models for failure probabilities and unavailabilities of components and sub-systems, which are equipped with reserve components or subject to functional tests and repair, are presented. The expressions derived are then used to calculate the expected value of the structure function in order to determine reliability parameters for the system under investigation, as shown in the preceding section.

9.5.1 Systems with Reserve Elements

Basically two types of reserve are in use. The so-called ‘hot reserve’ is characterized by the fact that several components are working at the same time, although fewer or even one of them would suffice to realize the corresponding task. In such a case we are dealing with a parallel configuration in the sense of reliability, i.e. a redundant system. The ‘cold reserve’ consists of a main component and a reserve component which takes over the function of the main component in case that should fail. Several reserve components are possible as well which enter into operation one after the other following the failure of the preceding component. Additionally, intermediate situations are possible. For example reserve components running idly during the operation of the main component so that they would be able to take over the function of the main component immediately when demanded without a prior warming-up time. Such a reserve is called ‘warm reserve’.

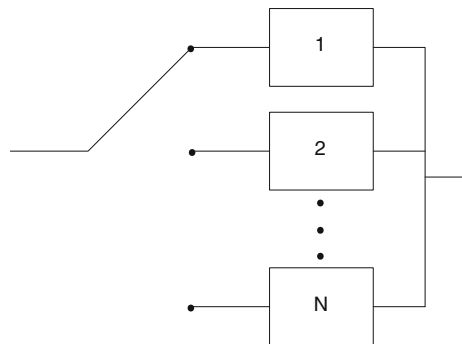
In what follows only the ‘cold reserve’ is treated since redundant systems were already discussed. For building the model it is assumed that the reserve components enter into operation quickly enough for avoiding an interruption of system functioning. Additionally, the switching process from one component to another is assumed to be perfect (probability of success equal to 1). The more realistic case of this not being true is treated in Example 9.30. The reserve components are regarded as being intact when they enter into operation. Figure 9.22 shows schematically a system of N components, $N - 1$ of which are reserve components.

In the case $N = 2$ the following expression is obtained for the failure probability if both components are independent from each other

$$q_S(t) = \int_0^t F_1(t') \cdot f_2(t - t') \cdot dt' \quad (9.77)$$

Equation (9.77) describes the probability of the first component failing in point of time t' and the second component, which then starts its operation, during the remaining time period $t - t'$. The integration accounts for the fact that t' may be

Fig. 9.22 Schematic of a system of N components, $N - 1$ of which are reserve components



any arbitrary point in time from the interval $[0, t]$. If component lifetimes are described by exponential distributions [vid. Eqs. (9.25) and (9.26)], Eq. (9.77) becomes

$$\begin{aligned} q_S(t) &= \int_0^t [1 - \exp(-\lambda_1 t')] \cdot \lambda_2 \cdot \exp[-\lambda_2 \cdot (t - t')] \cdot dt' \\ &= 1 - \exp(-\lambda_1 \cdot t) - \frac{\lambda_2}{\lambda_2 - \lambda_1} \cdot [\exp(-\lambda_1 \cdot t) - \exp(-\lambda_2 \cdot t)] \end{aligned} \quad (9.78)$$

In particular, if $\lambda_1 = \lambda_2 = \lambda$ holds, Eq. (9.78) becomes

$$q_S(t) = 1 - \exp(-\lambda \cdot t) \cdot (1 + \lambda \cdot t) \quad (9.79)$$

Equation (9.79) results from the right hand side of Eq. (9.78) by applying the rule of de L'Hospital.

An integral of the type figuring in Eq. (9.78) is called faltung or convolution integral. Its treatment using Laplace transforms facilitates the extension of Eq. (9.79) to the general case of N components. For this purpose

$$q_S^{(N)}(t) = \int_0^t q_S^{(N-1)}(t') \cdot f_N(t - t') \cdot dt' \quad (9.80)$$

has to be evaluated. In Eq. (9.80) the superscript indicates the number of the component. The Laplace transform of Eq. (9.80) is

$$\tilde{q}_S^{(N)}(s) = \tilde{q}_S^{(N-1)}(s) \cdot \tilde{f}_N(s) \quad (9.81)$$

Equation (9.81), in which s is the parameter of the Laplace transform and the tilde denotes the transform, is a recursion, which can also be written as follows

$$\tilde{q}_S^{(N)}(s) = \tilde{q}_S^{(1)}(s) \cdot \prod_{n=2}^N \tilde{f}_n(s) \quad (9.82)$$

If we assume that the lifetimes of all components are exponentially distributed and in addition described by the same failure rate the following Laplace transforms are obtained

$$\begin{aligned}
q_S^{(1)}(t) &= F(t) = 1 - \exp(-\lambda \cdot t) \quad \text{becomes} \\
\tilde{q}_S^{(1)}(s) &= \int_0^\infty [1 - \exp(-\lambda \cdot t)] \cdot \exp(-s \cdot t) dt = \frac{1}{s} - \frac{1}{\lambda + s} \quad \text{and} \\
f_2(t) &= f_3(t) = \dots = f_N(t) = f(t) = \lambda \cdot \exp(-\lambda \cdot t) \quad \text{becomes} \\
\tilde{f}(s) &= \int_0^\infty \lambda \cdot \exp(-\lambda \cdot t) \cdot \exp(-s \cdot t) dt = \frac{\lambda}{\lambda + s}
\end{aligned} \tag{9.83}$$

Inserting the expressions of Eq. (9.83) in Eq. (9.82) we obtain

$$\tilde{q}_S^{(N)}(s) = \left(\frac{1}{s} - \frac{1}{\lambda + s} \right) \cdot \left(\frac{\lambda}{\lambda + s} \right)^{N-1} \tag{9.84}$$

The inverse of Eq. (9.84) gives the failure probability of the system

$$q_S^{(N)}(t) = 1 - e^{-\lambda \cdot t} \cdot \sum_{n=0}^{N-1} \frac{(\lambda \cdot t)^n}{n!} \tag{9.85}$$

The corresponding survival probability is

$$p_S^{(N)}(t) = e^{-\lambda \cdot t} \cdot \sum_{n=0}^{N-1} \frac{(\lambda \cdot t)^n}{n!} \tag{9.86}$$

Equation (9.86) represents the sum probability of the Poisson distribution

The mean time to failure (MTTF) of the system is obtained in analogy with Eq. (9.17) from

$$T_s = \int_0^\infty p_S^{(N)}(t) \cdot dt = \frac{N}{\lambda} \tag{9.87}$$

as shown in the following Example.

Example 9.19 System with a cold reserve

The survival probability of a system of two electric motors, one of which is a reserve, is to be increased. This is done by adding another motor. The failure rate of any one of the motors is $\lambda = 10 \times 10^{-6} \text{ h}^{-1}$. Obtain

- (a) the failure probability of the original and the modified systems for $t = 8,000 \text{ h}$ and

- (b) the expression of the average lifetime (mean time to failure) of the system and its numerical value for the original and modified systems.

Solution

- (a) according to Eq. (9.79) we obtain for the original system

$$q_s^{(2)}(t = 8,000 \text{ h}) = 3.03 \times 10^{-3}$$

and according to Eq. (9.85) for the modified system

$$q_s^{(3)}(t = 8,000 \text{ h}) = 8.04 \times 10^{-5}$$

The Laplace transform of the survival probability is [cf. Eq. (9.86)]

$$\tilde{p}_s^{(N)}(s) = \int_0^{\infty} e^{-s \cdot t} \cdot p_s^{(N)}(t) \cdot dt$$

Comparing this with the result of Eq. (9.87) one obtains

$$T_s = \tilde{p}_s^{(N)}(0)$$

On the other hand we have

$$\tilde{p}_s^{(N)}(s) = \frac{1}{s} - \tilde{q}_s^{(N)}(s)$$

Using the result of Eq. (9.84) one obtains

$$\begin{aligned} \tilde{p}_s^{(N)}(s) &= \left(\frac{(\lambda + s)^{N-1} - \lambda^{N-1}}{s \cdot \lambda^{N-1}} + \frac{1}{s + \lambda} \right) \cdot \left(\frac{\lambda}{s + \lambda} \right)^{N-1} \\ &= \left(\frac{\lambda^{N-1} + (N-1) \cdot \lambda^{N-2} \cdot s + \dots + s^{N-1} - \lambda^{N-1}}{s \cdot \lambda^{N-1}} + \frac{1}{s + \lambda} \right) \cdot \left(\frac{\lambda}{s + \lambda} \right)^{N-1} \end{aligned}$$

and hence

$$\tilde{p}_s^{(N)}(0) = \frac{(N-1) \cdot \lambda^{N-2}}{\lambda^{N-1}} + \frac{1}{\lambda} = \frac{N}{\lambda}$$

This gives $T_s = 2 \times 10^5 \text{ h}$ for the original system and $T_s = 3 \times 10^5 \text{ h}$ for the modified system. $\square$

9.5.2 Maintenance Models

If components are not repaired, unavailability and failure probability are identical. If there is repair, this is no longer true. A high availability is not identical with a high survival probability. For example, a fictitious cable car whose cables break several times a day has a small survival probability. However, if it were possible to repair the cable within a short period of time, its availability would be high. Thus, which of the two parameters is appropriate for characterizing a system depends on the circumstances.

In general the survival probability is of interest if a system has to maintain its function during a certain period of time (e.g. a rocket). If, on the other hand, a system has to function on demand, as for example a trip system, the availability is the adequate parameter. Of course, combinations of both parameters can also be appropriate. A standby system like an emergency power supply needs a high availability (probability to start) and a high survival probability (functioning until the grid supply is restored, i.e. until mission time t).

9.5.2.1 Recurrent Functional Tests

Often components of technical systems are tested in certain time intervals. This is especially true for stand-by components. In what follows this kind of test is modelled. The mathematical model makes use of the following assumptions:

- component lifetimes are exponentially distributed,
- the time intervals between functional tests, θ , are constant,
- failures are only discovered on test,
- the time needed for the test and a possibly required repair or replacement is much smaller than the average lifetime of the component and hence taken to be equal to 0,
- in case the component has failed, it is either replaced or repaired in such a way that it is “as good as new”, i.e. lifetimes are distributed with the same failure rate as before the repair.

We then have the for the unavailability

$$u(t) = 1 - \exp[-\lambda \cdot (t - n \cdot \theta)] \quad (t \geq 0; n = 0, 1, \dots) \quad (9.88)$$

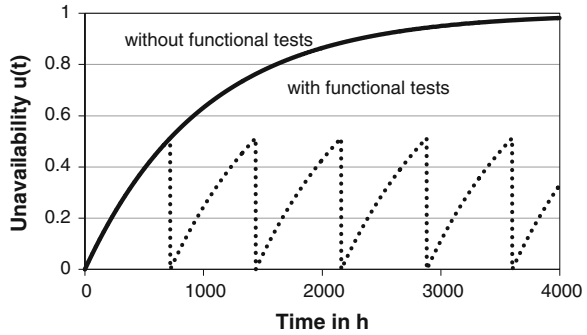
In Eq. (9.88) λ is the failure rate of the component and n the whole-numbered part of the quotient t/θ , e.g. $t/\theta = 1.84$ becomes 1.

Equation (9.88) leads to the so-called sawtooth curve, for which Fig. 9.23 gives an example.

The maximum unavailability is reached immediately before the functional test, i.e.

$$u_{\max} = 1 - \exp(-\lambda \cdot \theta) \approx \lambda \theta = \frac{\theta}{T} \quad (9.89)$$

Fig. 9.23 Time-dependent unavailability of a component with $\lambda = 1,000 \times 10^{-6} \text{ h}^{-1}$ without and with functional tests in time intervals of $\theta = 720 \text{ h}$



In Eq. (9.89) $T = 1/\lambda$ is the average lifetime of the component. The time-averaged unavailability of the component is

$$\begin{aligned} \bar{u} &= \frac{1}{\theta} \cdot \int_{n \cdot \theta}^{(n+1) \cdot \theta} \{1 - \exp[-\lambda \cdot (t - n \cdot \theta)]\} dt \\ &= 1 + \frac{1}{\lambda \theta} \cdot (\exp(-\lambda \theta) - 1) \approx \frac{\lambda \theta}{2} = \frac{\theta}{2T} \end{aligned} \quad (9.90)$$

The approximations in the above equations are obtained by expanding the exponential function in a Taylor series and truncating it with its second term for Eq. (9.89) and with its third term for Eq. (9.90). This represents a good approximation if the argument of the exponential function is $\ll 1$.

It must be emphasized that a component whose lifetime is exponentially distributed cannot be improved by maintenance. For an improvement would imply a reduction of its failure rate. In the present model it is ensured that the unavailability is equal to zero after every functional test. This is achieved by determining in the first place whether it is still capable of functioning or has failed. In the latter case the component is either repaired or replaced. If it is still capable of functioning it is “as good as new” because components with a constant failure rate do not age by definition. If it has to be repaired, “as good as new” is a hypothesis usually corroborated in plants with a good safety culture.

The above model is now extended by accounting for the duration of the functional test or repair, T_r . Since the functional tests are recurrent it suffices to consider the first time interval. During the period of time $T_r + \theta$, which represents a complete time interval from the start of stand-by after the functional test until the end of the subsequent functional test, the component is not available during $T_r + \theta - t$, if it has failed in point of time t . Hence, we obtain the unavailability

$$\begin{aligned}
\bar{u} &= \frac{1}{T_r + \theta} \cdot \left[T_r + \int_0^\theta (\theta - t) \cdot f(t) \cdot dt \right] \\
&= \frac{1}{T_r + \theta} \cdot \left[T_r + \theta \cdot \int_0^\theta f(t) \cdot dt - [F(t) \cdot t]_0^\theta + \int_0^\theta F(t) \cdot dt \right] \\
&= \frac{1}{T_r + \theta} \cdot \left[T_r + \int_0^\theta F(t) \cdot dt \right]
\end{aligned} \tag{9.91}$$

If component lifetimes are exponentially distributed, $F(t) = 1 - \exp(-\lambda t)$ is inserted in Eq. (9.91) and we have

$$\begin{aligned}
\bar{u} &= \frac{1}{T_r + \theta} \cdot \left[T_r + \int_0^\theta [1 - \exp(-\lambda \cdot t)] dt \right] \\
&= 1 + \frac{\exp(-\lambda \cdot \theta) - 1}{\lambda \cdot (T_r + \theta)}
\end{aligned} \tag{9.92}$$

The time interval between functional tests, which minimizes the time-averaged unavailability, θ_{opt} , is obtained as follows

$$\frac{d\bar{u}}{d\theta} = 0 \tag{9.93}$$

Applying the condition of Eq. (9.93) to Eq. (9.92) we have

$$\exp(-\lambda \cdot \theta) = 1 + \lambda \cdot (T_r + \theta) \tag{9.94}$$

Equation (9.94) is transcendental, but can easily be solved if $\exp(-\lambda \cdot \theta)$ is approximated by $1 + \lambda \cdot \theta + 0.5 \cdot (\lambda \cdot \theta)^2$, which is permitted if $\lambda \cdot \theta \ll 1$. One then obtains

$$\theta_{\text{opt}} = \sqrt{2 \cdot \frac{T_r}{\lambda}} = \sqrt{2 \cdot T_r \cdot T} \tag{9.95}$$

Example 9.20 Recurrent functional tests

A pump has a failure rate of $\lambda = 97 \times 10^{-6} \text{ h}^{-1}$. Its function is tested monthly ($\theta = 720 \text{ h}$). Calculate

- the time-dependent unavailability as well as the maximum and time-averaged unavailabilities,

- (b) the time-averaged unavailability, if the functional test takes $T_r = 5$ h,
 (c) the optimum interval between functional tests.

Solution

- (a) Eq. (9.88) gives using $T = 1/\lambda = 10,309.3$ h

$$u(t) = 1 - \exp[-97 \cdot 10^{-6} \text{h}^{-1}(t - 720 \text{ h} \cdot n)] = 1 - \exp\left(-\frac{t - 720 \cdot n}{10,309.3}\right)$$

$$n = 0, 1, \dots$$

The maximum unavailability is calculated with Eq. (9.89) to be

$$u_{\max} = 6.75 \times 10^{-2}$$

Equation (9.90) gives the time-averaged unavailability

$$\bar{u} = 3.41 \times 10^{-2}$$

- (b) Based on Eq. (9.92) we have

$$\bar{u} = 4.1 \times 10^{-2}$$

- (c) The optimal value for the test interval is calculated with Eq. (9.95), i.e.

$$\theta_{\text{opt}} = \sqrt{2 \cdot T_r \cdot T} = \sqrt{2 \cdot 5 \text{ h} \cdot 10,309.3 \text{ h}} = 321.08 \text{ h}$$

The corresponding time-average unavailability then amounts to

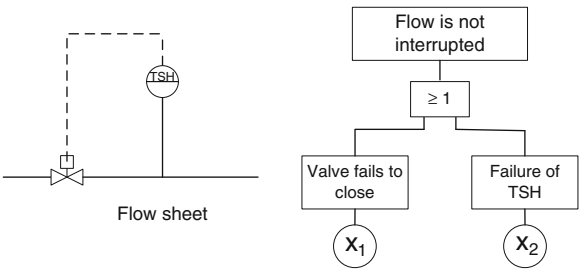
$$\bar{u} = 3.05 \times 10^{-2}$$

□

Example 9.21 Model for an interruption of flow due to high temperature

The flow of a hot medium is to be interrupted if its temperature is too high. The system, which is shown in Fig. 9.24 is successful if the temperature switch TSH responds to high temperature and successfully closes the valve.

Fig. 9.24 Temperature-induced flow interruption and the corresponding fault tree model



We are dealing with an ‘OR’-gate. According to Eq. (9.61) we have the following structure function

$$\Psi(x_1, x_2) = x_1 + x_2 - x_1 \cdot x_2$$

The reliability data needed for quantification are listed in Table 9.17.

Table 9.17 Reliability data for evaluating the fault tree of Fig. 9.24

Primary event x_i	Component	Failure rate λ in 10^{-6} h^{-1}	Test interval θ in h	Unavailability u_i according to Eq. (9.90)
x_1	Valve	4.2	8,760	1.82×10^{-2}
x_2	Temperature switch	38.0	8,760	1.49×10^{-1}

The unavailability of the system is obtained according to Sect. 9.4.5 by forming the expected value of the structure function, i.e.

$$\begin{aligned} E[\Psi(x_1, x_2)] &= E[x_1] + E[x_2] - E[x_1] \cdot E[x_2] = u_1 + u_2 - u_1 \cdot u_2 \\ &= 1.82 \times 10^{-2} + 0.149 - 1.82 \times 10^{-2} \times 0.149 = 0.16 \end{aligned}$$

□

Example 9.22 Model for an interruption of flow due to high temperature activated by a 2-out-of-three voting system

Since in the preceding example the main contribution to the unavailability of the system is made by the temperature switch, the latter is designed as a two-out-of-three voting configuration. The corresponding flow sheet and fault tree model are shown in Fig. 9.25.

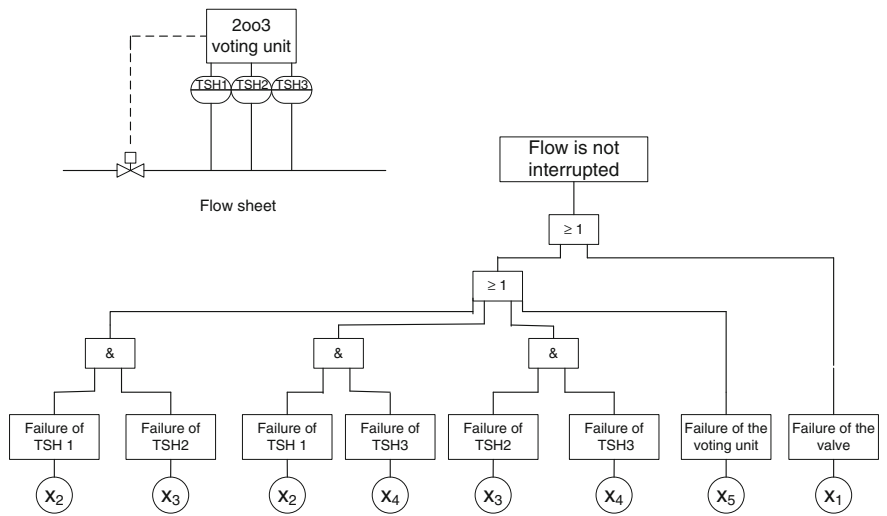


Fig. 9.25 Flow sheet and fault tree model for temperature-induced flow interruption using a two-out-of-three activation

The reliability data needed for quantification are listed in Table 9.18.

Table 9.18 Reliability data for evaluating the fault tree of Fig. 9.25

Primary event x_i	Component	Failure rate λ in 10^{-6} h^{-1}	Test interval θ in h	Unavailability u_i according to Eq. (9.90)
x_1	Valve	4.2	8,760	1.82×10^{-2}
x_2 – x_4	Temperature switches	38.0	8,760	1.49×10^{-1}
x_5	2003 voting unit	0.85	8,760	3.7×10^{-3}

Inspection of the fault tree leads to the following minimal cut sets:

$$\kappa_1 = x_1; \kappa_2 = x_2 \cdot x_3; \kappa_3 = x_2 \cdot x_4; \kappa_4 = x_3 \cdot x_4; \kappa_5 = x_5$$

The expected value of the structure function and the unavailability are approximated as follows [cf. Eq. (9.75)]

$$E[\Psi(x_1, \dots, x_5)] \approx \sum_{i=1}^5 E[\kappa_i] = u_1 + u_2 \cdot u_3 + u_2 \cdot u_4 + u_3 \cdot u_4 + u_5 = 0.089$$

The simultaneous failure of two temperature switches (minimal cut sets $\kappa_2 \dots \kappa_4$) leads to an unavailability of 0.022, i.e. 25 % of the total unavailability. □

Example 9.23 Model for an interruption of flow due to high temperature with redundant valves activated by a two-out-of-three (2oo3) voting system

The configuration of the Example 9.22 is extended by providing two redundant valves, V-1 and V-2, for interrupting the flow, as can be seen from Fig. 9.26.

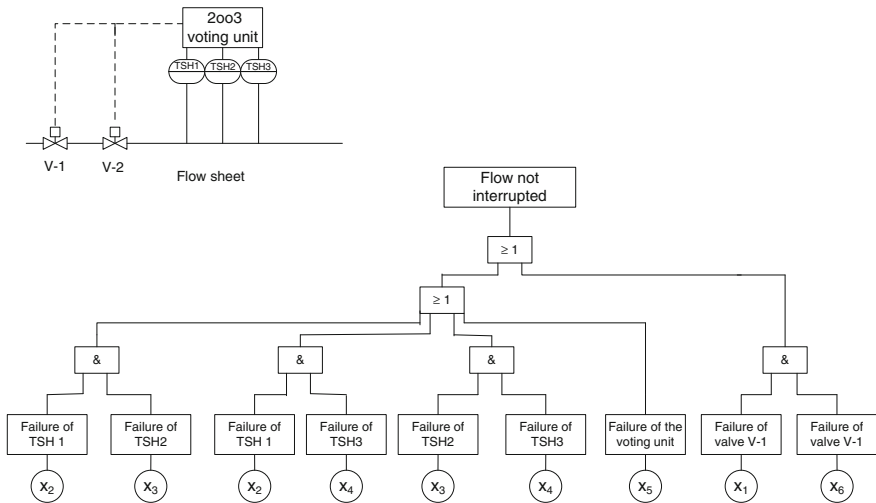


Fig. 9.26 Flow sheet and fault tree model for temperature-induced flow interruption by two valves activated by a two-out-of-three activation

Compared with Example 9.22 only the minimal cut set describing the failure of the valve is modified due to the additional valve. Hence, we have

$$K_1 = x_1 \cdot x_6; K_2 = x_2 \cdot x_3; K_3 = x_2 \cdot x_4; K_4 = x_3 \cdot x_4; K_5 = x_5$$

The expected value of the structure function and the unavailability are approximated as follows [cf. Eq. (9.75)]

$$E[\Psi(x_1, \dots, x_5)] \approx \sum_{i=1}^5 E[k_i] = u_1 \cdot u_6 + u_2 \cdot u_3 + u_2 \cdot u_4 + u_3 \cdot u_4 + u_5 = 0.071$$

If functional tests were carried out every half year instead of annually the unavailability of the system would drop to 0.019. $\square$

Example 9.24 Level and pressure switches for interrupting the filling of a vessel

A vessel is filled 26 times per year. The time intervals between the moments of filling are equally long, i.e. 2 weeks. If the filling is not stopped the vessel fails.

Flow interruption is effected by the level gauge LSH1 which activates the solenoid valve VSOL1. This in turn closes the shut-off valve V1 (the shut-off valve is fail-safe on instrument air failure with an idealized failure probability of 0). For

safety reasons there is a pressure switch which gives a closing signal to VSOL1 and V1 if the pressure is too high. In addition to this basic concept there are further self-explanatory configurations, which are shown as well in Fig. 9.27. The data for quantification are listed in Table 9.19.

- Compare the following cases:
- (a) PSH1 and LSH1 activate a single shut-off valve
 - (b) two shut-off valves are arranged geometrically in series; the first valve is activated by LSH1 and the second by PSH1
 - (c) two shut-off valves are arranged geometrically in series; LSH1 und PSH1 activate both valves

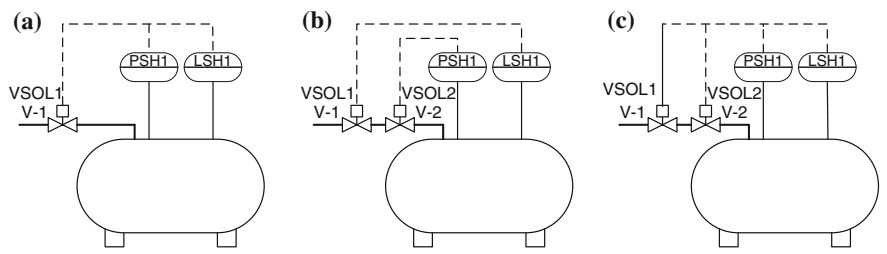


Fig. 9.27 Flow sheets of vessels for storing a liquid under an inert gas pressure pad (without safety valve with level and pressure switches for automatic shut-off)

Table 9.19 Data for quantifying the fault trees of Figs. 9.28, 9.29, 9.30

Primary event x_i	Description	Failure rate	Test interval θ (h)
x_1	Filling takes place	Frequency: 26 a^{-1}	
x_2	LSH1 fails	$\lambda = 7.6 \times 10^{-6} \text{ h}^{-1}$	336
x_3	PSH1 fails	$\lambda = 2.1 \times 10^{-6} \text{ h}^{-1}$	8,760
x_4	V1 fails	$\lambda = 16.8 \times 10^{-6} \text{ h}^{-1}$	336
x_5	VSOL1 fails	$\lambda = 4.2 \times 10^{-6} \text{ h}^{-1}$	336
x_6	V2 fails	$\lambda = 16.8 \times 10^{-6} \text{ h}^{-1}$	8,760/336
x_7	VSOL2 fails	$\lambda = 4.2 \times 10^{-6} \text{ h}^{-1}$	8,760/336

Note Every filling process represents a functional test for the components involved. The test interval therefore is 2 weeks (336 h). The function of the remaining components is tested annually

Solution

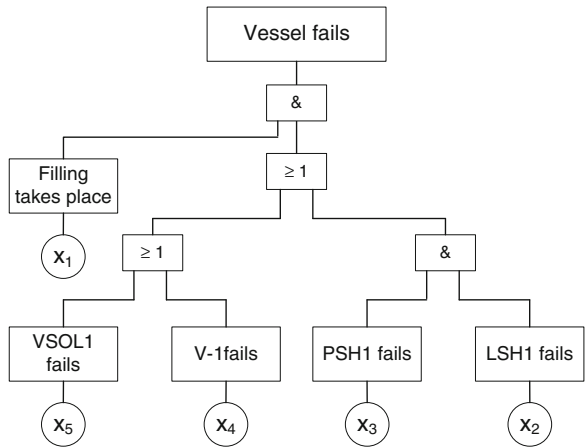
The unavailabilities of the components are given in Table 9.20.

Table 9.20 Frequency of occurrence and unavailabilities for quantifying the primary events of fault trees of Figs. 9.28, 9.29, 9.30

Primary event	Description	Unavailability according to Eq. (9.90)	Test interval θ (h)
x1	Filling takes place	Frequency: 26 a^{-1}	
x2	LSH1 fails	1.28×10^{-3}	336
x3	PSH1 fails	9.14×10^{-3}	8,760
x4	V1 fails	2.82×10^{-3}	336
x5	VSOL1 fails	7.05×10^{-4}	336
x6	V2 fails	$7.01 \times 10^{-2}/2.82 \times 10^{-3}$	8,760/336
x7	VSOL2 fails	$1.82 \times 10^{-2}/7.05 \times 10^{-4}$	8,760/336

(a) PSH1 and LSH1 activate a single shut-off valve

Fig. 9.28 Fault tree for the configuration a) for the undesired event “vessel fails”



The fault tree has the following minimal cut sets:

$$K_1 = x_1 \cdot x_4; K_2 = x_1 \cdot x_5; K_3 = x_1 \cdot x_2 \cdot x_3$$

The expected frequency for vessel failure is approximated according to Eq. (9.75)

$$E[\Psi(x_1, \dots, x_4)] \approx 26 \text{ a}^{-1} \cdot (2.82 \times 10^{-3} + 7.05 \times 10^{-4} + 1.28 \times 10^{-3} \times 9.14 \times 10^{-3}) = 9.2 \times 10^{-2} \text{ a}^{-1}$$

- (b) two shut-off valves are arranged geometrically in series; LSH1 activates the first shut-off valve and PSH1 the second one

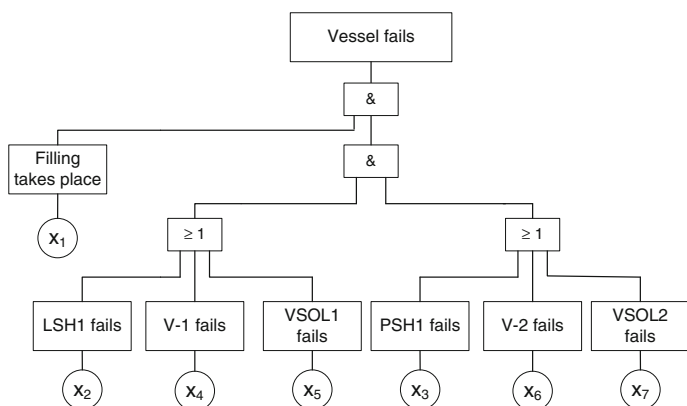


Fig. 9.29 Fault tree for the configuration (b) for the undesired event “vessel fails” (each shut-off valve is activated by its dedicated instrument)

The fault tree of Fig. 9.29 has the following minimal cut sets:

$$K_1 = X_1 \cdot X_2 \cdot X_3; K_2 = X_1 \cdot X_2 \cdot X_6; K_3 = X_1 \cdot X_2 \cdot X_7$$

$$K_4 = X_1 \cdot X_4 \cdot X_3; K_5 = X_1 \cdot X_4 \cdot X_6; K_6 = X_1 \cdot X_4 \cdot X_7$$

$$K_7 = X_1 \cdot X_5 \cdot X_3; K_8 = X_1 \cdot X_5 \cdot X_6; K_9 = X_1 \cdot X_5 \cdot X_7$$

The expected frequency for vessel failure is approximated according to Eq. (9.75)

$$\begin{aligned} E[\Psi(x_1, \dots, x_7)] &\approx 26 a^{-1} \cdot (1.28 \times 10^{-3} \cdot 9.14 \times 10^{-3} + 1.28 \times 10^{-3} \cdot 7.01 \\ &\quad \times 10^{-2} + 1.28 \times 10^{-3} \cdot 1.82 \times 10^{-2} + 2.82 \times 10^{-3} \cdot 9.14 \\ &\quad \times 10^{-3} + 2.82 \times 10^{-3} \cdot 7.01 \times 10^{-2} + 2.82 \times 10^{-3} \cdot 1.82 \\ &\quad \times 10^{-2} + 7.05 \times 10^{-4} \cdot 9.14 \times 10^{-3} + 7.05 \times 10^{-4} \cdot 7.01 \\ &\quad \times 10^{-2} + 7.05 \times 10^{-4} \cdot 1.82 \times 10^{-2}) = 1.22 \times 10^{-2} a^{-1} \end{aligned}$$

- (c) two shut-off valves are arranged geometrically in series; LSH1 and PSH1 activate both shut-off valves

This case is modelled by the fault tree of Fig. 9.30

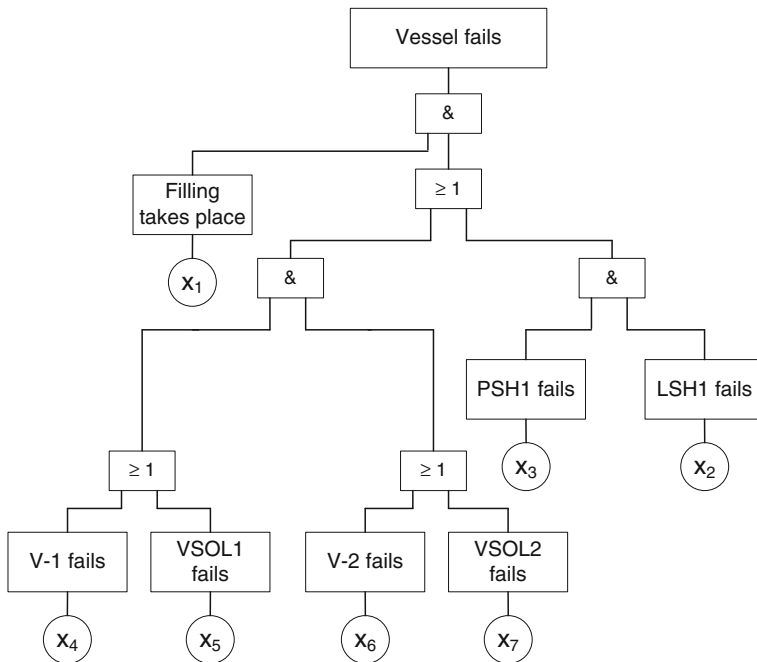


Fig. 9.30 Fault tree for the configuration (c) for the undesired event “vessel fails” (each shut-off valve is activated by both instruments)

The fault tree of Fig. 9.30 has the following minimal cut sets:

$$\begin{aligned} \kappa_1 &= X_1 \cdot X_2 \cdot X_3; \kappa_2 = X_1 \cdot X_4 \cdot X_6; \kappa_3 = X_1 \cdot X_4 \cdot X_7; \kappa_4 = X_1 \cdot X_5 \cdot X_6; \kappa_5 \\ &= X_1 \cdot X_5 \cdot X_7 \end{aligned}$$

The expected frequency for vessel failure is approximated according to Eq. (9.75)

$$\begin{aligned} E[\Psi(x_1, \dots, x_7)] &\approx 26 \text{ a}^{-1} \cdot (1.28 \times 10^{-3} \cdot 9.14 \times 10^{-3} + 2.82 \times 10^{-3} \cdot 2.82 \\ &\quad \times 10^{-3} + 2.82 \times 10^{-3} \cdot 7.05 \times 10^{-4} + 7.05 \times 10^{-4} \cdot 2.82 \\ &\quad \times 10^{-3} + 7.05 \times 10^{-4} \cdot 7.05 \times 10^{-4}) = 6.27 \times 10^{-4} \text{ a}^{-1} \end{aligned}$$

This configuration is called ‘intermeshed’. It has superior characteristics. If, however, events of encompassing impacts like fires are included in the analysis, the separated configuration might prove superior. It permits a more efficient spatial segregation of the redundant chains (switch-solenoid-valve-shut-off valve) and would thus reduce the probability of a fire to affect the redundancies at the same time.

It should therefore be noted that an extension of the scope of the analysis influences its result and may occasionally even contradict the results from an analysis with a more restricted scope. Only events with a small influence may therefore be neglected. $\square$

9.5.2.2 Components Which are Repaired According to the Theory of Markov Processes

If components announce their failures themselves (self-announcing components) or we are dealing with components which are essential for the production process we may assume that their failure is immediately noticed. If it is further assumed that repair begins after the failure has been detected then this type of component can be modelled by a Markov process [47]. For this purpose the following assumptions are made:

- the component lifetimes are exponentially distributed,
- the durations of repairs are also exponentially distributed,
- repair restores the component to its original state (the same failure rate as before its failure is applicable after repair).

A Markov process describes the states of a system (enumerably many states are admitted) as a function of time. Its characteristic is that the progression of the process at any point in time t only depends on its state in t and not on states prior to t . If, in addition, it is homogeneous, as is supposed here, the probability of the transition of the state of the system at point in time t to its state at point in time $t + \Delta t$ depends only on the duration of Δt and not on the point in time t . A further assumption is that the probability of more than one change of state in Δt can be neglected. In order to formulate the model the following quantities are needed:

- $P_0(t)$: probability that the component functions at point in time t
- $P_{00}(\Delta t)$: probability that the component maintains its function during time interval Δt
- $P_1(t)$: probability that the component is in failed state at point in time t
- $P_{11}(\Delta t)$: probability that the component remains failed during time interval Δt
- $P_{01}(\Delta t)$: probability that the component fails during the time interval Δt (transition from state 0 to state 1)
- $P_{10}(\Delta t)$: probability that the component is repaired during time interval Δt (transition from state 1 to state 0)
- $P_0(t + \Delta t)$: probability that the component functions at point in time $t + \Delta t$
- $P_1(t + \Delta t)$: probability that the component is in failed state at point in time $t + \Delta t$

The state of functioning at point in time $t + \Delta t$ can be reached by two mutually exclusive ways:

- the component functions at point in time t and maintains this state during $[t, t + \Delta t]$: $P_0(t) \cdot P_{00}(\Delta t)$,

- the component is in failed state at point in time t and is repaired during $[t, t + \Delta t]$: $P_1(t) \cdot P_{10}(\Delta t)$.

From this follows

$$P_0(t + \Delta t) = P_0(t) \cdot P_{00}(\Delta t) + P_1(t) \cdot P_{10}(\Delta t) \quad (9.96)$$

In analogy to this the probability of a component being in failed state (not available) at point in time $t + \Delta t$ is obtained:

- the component is in failed state at point in time t and maintains this state during $[t, t + \Delta t]$: $P_1(t) \cdot P_{11}(\Delta t)$,
- the component functions at point in time t and fails during $[t, t + \Delta t]$: $P_0(t) \cdot P_{01}(\Delta t)$.

Thus we have

$$P_1(t + \Delta t) = P_1(t) \cdot P_{11}(\Delta t) + P_0(t) \cdot P_{01}(\Delta t) \quad (9.97)$$

Since with a homogeneous Markov process the probabilities of transition, $P_{00}(\Delta t)$, $P_{11}(\Delta t)$, $P_{01}(\Delta t)$ and $P_{10}(\Delta t)$, do not depend on the point in time t but only on the duration of the time interval Δt the corresponding rates (failure and repair rate) must be constants.

The only probability distribution satisfying this requirement is the exponential distribution, which gives for this case

$$\begin{aligned} P_{01}(\Delta t) &= 1 - \exp(-\lambda \cdot \Delta t) \approx \lambda \cdot \Delta t \\ P_{00}(\Delta t) &= \exp(-\lambda \cdot \Delta t) \approx 1 - \lambda \cdot \Delta t \end{aligned} \quad (9.98)$$

In Eq. (9.98) λ is the failure rate. Analogously one describes repair by the repair rate μ , which is the reciprocal value of the mean duration of repair (mean time to repair: MTTR), i.e. $\mu = 1/T_r$

$$\begin{aligned} P_{10}(\Delta t) &= 1 - \exp(-\mu \cdot \Delta t) \approx \mu \cdot \Delta t \\ P_{11}(\Delta t) &= \exp(-\mu \cdot \Delta t) \approx 1 - \mu \cdot \Delta t \end{aligned} \quad (9.99)$$

Using Eqs. (9.98) and (9.99) in Eqs. (9.96) and (9.97) and expanding $P_0(t + \Delta t)$ and $P_1(t + \Delta t)$ in Taylor series, which are truncated after the second term, we obtain

$$\begin{aligned} P_0(t) + \frac{dP_0}{dt} \cdot \Delta t &= P_0(t) \cdot (1 - \lambda \cdot \Delta t) + P_1(t) \cdot \mu \cdot \Delta t \\ P_1(t) + \frac{dP_1}{dt} \cdot \Delta t &= P_1(t) \cdot (1 - \mu \cdot \Delta t) + P_0(t) \cdot \lambda \cdot \Delta t \end{aligned} \quad (9.100)$$

After cancelling equal terms on both sides of Eq. (9.100) and dividing them by Δt we obtain the following system of two simultaneous linear differential equations of first order

$$\begin{aligned}\frac{dP_0}{dt} &= -\lambda \cdot P_0(t) + P_1(t) \cdot \mu \\ \frac{dP_1}{dt} &= -\mu \cdot P_1(t) + P_0(t) \cdot \lambda\end{aligned}\quad (9.101)$$

The following initial conditions can be considered for Eq. (9.101):

$$\begin{aligned}P_0(0) &= 1 \\ P_1(0) &= 1 - P_0(0) = 0\end{aligned}\quad (9.102)$$

i.e. the component functions initially (at point in time $t = 0$) or

$$\begin{aligned}P_0(0) &= 0 \\ P_1(0) &= 1 - P_0(0) = 1\end{aligned}\quad (9.103)$$

i.e. the component is in failed state initially (at point in time $t = 0$).

The solution of Eq. (9.101) is obtained using Laplace transforms. This gives

$$\begin{aligned}s \cdot \tilde{P}_0 - P_0(0) &= -\lambda \cdot \tilde{P}_0 + \tilde{P}_1 \cdot \mu \\ s \cdot \tilde{P}_1 - P_1(0) &= -\mu \cdot \tilde{P}_1 + \tilde{P}_0 \cdot \lambda\end{aligned}\quad (9.104)$$

where we use $\tilde{P}_0 = \int_0^\infty P_0(t) \cdot e^{-s \cdot t} dt$ and $\tilde{P}_1 = \int_0^\infty P_1(t) \cdot e^{-s \cdot t} dt$. After rearrangement Eq. (9.104) becomes

$$\tilde{P}_0 = \frac{P_0(0) \cdot (s + \mu)}{(s + \lambda) \cdot (s + \mu) - \lambda \cdot \mu} + \frac{P_1(0) \cdot \mu}{(s + \lambda) \cdot (s + \mu) - \lambda \cdot \mu}\quad (9.105)$$

The inversion of the Laplace transforms of Eq. (9.105) with the initial conditions of Eq. (9.102) gives the availability

$$P_0(t) = \frac{\mu}{\lambda + \mu} \cdot \left[1 + \frac{\lambda}{\mu} \cdot \exp(-(\lambda + \mu) \cdot t) \right]\quad (9.106)$$

and the unavailability

$$P_1(t) = \frac{\lambda}{\lambda + \mu} \cdot [1 - \exp(-(\lambda + \mu) \cdot t)]\quad (9.107)$$

Using the initial conditions of Eq. (9.103) we obtain for the availability

$$P_0(t) = \frac{\mu}{\lambda + \mu} \cdot [1 - \exp(-(\lambda + \mu) \cdot t)] \quad (9.108)$$

and for the unavailability

$$P_1(t) = \frac{\lambda}{\lambda + \mu} \cdot \left[1 + \frac{\mu}{\lambda} \cdot \exp(-(\lambda + \mu) \cdot t) \right] \quad (9.109)$$

Despite differing initial conditions both solutions lead to the same asymptotic results for the availability

$$\lim_{t \rightarrow \infty} P_0(t) = \frac{\mu}{\lambda + \mu} = \frac{T}{T_r + T} \quad (9.110)$$

and the unavailability

$$\lim_{t \rightarrow \infty} P_1(t) = \frac{\lambda}{\lambda + \mu} = \frac{T_r}{T_r + T} \quad (9.111)$$

It can be seen that the asymptotic availability is given by the average component lifetime divided by a cycle consisting of the sum of the average lifetime and the average repair time.

The Markov procedure enables one to treat more complex situations as well. For example, the time until detection of the failure, the waiting time until the start of repair work or restrictions during repair can be accounted for. The necessary extensions (every additional state leads to an additional equation) are treated for instance in [47]. However, the application of such extended models in analyzing real systems mostly fails due to a lack of empirical data for calculating the transition probabilities. Apart from that the calculational effort increases, if additional states are included.

Example 9.25 Treatment of the repair of a component as a Markov process

A failure rate of $\lambda = 97 \times 10^{-6} \text{ h}^{-1}$ applies to a pump. The average time needed for its repair is known to be $T_r = 5 \text{ h}$. $T_d = 3 \text{ h}$ are required on the average until its failure is detected.

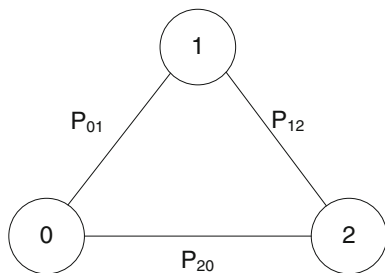
Determine the asymptotic (stationary) unavailability. The result is to be compared with that obtained in case of immediate detection of the failure.

Solution

The system described above can adopt three mutually exclusive states:

- 0: functioning
- 1: failed, but the failure has not yet been detected
- 2: under repair

Fig. 9.31 Markov transition diagram for a repair process



This is illustrated by Fig. 9.31.

In analogy to the derivation of Eq. (9.99) the following system of equations is established:

$$\begin{aligned}\frac{dP_0}{dt} &= -\lambda \cdot P_0(t) + \mu \cdot P_2(t) \\ \frac{dP_1}{dt} &= -\eta \cdot P_1(t) + \lambda \cdot P_0(t) \\ \frac{dP_2}{dt} &= -\mu \cdot P_2(t) + \eta \cdot P_1(t)\end{aligned}$$

where

$$\eta = \frac{1}{T_d}, \mu = \frac{1}{T_r}, \lambda = \frac{1}{T}$$

In the stationary case the parameters do not vary with time, i.e.

$$\frac{dP_0}{dt} = \frac{dP_1}{dt} = \frac{dP_2}{dt} = 0$$

We then have

$$\begin{aligned}-\lambda \cdot P_0(t) + \mu \cdot P_2(t) &= 0 \\ -\eta \cdot P_1(t) + \lambda \cdot P_0(t) &= 0 \\ -\mu \cdot P_2(t) + \eta \cdot P_1(t) &= 0\end{aligned}$$

Additionally $P_0 + P_1 + P_2 = 1$ has to hold, since the three states are the only ones which can be adopted by the component. The availability of the component is

$$P_0 = \frac{\mu \cdot \eta}{\eta \cdot \lambda + \eta \cdot \mu + \lambda \cdot \mu} = \frac{T}{T_r + T + T_d}$$

For the component unavailability we have

$$1 - P_0 = \frac{T_r + T_d}{T_r + T + T_d} = 7.75 \times 10^{-4}$$

If detection of the failure is immediate [cf. Eqs. (9.110) and (9.111)], we obtain an unavailability of

$$1 - P_0 = 4.85 \times 10^{-4}$$

It is obvious that the difference between the two models is considerable in this case. Equation (9.111) leads to the same result as the foregoing consideration if T_r is replaced there by the sum $T_r + T_d$. This is also true if additional waiting times are to be taken into account, for example caused by the unavailability of a person for carrying out the repair. Hence we can replace T_r in Eq. (9.111) by the sum of all times leading to component unavailability for whatever reason, which is simply called ‘downtime’. $\square$

Example 9.26 Unavailability of an emergency cooling system pump

After the start of the emergency cooling system of a nuclear power station the radiation level drops to a value which permits a repair of the emergency cooling pump only after 48 h. It is assumed that the pump starts on demand. For its failure during operation a rate of $\lambda = 42 \times 10^{-6} \text{ h}^{-1}$ applies; the average time for repair amounts to $T_r = 20 \text{ h}$.

Calculate the time-dependent unavailability of the pump.

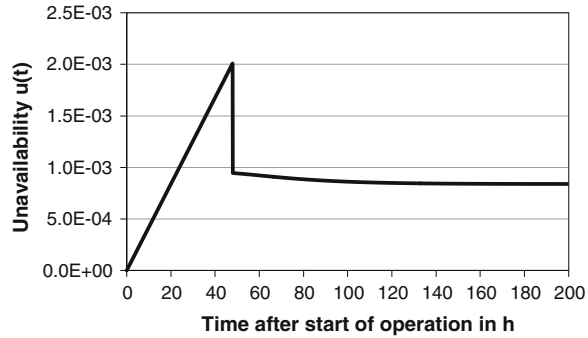
Solution

During the initial phase ($t < 48 \text{ h}$) the unavailability is equal to the failure probability (identity of the parameters in case the component is not subject to repair). Thus the availability of the pump is calculated according to Eq. (9.24) and its unavailability according to Eq. (9.25). Thereafter Eq. (9.105) must be used. The boundary condition of Eq. (9.102), i.e. the component functions initially, is to be applied with a probability of $\exp(-42 \times 10^{-6} \text{ h}^{-1} \cdot 48 \text{ h})$ and the complementary one according to Eq. (9.103) with a probability of $1 - \exp(-42 \times 10^{-6} \text{ h}^{-1} \cdot 48 \text{ h})$. This means that the unavailability of the pump is calculated according to Eqs. (9.107) and (9.108). Hence we have

$$u(t) = \begin{cases} 1 - \exp(-\lambda \cdot t) & 0 \leq t \leq 48 \text{ h} \\ \exp(-\lambda \cdot t) \cdot \frac{\lambda}{\lambda + \mu} \cdot [1 - e^{-(\lambda + \mu) \cdot t}] + [1 - \exp(-\lambda \cdot t)] \cdot \frac{\lambda}{\lambda + \mu} \cdot [1 + \frac{\mu}{\lambda} \cdot e^{-(\lambda + \mu) \cdot t}] & t > 48 \text{ h} \end{cases}$$

The time-dependent unavailability of the pump is shown in Fig. 9.32.

Fig. 9.32 Time-dependent unavailability of an emergency cooling pump after start of operation ($\lambda = 42 \times 10^{-6} \text{ h}^{-1}$; $\mu = 1/T_r = 0.05$)



9.6 Dependent Failures

So far it has been assumed that the primary events of a fault tree are independent of one another. However, this is not always true. Failures of components from the same production may occur due to a manufacturing flaw which affects all of them. A corrosive atmosphere may shorten the lifetimes of all components exposed to it. Errors in testing and maintenance may occur, for example an erroneous calibration of several redundant measuring devices. These examples belong to a class of failures called 'dependent failures'. They are discussed in detail in [48]. Dependent failures are failures which occur simultaneously or within a short interval of time so that several components are not available simultaneously. This type of failures is especially grave if it affects redundant sub-systems or systems. An overview of the different types of failures is provided by Fig. 9.33.

In general three types of dependent failures are distinguished:

- (1) Functional failures of two or more redundant components resulting from a single preceding failure (e.g. failure of several redundant pressure switches following exposure to moisture because of a pipe leak). They are called propagating or secondary failures [3];

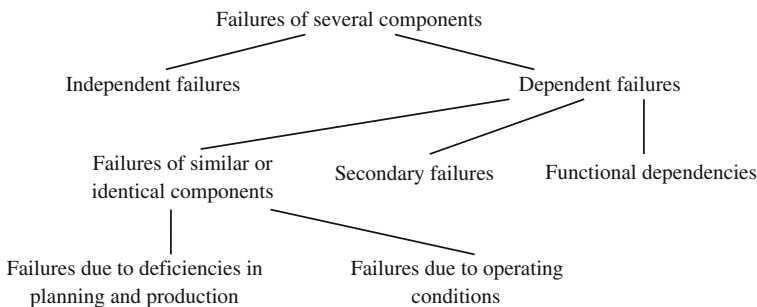


Fig. 9.33 Types of failures of several components (according to [49])

- (2) Functional failures of two or more redundant components caused by functional dependencies, i.e. derived directly from the structure of the system. Functional dependencies may result from a common auxiliary system (e.g. instrument air supply or energy supply). They are denominated commanded failures according to [3].
- (3) Functional failures of two or more similar or identical redundant components due to a single shared cause. They are referred to as common cause failures (CCF) [3].

In order to adequately treat dependent failures in a reliability analysis, secondary failures (1) and failures of components due to functional dependencies (2) are accounted for as far as possible by a detailed fault tree model. Common cause failures (3) require a separate treatment. The procedure for all three failure types is explained below. Yet, before that possible causes of dependent failures are classified.

9.6.1 Causes

A classification of dependent failures is helpful for their analysis. According to [49] we distinguish the following causes:

- planning errors,
- wrong functional assessment,
- design and construction errors,
- manufacturing errors,
- errors during operation,
- faults when operating or maintaining the system,
- extreme environmental or operating conditions,
- impacts from neighbouring systems or external impacts.

Planning errors cause wrong designs and construction flaws and lead to wrong or insufficient instructions in the operating manual. Planning errors stem, for example, from mutual dependencies which have not been identified or sufficiently accounted for as the dependence of human error probabilities on environmental influences or impairment of components due to changes in environmental conditions caused by an accident.

Wrong functional assessments refer to system flaws resulting from erroneous judgments on the time-behaviour of process variables or insufficient instrumentation to measure them. This may render detection of accident initiation impossible. Furthermore, it is conceivable that due to wrong assessments only insufficient measures against accidents are implemented.

Manufacturing errors are deficiencies originating in the manufacturing process (including quality assurance), the installation or assembly on the site or the commissioning.

Operator errors may be the cause of dependent failures, for example unprofessional maintenance like miscalibration or valves left in wrong position.

Extreme environmental or operating conditions may result from accidents. Increased temperature, humidity or pressure are examples. If components are not designed for such conditions they are expected to fail.

Secondary or consequential failures caused by impacts from neighbouring systems are conceivable. For example, ejected missiles, pipe whip or impacts from fluid jets in a system may cause destructions in a neighbouring system.

Possible external events are fires, flooding lightning, storm, earthquake, explosion, aircraft crash etc. They will usually affect several components at the same time.

9.6.2 Countermeasures

The measures listed below, which in part were devised to reduce the probability of occurrence of independent failures, are also suited to reduce the probability of occurrence of dependent failures:

- proven construction and standardization,
- redundancy,
- diversity,
- segregation,
- equipment for early fault detection,
- regular functional tests,
- fail-safe design,
- separation of operational from safety systems,
- simple system structure,
- quality assurance in planning construction, and commissioning,
- quality assurance during operation,
- evaluation of operating experience.

Below the different concepts are discussed in some detail.

If proven and standardized components are used and unnecessary innovations are avoided, the experience with the component type in question is an advantage. Based on the experience design flaws, which possibly existed in the phase immediately following market introduction, have probably already been eliminated.

As mentioned before, a redundancy implies that more than one component or sub-system is implemented for the same task. A redundancy may also concern actions of the operators, if, for example, the action of one operator is checked by another one. A redundancy reduces the probability of independent failures as well as that of certain dependent failures. The occurrence of dependent failures does not necessarily imply simultaneity. It may rather be the simultaneous unavailability of several components. This may also occur if the components failed one after

another and are all not available when the corresponding sub-system is demanded. If the failed component is self-announcing or recurrent functional tests are carried out it is conceivable that a failure is detected and repaired. The sub-system would then be available. Furthermore it is possible that during the repair the cause of the failure is identified and thus measures are taken to make its repetition less probable.

The concept of diversity implies that the components of a redundant sub-system or system realizing the same function are of different designs. Thus it can be avoided that possible design or manufacturing flaws affect all redundant components. Diversity is a requirement which counteracts standardization and renders maintenance more difficult. Diversity is encountered especially in the protection system of nuclear reactor which is activated by two different criteria, e.g. power too high and pressure too high. An example from the process industry is to avoid overfilling by level and pressure measurements. Different criteria of activation necessarily lead to diversity in instrumentation. However, it must be ensured that the measuring chains do not contain the same component type, e.g. the same amplifier, which would obstruct the ends of diversity. If the action of a person is checked by another person, diversity is granted, because people are different by nature.

Segregation, which can be realized by thick walls separating the individual trains of a redundant system, protects against secondary failures and external effects.

Quick detection of failures increases the availability of systems. That is why so-called self-announcing components are used. They signal their own failure and enable one to detect dependent failures as well.

The fail-safe principle prevents failures from causing hazardous system states. A good example are the control rods of pressurized water reactors, which are held by magnets. In case of electricity supply failure these are demagnetized and the control rods drop into the nuclear core by gravity. The emergency discharge valve of the reactor of case study 4.2 is opened by a spring if compressed air fails and thus provides an example of fail-safe behaviour.

The separation of operating and safety systems prevents components shared by the operating and the safety systems from reducing the availability of the latter in case of their failure.

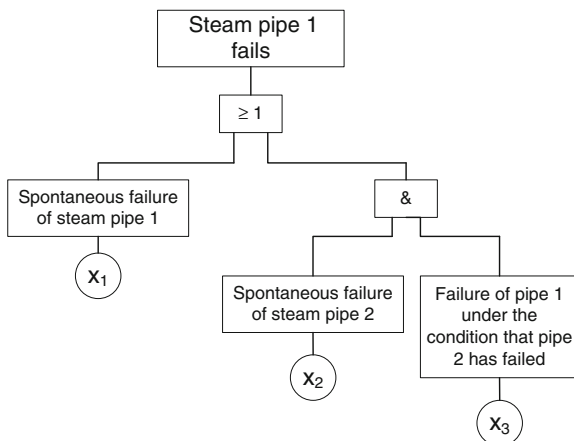
A simple system structure facilitates the detection of possible causes of failures.

Quality assurance covering planning, manufacturing and commissioning of components and systems reduces the probability of dependent failures.

The quality assurance during plant operation comprises, for example, the following measures:

- good and permanent training of personnel,
- comprehensive operating manual, which is easy to understand and describes measures for handling accidents,
- restriction of access to certain areas of the plant to authorized personnel,
- functional tests after maintenance,

Fig. 9.34 Fault tree model of a secondary failure



- documentation of maintenance work,
- redundancy and diversity of persons carrying out maintenance work (e.g. two collaborators with different education).

Operating experience with technical plants shows that errors cannot be avoided even if plant designers and operators are very experienced. Therefore it makes sense to maintain a documentation of safety-relevant incidents like for example [23, 50], which may be one of the bases of a safety analysis.

9.6.3 Secondary Failures

The treatment of secondary failures, also called consequential failures is illustrated by an example. The fault tree of Fig. 9.34 models the failure of two pipes geometrically arranged in parallel. Apart from a spontaneous failure of pipe 1 (primary event x_1) pipe 2 may fail spontaneously (primary event x_2) and as a consequence damage pipe 1 (primary event x_3) by pipe whip or impinging steam jets.

The dependence of the failure of pipe 1 on the rupture of pipe 2 is expressed by a conditional probability to be assigned to primary event x_3 . The latter represents a so-called pseudo-event. Its probability of occurrence must be derived from statistics, if available, or pertinent model calculations. In this case the models would be from the areas of fracture mechanics and thermohydraulics. If no information is available, estimates are the only recourse. A pessimistic estimate is a value of 1, i.e. the failure of pipe 2 always causes pipe 1 to fail.

The fault tree of Fig. 9.34 has the following cut sets

$$K_1 = x_1; K_2 = x_2 \cdot x_3$$

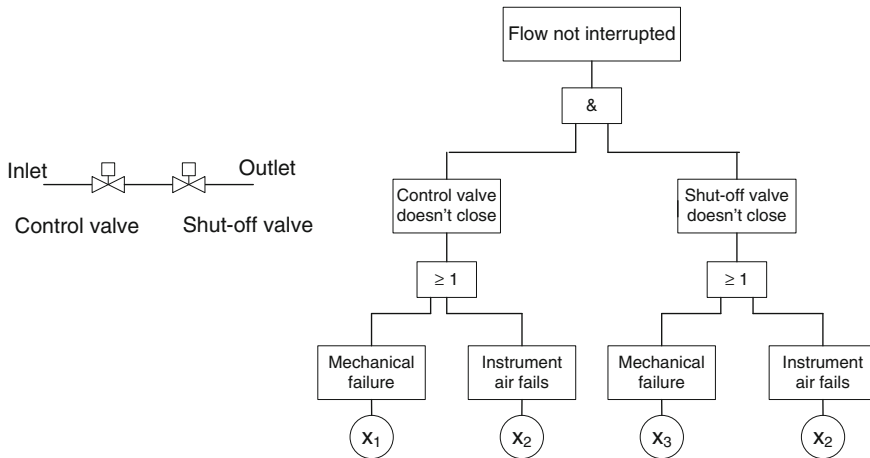


Fig. 9.35 Fault tree model for a functional dependence

These happen to be already minimal. The corresponding structure function is

$$\Psi(x_1, x_2, x_3) = x_1 + x_2 \cdot x_3 - x_1 \cdot x_2 \cdot x_3$$

By introducing pseudo-events the fault tree becomes more complex. This may lead to a more laborious evaluation.

9.6.4 Functional Dependencies

An example is to serve for explaining the analysis of functional dependencies. Figure 9.35 shows a fault tree modelling the failure of a system of two redundant valves. The system failure can be caused either by the simultaneous failure of both valves in open position or the failure of the supply of instrument air.

In such a case the probability is assigned to the primary events on the basis of the corresponding failure rates for independent failures. The fault tree of Fig. 9.35 has the following cut sets:

$$K_1 = x_1 \cdot x_3; K_2 = x_1 \cdot x_2; K_3 = x_2 \cdot x_3; K_4 = x_2$$

After eliminating the non-minimal cut sets the following minimal cut sets remain:

$$K_1 = x_1 \cdot x_3; K_4 = x_2$$

It is obvious that the failure of instrument air alone is sufficient to cause the undesired event. The structure function representing the fault tree is

$$\Psi(x_1, x_2, x_3) = x_1 \cdot x_3 + x_2 - x_1 \cdot x_2 \cdot x_3$$

Of course, it would make sense in this case to use fail-safe valves, i.e. valves which close on instrument air failure. Then air failure would not cause the undesired event unless none of the two valves would adopt its rest position (closed), which might occur with a certain—even if small—probability.

9.6.5 Common Cause Failures

After analyzing the preceding two classes of failures those dependent failures which are due to a common (shared) cause (CCF) remain to be explained. The common cause may be a design or construction flaw or a maintenance error, e.g. unsuitable lubricants used for pump bearings. CCFs are introduced into the fault tree in addition to the independent failures of the components involved. Probabilities are assigned to them using model-based evaluations of operating experience.

The treatment of CCFs is impaired by the dearth of observations. This results from the fact that CCFs occur more seldom than independent failures. Furthermore, the observation time is counted only once for the redundant system whilst with independent failures the accumulated time of observation is the product of the time of observation and the number of redundant components in the redundant system.

In addition, the probability of individual events depends on the degree of redundancy of the observed system. For example, the probability of a common cause failure of two components in a system with two redundant components is not the same as that in a system with four redundant components, even if all parameters with relevance for the failure behaviour are identical. This is because one generally believes that CCFs are caused by hidden component flaws or hidden environmental influences and the number of components affected depends on the number of redundant component present (e.g. the same cause affecting two components in a twofold redundant system could only affect one in a non-redundant system and three in a threefold redundant system). Thus, conversions and adaptations are necessary, as described in detail in [48].

Basically two classes of models are distinguished

- shock models,
- non-shock models.

With shock models two failure mechanisms are contemplated:

- (1) Failures due to independent causes occurring at random points in time.
- (2) Failures of one or several components due to a common cause, namely a sudden strong load (shock) impacting the system at a random point in time.

Modelling of the failure type of class (2) requires one to determine the expected frequency of the shock events and the corresponding conditional probabilities of component failures caused by them. The binomial failure rate model (BFR) is the best known model of this class. For its application observed CCF events are used to calculate the parameter of the binomial distribution [u in Eq. (9.36)]. This then enables one to determine the probabilities of failure combinations (e.g. three-out-of-four redundant components) including for combinations which have not been observed.

With non-shock models failure probabilities are directly derived from observations. The following models are inscribed in this group:

- Basic Parameter Model,
- Beta Factor Model,
- Multiple Greek Letter Model,
- Alpha Factor Model.

In what follows only the Beta Factor Model is treated. As to the remaining models the reader is referred to the literature, e.g. [48].

The Beta Factor Model is a one parameter model in which the total failure rate of a component is split into an independent part and one due to common cause, i.e.

$$\lambda = \lambda_{\text{in}} + \lambda_{\text{CCF}} \quad (9.112)$$

In Eq. (9.112) λ_{in} is the failure rate for independent failures and λ_{CCF} that for dependent failures. Using the parameter β , which represents the ratio of the number of common cause failures to the total number of failures, we obtain the following relationships:

$$\begin{aligned} \lambda_{\text{in}} &= (1 - \beta) \cdot \lambda \\ \lambda_{\text{CCF}} &= \beta \cdot \lambda \end{aligned} \quad (9.113)$$

Hence we have

$$\beta = \frac{\lambda_{\text{CCF}}}{\lambda_{\text{in}} + \lambda_{\text{CCF}}} \quad (9.114)$$

as the ratio of the CCF failure rate to the total failure rate.

The Beta Factor Model was originally developed for treating CCFs in twofold redundant systems of U.S. nuclear power reactors. A factor of $\beta = 0.1$ resulted. An evaluation of data of the collection in process plants described in [40] gave $\beta = 0.084$, which insinuates that $\beta = 0.1$ is a conservative value for analyses of process plants from the class investigated in [40].

However, the application of the model to systems with higher degrees of redundancy is problematic. This was reason for extending the Beta Factor Model to the Multiple Greek Letter (MGL) Model [48].

9.6.6 Closing Remark

The treatment of CCFs requires a substantial amount of engineering judgment. The models can only give support in interpreting and representing available data since usually only very few multiple failures are observed and the evaluation results are therefore affected by large uncertainties.

Example 9.27 Application of the Beta Factor Model

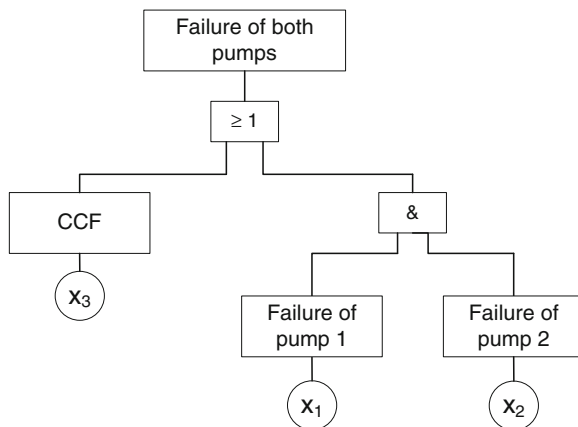
A reliability data evaluation in process plants comprised observations of two-fold redundant pump configurations in standby; $k_{in} = 9$ single failures and $k_{CCF} = 1$ failure of both pumps were observed in 100 test cycles. The accumulated observation time was 100 years. Calculate the

- β factor
- failure probability of the twofold redundant configuration for $t = 500$ h (before the first functional test)
- time-averaged unavailability if $\theta = 720$ h

Solution

The pertinent fault tree is shown in Fig. 9.36.

Fig. 9.36 Fault tree for a standby system of two pumps



The minimal cut sets of the fault tree are:

$$K_1 = X_1 \cdot X_2; K_2 = X_3$$

- On the basis of Eq. (9.34) we obtain with $t_{in} = 100 a \cdot 8,760 \text{ h/a} = 876,000 \text{ h}$ and $t_{CCF} = 100 a/2 \cdot 8,760 \text{ h/a} = 438,000 \text{ h}$

$$\hat{\lambda}_{in} = \frac{k_{in}}{t_{in}} = \frac{9}{876,000 \text{ h}} = 1.03 \times 10^{-5} \text{ h}^{-1}$$

$$\hat{\lambda}_{CCF} = \frac{k_{CCF}}{t_{CCF}} = \frac{1}{438,000 \text{ h}} = 2.28 \times 10^{-6} \text{ h}^{-1}$$

According to Eq. (9.112) we have

$$\beta = \frac{\lambda_{CCF}}{\lambda_{in} + \lambda_{CCF}} = \frac{2.28 \times 10^{-6} \text{ h}^{-1}}{1.03 \times 10^{-5} \text{ h}^{-1} + 2.28 \times 10^{-6} \text{ h}^{-1}} = 0.18$$

- (b) The expected value of the structure function is the failure probability of the system

The failure probabilities are calculated using Eq. (9.25), which gives

$$F_{in} = 1 - \exp(-\lambda_{in} \cdot t) = 1 - \exp(-1.03 \times 10^{-5} \text{ h}^{-1} \cdot 500 \text{ h}) = 5.14 \times 10^{-3}$$

$$F_{CCF} = 1 - \exp(-\lambda_{CCF} \cdot t) = 1 - \exp(-2.28 \times 10^{-6} \text{ h}^{-1} \cdot 500 \text{ h}) = 1.14 \times 10^{-3}$$

$$q_s = E(\Psi) = E(x_1 \cdot x_2 + x_3 - x_1 \cdot x_2 \cdot x_3)$$

$$= 2.64 \times 10^{-5} + 1.14 \times 10^{-3} - 3.01 \times 10^{-8} = 1.17 \times 10^{-3}$$

where the contribution of the CCF is 97.4 %.

- (c) Equation (9.90) gives

$$u_{in} = 3.70 \times 10^{-3} \quad \text{and} \quad u_{CCF} = 8.20 \times 10^{-4}$$

We obtain from the structure function

$$u_s = E(\Psi) = E(x_1 \cdot x_2 + x_3 - x_1 \cdot x_2 \cdot x_3)$$

$$= 1.37 \times 10^{-5} + 8.20 \times 10^{-4} - 1.12 \times 10^{-8} = 8.34 \times 10^{-4}$$

□

9.7 Human Error

In the preceding sections only failures of technical components were treated. This is not enough for the analysis of a technical system. Building, operating and maintaining a technical plant requires human interventions. The extent to which these are necessary depends on the degree of automation of the plant. In general

there is a tendency to increase the degree of automation. Nevertheless the contribution of human error to accidents remains substantial. For the accident sequences investigated in [51] its contribution amounts to about 30 % on the average reaching up to 70 % in some cases. On the other hand the possibility exists that accident sequences may be terminated by adequate human intervention or at least their consequences be reduced. In the context of probabilistic analyses human intervention and, in particular, the possibility of committing errors must be quantified. For this purpose human errors are treated in analogy with component failures, i.e. they are introduced into the fault tree as primary events [52]. It goes without saying that this can only be an approximation since human behaviour cannot be standardized like the operating behaviour of technical components.

Human error is defined as an act outside the tolerance bounds. These are determined by the technical boundary conditions and may therefore be influenced—within limits—by the designer in the sense that the tolerance region becomes large (fault-tolerant design). This reduces the probability of human error.

Before dealing with modelling human error, a classification of errors is useful. This can be done in many ways. A universally accepted classification does not exist. In what follows the classifications of [52] are presented. Accordingly two broad categories of human error may be distinguished:

- human error due to the work environment, and
- human error rooted in the personality (e.g. physical constitution, skills, motivations, expectations) or caused by factors which may be influenced by personal decisions (e.g. drinking of alcohol).

Systems analysis usually only deals with human error due to the work environment. The following classification can be found for this. It is based on the possibilities for human error derived from the ways of human information processing [52].

- Error of omission: failure to initiate performance of a system-required task or action;
- Error of commission: incorrect performance of a system-required task or action, given that the task or action is attempted, or the performance of some extraneous task or action which is not required by the system and which has the potential for contributing to some system-defined failure;
- Error of sequence: performance of a task or action disregarding the correct sequence;
- Time error: performance of a task or action outside the fixed time (e.g. too slow, too fast, too late);
- Extraneous task: task or action which is not required by the system and which has the potential for contributing to some system-defined failure.

The actions mentioned above are composed of one or several tasks or steps. Intentional errors such as sabotage are normally not addressed, since their probability can virtually not be determined.

Furthermore the following distinctions are useful:

- random error: act outside the tolerance limits not following a given scheme;
- systematic error: act outside the tolerance limits following a given scheme;
- sporadic errors: rare acts outside the tolerance limits.

Errors made by humans when interacting with technical plants do not always have to impair them seriously. This is especially true for so-called fault-tolerant or fault-forgiving systems. Thus, only errors are of interest here which have detrimental consequences.

The basic approach to determining a probability for a human error, q_H , is statistical observation. We use

$$\hat{q}_H = \frac{m}{N} \quad (9.115)$$

In Eq. (9.115) m is the number of failures made in realizing a certain task and N the number of opportunities of committing such an error. The tasks and actions are assigned to different categories of behaviour. However, probabilities from observation cannot be assigned with equal ease to any of the categories:

- skill-based actions or behaviour (quantification possible);
- rule-based actions or behaviour (quantification possible);
- knowledge-based actions or behaviour (quantification mostly impossible).

According to [53] these categories of behaviour are defined as follows:

- *skill-based actions or behaviour* The performance of more or less subconscious routines governed by stored patterns of behaviour, e.g. the performance of memorized immediate emergency actions to control an incipient runaway or an initiating event like stirrer failure, or the use of a hand tool by a person experienced with the tool. The distinction between skill-based actions and rule-based actions is often arbitrary, but is primarily in terms of the amount of conscious effort involved; in a layman's terms, the amount of "thinking" required.
- *rule-based actions or behaviour* Behaviour in which a person follows remembered or written rules, e.g. performance of written post-diagnosis actions or calibrating an instrument or using a checklist to restore manual valves to their normal operating status after maintenance. Rule-based tasks are usually classified as step-by-step tasks unless the operators have to continually divide their attention among several such tasks without specific written cues each time they should shift attention to a different task. In the latter case, in which there is considerable reliance on memory, the overall combination may be classified as a dynamic task, especially in a post accident condition.
- *knowledge-based actions or behaviour* This is understood to be the behaviour in novel situations which require the operator to find solutions to problems. After

identifying the characteristics of the disturbance necessary actions are derived from general objectives and the actions are planned based on the operator's knowledge of the functional and physical properties of the system and its dynamic behaviour.

9.7.1 Procedure for Analyzing Human Actions

For analyzing human actions in operating technical plants usually the following steps are carried out:

- plant familiarization:
 - collection of information,
 - plant visit,
 - examination of operating regulations/information from technical systems analysis.
- qualitative evaluation:
 - determination of requirements for the action (or task),
 - valuation of the circumstances for carrying out the action,
 - fixing of the objectives,
 - identification of performance shaping factors and interactions influencing human actions,
 - identification of the potential for human error,
 - modelling of human actions.
- quantitative evaluation
 - determination of probabilities for human error,
 - quantification of performance shaping factors and interactions,
 - assignment of probabilities for error recovery (possibly by a second person),
 - implementation in the technical systems analysis (e.g. as a primary event in a fault tree).

It is fundamental for assessing human error in systems analyses to identify and describe the human acts with importance for the event sequence under analysis (qualitative assessment). This corresponds to the task analyses, which are characteristic of ergonomic studies. Firstly, the important actions, the moment in time at which they are required and the time period available for their execution have to be determined. Furthermore, the requirements for the action, the information necessary, respectively available, the possibilities of correction in case of omission or faulty execution must be established. Additionally, other factors of important influence on human reliability such as the state of knowledge on the process in question, ergonomically favourable or disadvantageous layout of the workplace, the tools or the environment are identified. On the basis of this task analysis reliability data (normally failure probabilities on demand) are assigned to the tasks identified. They stem from existing data collections (cf. Table 9.21).

Table 9.21 Excerpt of data for quantifying human error with indication of the 5th percentile, q_{05} , the median, q_{50} , and the 95th percentile, q_{95} (according to [52])

Action	Basic failure probability		
	q_{H05}	q_{H50}	q_{H95}
Response to an alarm with signal horn and light signal	0.00005	0.0001	0.001
Reading of an analogue meter	0.001	0.003	0.01
Reading of a digital meter	0.0005	0.001	0.005
Discovery of an instrument failure, if there is no failure signal	0.02	0.1	0.2
Changing of the position of a manual valve			
- with position indicator on the valve	0.0005	0.001	0.01
- with position indicator away from the valve	0.001	0.002	0.01
- without position indicator	0.003	0.01	0.1
General human error (error of omission or commission)	0.0033	0.01	0.03
Discovery of the wrong position of a valve on control without a checklist	0.1	0.5	0.9

The uncertainties of the failure probabilities are treated using log-normal distributions (vid. Sect. 9.3.4 and Appendix C). Since this distribution is defined on $[0, \infty]$ this is an inappropriate choice for a probability, which is defined on $[0, 1]$. The choice is explained historically.

The values from [52] apply for “optimal” conditions. If conditions are not optimal, they are modified by multipliers >1 . These are called performance shaping factors (PSF) and determined on the basis of an assessment of the impact of the circumstances for the action.

If no data are available for complex sequences of actions, these must be decomposed into individual steps down to the level at which data are available. If no probabilities can be encountered for a step to be assessed recourse must be had to analogies or estimates (vid. Case Study 9.1).

During the elaboration of a fault tree the identified and analyzed human actions are assigned to the corresponding systems and components.

It is important for the assessment to account for possible dependencies. Such dependencies can exist both between the actions of several persons and several consecutive actions performed by one and the same person (e.g. because of high stress).

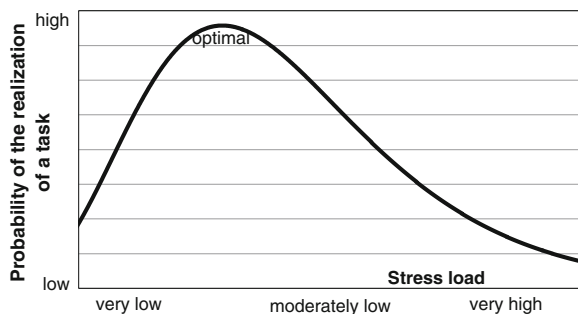
For analyzing and quantifying human error nowadays mostly the **Technique for Human Error Rate Prediction (THERP)** procedure is applied. The method is documented in [52] along with a comprehensive data collection. Despite numerous further developments in the field it remains the procedure most suitable for practical applications.

9.7.2 Important Factors of Influence on Human Reliability

In what follows several important factors of influence on human reliability are briefly presented and hints are given on important aspects for analysis and quantification.

- **Ergonomic layout of the control room:** An increase of failure probabilities is to be assumed if the arrangement, labelling and design of the control mechanism are such that error is enhanced. This may be the case, for example, if stereotypes are violated, or if labelling of instruments and buttons is confusing or hardly legible. A stereotype is the expected reaction of a human to an outside influence. For example, green (as with a traffic light) is associated with the expectation of safety, no danger etc. With electric equipment turning a button in a clockwise direction is associated with “more”, “stronger”, “louder” (stereotype of movement).
- **Feedback through indications and alarms:** The probability of human failure is reduced, if feedback through indications and alarms, which render the detection of an error probable, exists. The possibility of the discovery of an error is to be taken into account especially if the operator is warned immediately after committing it. This gives the opportunity for correction and applies most of all if system response to the error is rapid. Errors causing only slow variations of the process parameters are detected with correspondingly lower probability.
- **Human redundancy:** A further important way of detecting errors results from human redundancy, i.e. a decision or an act involves more than one person with adequate qualification. Redundancy is assumed as well if a person's acts are also controlled by another person. The requirement of diversity is always satisfied with human redundancy given the differences between persons. However, in contrast with technical components the possibility of mutual influence has to be considered (see below).
- **Psychical stress:** In assessing human error it has to be taken into consideration whether the plant personnel is under stress or not. Figure 9.37 shows the hypothetical relationship between stress and human reliability (probability of successfully carrying out a task).

Fig. 9.37 Hypothetical relationship between the probability of the realization of a task and the existing stress level (according to [52])



Optimum reliability is attained accordingly in case of moderate stress, which is high enough to fully capture the operator's attention.

Low stress decreases the attentiveness because uninteresting and little exacting tasks cause a decrease of attention. Low stress is applicable, for example, to routine control walks.

An optimum stress level exists in routine operations in the control room during normal operation of a plant, maintenance, and functional tests. These activities do not lead to excessive adaptation nor are they too simple and boring. Therefore reliable performance can be assumed.

Very high stress and hence a high probability for human error prevails shortly after the occurrence of an accident. With increasing time after the accident lower probabilities for human error may be assumed, in case the plant is brought under control by appropriate automatic or human interventions during accident progression thereby gradually reducing the stress level.

- **Qualification and training of operators:** It may normally be assumed that the staff of complex technical installations is carefully selected and hence has a sufficient qualification.

This may not apply to the same extent to training of the personnel. One has to distinguish between training before starting to work in the plant, hence the preparation for plant-specific tasks, and recurrent training aimed at maintaining the skills and knowledge. Whilst often efficient training before employment of personnel takes place, recurrent training is not so frequent. The latter has considerable importance for maintaining the necessary knowledge, especially for handling accident situations.

Frequently the effectiveness of existing training programmes is not checked. The quality and recurrence of training has therefore to be taken into account in assessing the reliability of the plant personnel.

- **Written instructions:** Normally lower failure probabilities are assumed for actions based on written instructions. Criteria to assess the quality of written instructions are, for example, good readability and clarity. If instructions concern actions for accident handling, additionally ready access, updating and clearness should be taken into account. Furthermore it should be noted that written instructions exonerate the operator, should the result of following them be negative.
- **Dependence of human acts:** An important influence factor in assessing human reliability is the interdependence of human acts. Two types are distinguished here: direct and indirect dependence.

There is direct dependence if the interdependence is between several acts. Similar tasks carried out by the same operator one after another may serve as an example (e.g. activation of two components, one immediately after the other). Indirect dependence implies that there is interdependence between several acts and a factor of common influence. Such a factor may, for example, be a measuring device wrongly set or calibrated, which is used to calibrate measuring channels.

Complete independence of human acts is to be expected if they are totally different or carried out considerably separated as to place and time. This implies, contrary to technical components where the same component is always represented by the same binary variable, that each human action satisfying the above condition is represented by a binary variable of its own. Humans are “self-repairing”.

According to [52] dependencies between actions carried out by one and the same person or actions jointly carried out by several persons (e.g. in the control room) are treated by different levels of dependence. One uses for the probability of a failure of the Nth task under the condition that the preceding task failed the following relationships for the different levels of dependence:

- zero dependence (according to Table 9.21):

$$q_{H,N} = q_{H50} \quad (9.116)$$

- low dependence:

$$q_{H,N} = \frac{1 + 19 \cdot q_{H50}}{20} \quad (9.117)$$

- moderate dependence:

$$q_{H,N} = \frac{1 + 6 \cdot q_{H50}}{7} \quad (9.118)$$

- high dependence:

$$q_{H,N} = \frac{1 + q_{H50}}{2} \quad (9.119)$$

- complete dependence:

$$q_{H,N} = 1 \quad (9.120)$$

The procedure described above in general is now illustrated by the following examples.

Example 9.28 Human error event tree of a hypothetical calibration task (according to [52])

The human error event tree of Fig. 9.38 describes a calibration procedure. A technician checks the setpoint values of three measuring devices. In the first place he has to adjust his test equipment. In doing this he might make a mistake which would entail a wrong calibration of all three measuring devices. As probability of

wrongly adjusting the test equipment $A = 0.01$ is used. This leads to the following event sequence.

It is assumed that the technician modifies the setpoint of the first measuring device due to the wrong adjustment of the test equipment ($B = 1$; complementary probability $b = 0$). If he then notices that the setpoint of the second measuring device has to be modified as well it is assumed that with a probability of 0.9 doubts as to the correct adjustment of the test equipment might arise. He would then check the test equipment with a probability of $c = 0.9$. If he has no doubt ($C = 0.1$) it is assumed that the conditional probability for modifying the setpoint of the third measuring device as well is $D = 1$. Thus we obtain a probability for a wrong setpoint of all three measuring devices of

$$q_H = 0.01 \cdot 1 \cdot 0.1 \cdot 1 = 0.001$$

Because medians have been multiplied with one another the result is not a median. This stems from several mathematical flaws which accompanied the development of the method. Instead of medians mean values should be used, because their sums and products (in case of independence only) lead to a result which is a mean value, too.

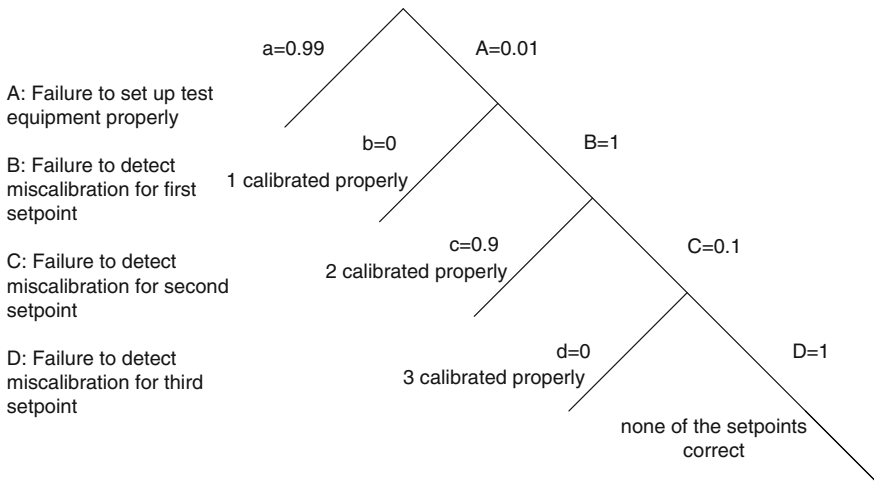


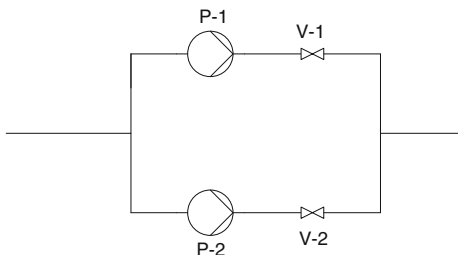
Fig. 9.38 Human error event tree for the wrong calibration of three measuring devices



Example 9.29 Human error in starting a pump

A system consists of two pumps (vid. Fig. 9.39). One of them is in standby as a reserve. The failure rate of each pump is $\lambda = 1.6 \times 10^{-5} \text{ h}^{-1}$ and that of each valve $\lambda = 1.0 \times 10^{-6} \text{ h}^{-1}$. The undesired event is that there is no flow. Calculate its probability for $t = 1,000 \text{ h}$.

Fig. 9.39 Example system with two pumps

**Solution**

We assume that the undesired event can only occur in case of pump failure or valve failure in closed position or both. A failure of the fluid supply to the system, pipe rupture or lack of information on the failure of the main pump as well as CCF because of technical failure and reserve pump starting failure are excluded for the sake of the example.

This leads to the fault tree of Fig. 9.40.

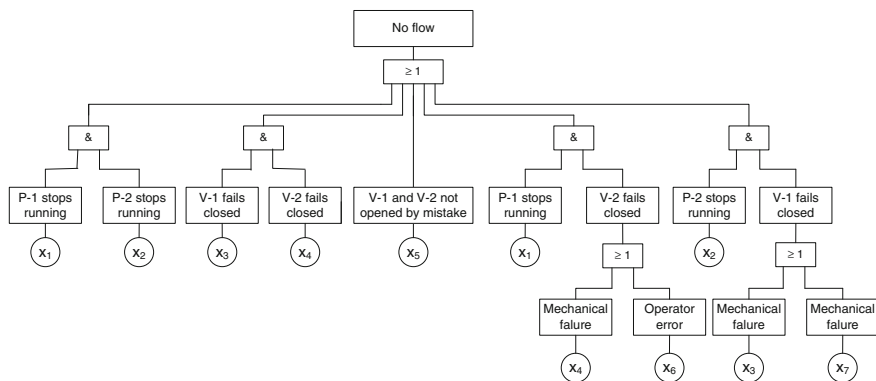


Fig. 9.40 Fault tree for a system of two pumps

The fault tree has the following minimal cut sets:

$$\begin{aligned} K_1 &= x_1 \cdot x_2; K_2 = x_3 \cdot x_4; K_3 = x_5; K_4 = x_1 \cdot x_4; K_5 = x_1 \cdot x_6; K_6 = x_2 \cdot x_3; \\ K_7 &= x_2 \cdot x_7 \end{aligned}$$

In developing the fault tree it was considered that after a functional test of the valves one might forget to open them again. This may occur independently ($q_{H50} = 0.01$, $q_{H05} = 0.0033$, $q_{H95} = 0.03$) or dependently. The mean value obtained from the preceding percentiles assuming a log-normal distribution is $q_H = 0.0125$.

Low dependence according to Eq. (9.112) is assumed for not opening both valves, where instead of the median the mean value is used in Eq. (9.112). This gives

$$q_{H,dependence} = q_H \cdot q_{H,2} = 0.0125 \cdot \frac{1 + 19 \cdot q_H}{20} = 0.0125 \cdot 0.062 = 0.000775$$

On quantifying the fault tree one has to observe that the probability of opening a single valve under the condition that the other one was opened must be used. It is

$$q'_H = q_H - q_{H,dependence} = 0.012$$

The probabilities of the minimal cut sets are obtained with the values for human error and the failure probabilities according to Eq. (9.25) as follows

$$\begin{aligned} E(\kappa_1) &= 2.52 \times 10^{-4}; E(\kappa_2) = 9.99 \times 10^{-7}; E(\kappa_3) = 7.75 \times 10^{-4}; E(\kappa_4) = 1.59 \times 10^{-5} \\ E(\kappa_5) &= 1.90 \times 10^{-4}; E(\kappa_6) = 1.59 \times 10^{-5}; E(\kappa_7) = 1.90 \times 10^{-4} \end{aligned}$$

The approximate failure probability of the system is calculated with Eq. (9.75), which gives

$$q_s = 1.44 \times 10^{-3}$$

It can easily be seen that the contribution of the minimal cut sets containing human error is 80.2 %.

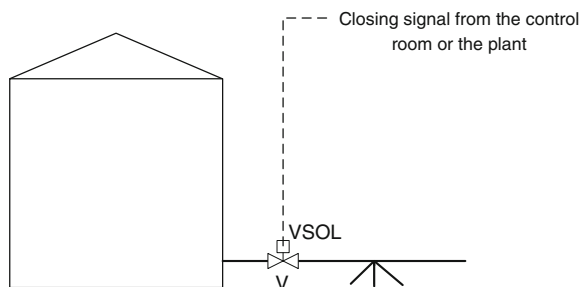
If high dependence according to Eq. (9.119) were assumed one would obtain

$$q_{H,dependence} = 0.0125 \cdot \frac{1 + 0.0125}{2} = 0.0063$$

and a final result of

$$q_s = 6.78 \times 10^{-3}$$

Fig. 9.41 Schematic representation of the storage tank and the pipe



In the latter case human error contributes 95.8 % to the failure probability. Hence, the assessment of the degree of dependence has a major influence on the final result in this case. $\square$

Case study 9.1 Isolation of a leak in an ammonia pipe [54]

The system shown in Fig. 9.25 serves for transporting ammonia at a temperature of $-30\text{ }^{\circ}\text{C}$ to a pressurized storage downstream, which supplies ammonia to a production process. A spontaneous rupture of the pipe is expected to occur with a frequency $2.7 \times 10^{-2} \text{ a}^{-1}$ and an uncertainty factor of $K_{95} = 10$. If the location of the rupture is such that the leak can be isolated larger releases of ammonia and accompanying health damage of the personnel can be prevented by closing the pneumatic valve V.

Valve V can be closed

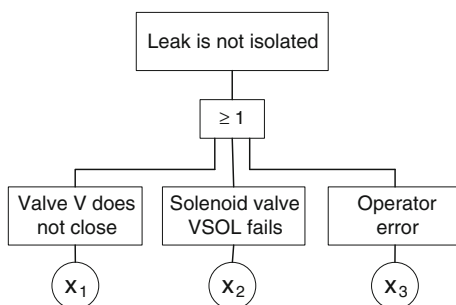
- locally (six places) or
- from the control room.

Two operators are present day and night. One of them is to leave the control room and to walk through the plant once every hour. The walk-around takes 10 min (Fig. 9.41).

Fault tree representation

The probability that the leak is not isolated can be assessed using the fault tree which is shown in Fig. 9.42.

Fig. 9.42 Fault tree for calculating the probability that the leak is not isolated



The leak is not isolated if

- valve V is stuck and can therefore not be closed (primary event x_1) or
- the solenoid valve VSOL fails (primary event x_2) or
- the operator does not push the button for closing the valve (primary event x_3)

Reliability data for technical components

For quantifying the fault tree the following reliability data are used:

- pneumatic valve: $\lambda = 18.6 \times 10^{-6} \text{ h}^{-1}$ ($K_{95} = 5$)
- solenoid valve: $\lambda = 13.0 \times 10^{-6} \text{ h}^{-1}$ ($K_{95} = 5$)

Frequent operational demands on the valve allow one to make the assumption that at least once per week its correct functioning is checked (operational demand as an equivalent for functional test). The unavailability is then approximated according to $u \cong (\lambda \cdot \theta)/2$ in Eq. (9.90) with $\theta = 168 \text{ h}$ giving:

- pneumatic valve: $u_1 = 0.0016$ and solenoid valve: $u_2 = 0.0011$

Calculation of the probability of the operator failing to actuate the valve

The following tasks have to be performed after the leak has occurred:

(1) Detection of the leak

It is conceivable to see that the leak has occurred, but only at daytime and if the operator looks out of the window or his colleague is on his walk-around. Therefore it is assumed conservatively that the leak is only detected by an increased smell of ammonia. An assessment showed that the threshold of smell perception is reached in the control room after about 5 min.

(2) Closing of valve V

According to the operating manual valve V has to be closed whenever a stronger than usual smell of ammonia is perceived. This is a safety-gearred measure. A conflict of interests is not possible because the production is not affected by a temporary interruption of ammonia flow to the pressurized storage, which in turn supplies the production process. The pressurized storage contains sufficient ammonia for several days of operation. For this reason closing the valve because of a false alarm would not be problematic.

The task is relatively simple. Yet, the event tree model has to account for the fact that we are dealing with a case of human redundancy (two operators). The event tree is presented in Fig. 9.27 and explained in what follows.

As already mentioned the smell of ammonia becomes so strong after five minutes that the operator who works permanently in the control room (main operator) might diagnose it to be caused by a leak. It is estimated that the

probability of not believing that the origin of the smell is a leak is 0.0013 (this is an analogy of a datum for not observing a compelling signal given in [52]). Since at this point in time the cause of the increased smell is still unclear the resulting high stress is accounted for by multiplying this probability with a performance shaping factor of 5. Therefore the value used in the evaluation is $q_H = 0.0065$ ($K_{95} = 3$).

The main operator then fails to close the valve with a probability of 0.016. Again a stress factor of 5 is applied because it is not yet clear whether the leak is located such that it can be isolated or not so that $q_H = 0.08$ ($K_{95} = 5$) is used.

The second operator may either be inside the control room or on his inspection walk. He is assumed to comply with his duty only with a probability of 0.5. He spends 5/6 of the remaining time inside the control room as well so that the total probability of being outdoors is

$$1 - (0.5 + 0.5 \cdot 5/6) \approx 0.08$$

An error factor of $K_{95} = 2$ is considered appropriate.

If the second operator is inside the control room his decision on whether the increased smell of ammonia is caused by a leak or not is influenced by the opinion of his colleague. If the main operator denies the existence of a leak, high dependence of the opinion forming process of the second operator is assumed. The corresponding model of Eq. (9.119) gives a conditional probability of 0.55 ($K_{95} = 2$). If, on the other hand, the second operator is convinced that there is a leak (complementary probability to the foregoing assessment) he carries out the task of closing analogously to his colleague, if he had diagnosed the situation as a leak, as explained above.

If the second operator is outdoors he will analyze the situation the same way as the main operator, because in this case the two operators would act independently.

The evaluation of the event tree of Fig. 9.43 leads to a probability of the valve not being closed of

$$u_{EB} = 0.083 \quad (K_{95} = 4.41)$$

Probability of a major release

Using the failure probabilities on demand (unavailabilities) for the technical components and the probability of human error we obtain a total probability for the leak not being isolated of

$$u_{\text{total}} = u_1 + u_2 + u_{EB} - u_1 u_2 - u_1 u_{EB} - u_2 u_{EB} + u_1 u_2 u_{EB} = 0.0855.$$

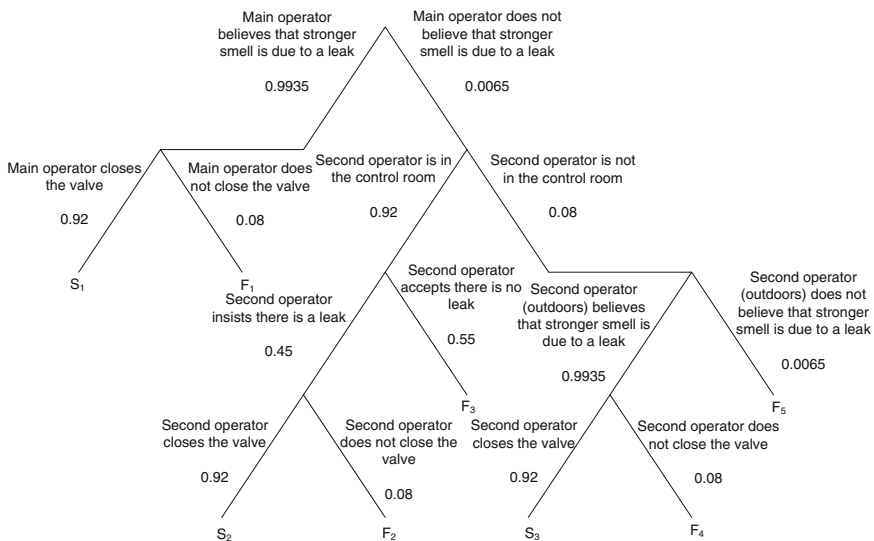
The evaluation accounts for the fact that the events are not mutually exclusive [cf. Eq. (9.62)]. The contribution of human error amounts to about 97 % in this case.

The expected frequency for the leak not being isolated then amounts to

$$H = 2.7 \times 10^{-2} \text{ a}^{-1} \cdot 0.0855 = 2.3 \times 10^{-3} \text{ a}^{-1}.$$

Uncertainties are accounted for by a Monte Carlo calculation (vid. Example 4.5) with $N = 5,000,000$ trials. The characteristic values of the distribution of the result are:

5th percentile	$4.74 \times 10^{-5} \text{ a}^{-1}$
Median	$6.52 \times 10^{-4} \text{ a}^{-1}$
Expected value	$2.32 \times 10^{-3} \text{ a}^{-1}$
95th percentile	$8.95 \times 10^{-3} \text{ a}^{-1}$
Error factor K_{95}	13.7



$$F = F_1 + F_2 + F_3 + F_4 + F_5 = 0.9935 \cdot 0.08 + 0.0065 \cdot 0.92 \cdot 0.45 \cdot 0.08 + 0.0065 \cdot 0.92 \cdot 0.55 + 0.0065 \cdot 0.08 \cdot 0.9935 \cdot 0.08 + 0.0065 \cdot 0.08 \cdot 0.0065 \approx 0.083$$

$$S = S_1 + S_2 + S_3 = 0.9935 \cdot 0.92 + 0.0065 \cdot 0.92 \cdot 0.45 \cdot 0.92 + 0.0065 \cdot 0.08 \cdot 0.9935 \cdot 0.92 \approx 0.917$$

$$F + S = 1$$

Fig. 9.43 Event tree for assessing human error (primary event x_3 in the fault tree of Fig. 9.42; S success, F failure)



Example 9.30 Fault tree model of a system with a cold reserve

A system consists of an operating and a reserve pump. It is to be modelled by a fault tree. The result should be compared with that from Eq. (9.79).

Two system configurations are to be distinguished:

1. The reserve pump is switched on by the operator
2. The reserve pump is switched on automatically

Data:

Probability for human error

No reaction to the alarm/reserve pump is not started: $q_H = 0.0015$

Failure rates:

Signal horn fails	$\lambda = 9.7 \times 10^{-6} \text{ h}^{-1}$
Flow switch or alarm fails	$\lambda = 92.7 \times 10^{-6} \text{ h}^{-1}$
Reserve pump does not start	$\lambda = 13.0 \times 10^{-6} \text{ h}^{-1}$
Failure of operating pump	$\lambda = 44.0 \times 10^{-6} \text{ h}^{-1}$
Mission time (reference time)	$t = 720 \text{ h}$
Time periods between functional tests	$\theta = 720 \text{ h}$

Solution

According to Eq. (9.79) we have

$$\begin{aligned}
 q_S(t) &= 1 - e^{-\lambda \cdot t} \cdot (1 + \lambda \cdot t) = 1 - \exp(-44.0 \times 10^{-6} \text{ h}^{-1} \cdot 720 \text{ h}) \\
 &\quad \times (1 + 44.0 \times 10^{-6} \text{ h}^{-1} \cdot 720 \text{ h}) \\
 &= 4.91 \times 10^{-4}
 \end{aligned}$$

A more realistic treatment of the problem leads to the fault trees of Fig. 9.44.

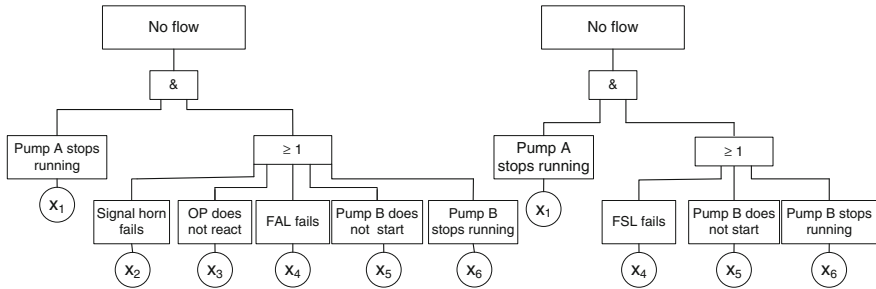


Fig. 9.44 Fault trees for the failure of a system with two pumps (*left* activation of the reserve pump by the operator; *right* automatic activation of the reserve pump)

Table 9.22 contains the data for evaluating the fault trees of Fig. 9.44 and Table 9.23 the corresponding minimal cut sets and their evaluation in terms of probabilities.

A probability of 1 is attached to the initiating event. Thereafter it is multiplied by the expected annual frequency of its occurrence.

The expected frequency of the undesired event in case of activation by the operator is calculated using Eq. (9.75), which gives

Table 9.22 Data for evaluating the fault trees of Fig. 9.44

Primary event	Description	Failure rate λ in 10^{-6} h^{-1}	Unavailability according to Eq. (9.90)
x_1	Pump A stops running ^b	44.0	0.385 a^{-1b}
x_2	Signal horn fails	9.7	3.48×10^{-3}
x_3	Operator (OP) does not react	$q_H = 0.0015^a$	0.0015
x_4	FAL/FSL fails	92.7	3.26×10^{-2}
x_5	Pump B does not start	13.0	4.67×10^{-3}
x_6	Pump B stops running	44.0	1.57×10^{-2}

^aFailure probability q_H ^bInitiating event, hence expected frequency of $44 \times 10^{-6} \text{ h}^{-1} \cdot 8,760 \text{ h a}^{-1}$ **Table 9.23** Probabilities of the minimal cut sets

Start of the reserve pump by the operator	Automatic start of the reserve pump
Expected values of the minimal cut sets	Expected values of the minimal cut sets
$E(\kappa_1) = E(x_1 \cdot x_2) = 3.48 \times 10^{-3}$	$E(\kappa_1) = E(x_1 \cdot x_4) = 3.26 \times 10^{-2}$
$E(\kappa_2) = E(x_1 \cdot x_3) = 0.0015$	$E(\kappa_2) = E(x_1 \cdot x_5) = 4.67 \times 10^{-3}$
$E(\kappa_3) = E(x_1 \cdot x_4) = 3.26 \times 10^{-2}$	$E(\kappa_3) = E(x_1 \cdot x_6) = 1.57 \times 10^{-2}$
$E(\kappa_4) = E(x_1 \cdot x_5) = 4.67 \times 10^{-3}$	
$E(\kappa_5) = E(x_1 \cdot x_6) = 1.57 \times 10^{-2}$	

$$E[\Psi(x_1, \dots, x_6)] \approx 0.385 \text{ a}^{-1} \cdot (3.48 \times 10^{-3} + 0.0015 + 3.26 \times 10^{-2} + 4.67 \times 10^{-3} + 1.57 \times 10^{-2}) = 5.8 \times 10^{-2} \text{ a}^{-1}$$

The expected frequency of the undesired event in the case of the automatic activation of the reserve pump amounts to

$$E[\Psi(x_1, x_4, x_5, x_6)] \approx 0.385 \text{ a}^{-1} \cdot (3.26 \times 10^{-2} + 4.67 \times 10^{-3} + 1.57 \times 10^{-2}) = 5.3 \times 10^{-2} \text{ a}^{-1}$$

Apparently automation is slightly better (active countermeasure instead of organizational/technical, cf. Sect. 4.2).

Furthermore it is evident that treating the system according to Eq. (9.79) leads to a more favourable result for the system. The reason is that necessary elements like information for activation of the reserve pump and its possible starting failure

are neglected. Additionally, the static method of fault tree analysis does not enable one to assign merely the residual running time after the failure of the main pump to the reserve pump. This is, however, done by the convolution integral in Eqs. (9.77)–(9.79). We rather use an operating time of 720 h for both pumps. □

Example 9.31 Modelling the protection of a tank against overfilling

The filling of a tank is monitored with the help of a level indicator with alarm LIA by the operator. The written operating instruction states that the pump P has to be switched off on alarm and the valve V has to be closed. For safety reasons an additional level switch LSHH is installed. It turns off the pump and closes the valve automatically. However, as in case of the Buncefield accident (vid. Table 1.1) it may remain in a deactivated position.

It is assumed conservatively that a successful termination of the filling process requires the valve to be closed and the pump to be stopped.

Furthermore it is assumed, that the tank is filled once per week ($h = 52 \text{ a}^{-1}$) and that the safety equipment is tested once per year. The flow sheet of the tank and the fault tree model are shown in Fig. 9.45. The data for quantifying the fault tree are found in Table 9.24.

Solution

The fault tree shows that both the operating level safeguard of the filling process and the automatic trip via LSHH have to fail in order for overfilling to occur.

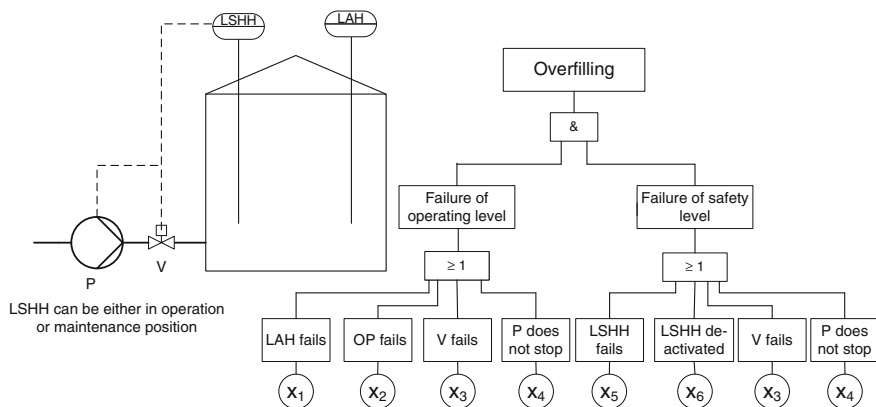


Fig. 9.45 Flow sheet and fault tree for the failure of the overfilling protection of a tank

Table 9.24 Data for quantifying the fault tree of Fig. 9.45

x_i		Primary event	Failure rate λ in 10^{-6} h^{-1}	Time between functional tests θ in h	Unavailability u_i according to Eq. (9.90)
x_1	LIA	Level alarm	22.2	168	1.9×10^{-3}
x_2	OP	Pump is not switched off by the operator	0.002*		0.002
x_3	V	Valve does not close	4.2	168	3.5×10^{-4}
x_4	P	Pump does not stop	9.6	168	8.1×10^{-4}
x_5	LSHH	Level switch fails	176.0	8760	0.49
x_6	LSHH deactivated	Level switch remains in maintenance position (deactivated)	0.002*		0.002

*probability

The analysis of the fault tree of Fig. 9.45 leads to the following minimal cut sets:

$$K_1 = x_1 \cdot x_5; K_2 = x_2 \cdot x_5; K_3 = x_1 \cdot x_6; K_4 = x_2 \cdot x_6; K_5 = x_3; K_6 = x_4$$

The expected value of the structure function and hence the unavailability of the operational safeguard and the safety trip amounts to

$$E[\Psi(x_1, \dots, x_6)] \approx \sum_{i=1}^5 E[k_i] = u_1 \cdot u_5 + u_2 \cdot u_5 + u_1 \cdot u_6 + u_2 \cdot u_6 + u_3 + u_4 = 0.0031$$

Events involving the deactivation position of the levels switch LSHH contribute 2.5×10^{-3} to the total unavailability.

The expected frequency of tank overfilling amounts to

$$H = 52 \text{ a}^{-1} \cdot 0.0031 = 0.16 \text{ a}^{-1}$$

If the conservative assumption that the pump must stop and the valve must close, is replaced by requiring that either the pump stops or the valve closes, we obtain the following minimal cut sets

$$K_1 = x_1 \cdot x_5; K_2 = x_2 \cdot x_5; K_3 = x_1 \cdot x_6; K_4 = x_2 \cdot x_6; K_5 = x_3 \cdot x_4$$

The expected frequency of tank overfilling then is

$$H' = 52 \text{ a}^{-1} \cdot 0.0019 = 0.099 \text{ a}^{-1}$$

This is a reduction to 62 % of the original result and demonstrates the influence of model assumptions on the result.

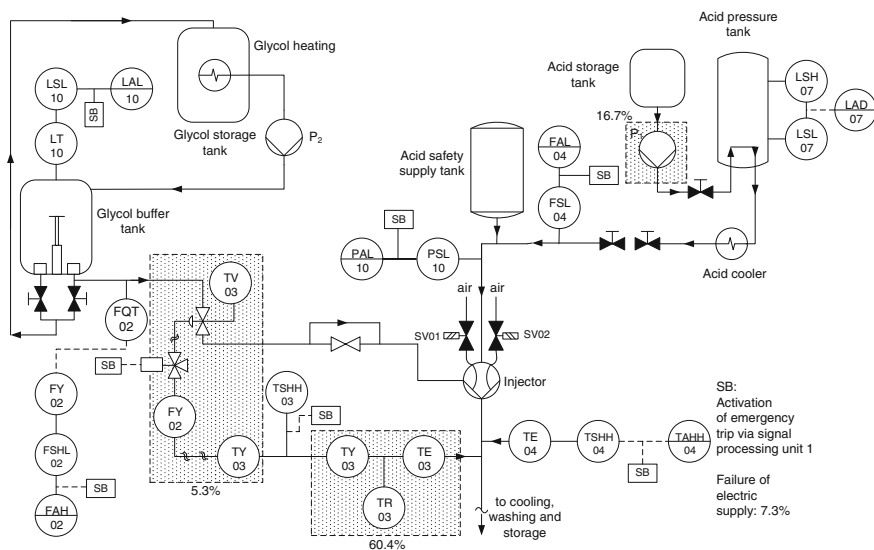


Fig. 9.46 P&I diagram of the continuous production of nitroglycol and relevant contributions to the expected frequency of an explosion (according to [55])

□

9.8 Case Studies

9.8.1 Fault Tree for the Trip System of a Plant for Producing Nitroglycol [2]

Process description and safety system

Figure 9.46 shows the P&I diagram of part of a plant for the continuous production of nitroglycol according to the injector nitration process (similar to a jet pump). The feed materials for the reaction are mixed acid (26 % of concentrated nitric acid, 62 % of oleum, 10 % H₂O and 2 % of nitroglycol from the spent acid recirculation) and glycol.

The nitrating acid is driven through the injector from the acid pressure tank, which is kept under a pressure of 500 kPa. Before that it is cooled to 0 °C in the acid cooler. It then sucks the glycol via control valve TV3 from the glycol buffer tank, where the glycol is heated to 30 °C. The exothermic reaction between glycol and acid is almost instantaneous (1–1.5 s). The explosive nitroglycol is produced, which forms an emulsion with the acid not consumed in the reaction. This emulsion is subsequently cooled and nitroglycol is separated from the spent acid in a centrifuge. The acidic nitroglycol is then mixed with a caustic solution and

washed in a washing column. After being separated from the soda solution the nitroglycol is stored.

The reaction conditions are practically adiabatic; the injector outlet temperature lies between 46 and 48 °C.

The reaction temperature is controlled by varying the glycol mass flow within a tolerance range around the setpoint corresponding to the fixed mass flow of nitrating acid. For this purpose the pneumatic control valve in the glycol line TV03 is activated by the temperature measurement T03 (TE03, TY03, TA03).

Fulfilment of the following conditions is essential for safe production, i.e. avoiding an explosion:

1. Maintaining an excess of nitrating acid corresponding to the glycol mass flow.
2. Not exceeding the upper limit of reaction temperature of about 52 °C.
3. Ensuring stable flow conditions in the injector.
4. Ensuring a composition of the nitrating acid according to specification.

In order to make sure that the above conditions are satisfied the following safety equipment is installed:

1. Acid feed

- interlock of the acid pump P1, which avoids start-up of the plant if the pump is switched off;
- pressure switch PSL 10 directly in front of the injector, which activates reactor trip if the pressure is too low;
- monitoring of flow in front of the injector via FSL04, which activates reactor trip if the flow is too low;
- monitoring of the level in the pressure vessel via LSHL 07, which activates an alarm (LAD 07) following deviations of the level from its setpoints. Reactor trip is then to be activated manually by the operator.

2. Glycol feed

- flow monitoring in the feed line, which activates reactor trip via FSHL02, if glycol mass flow is too high or too low;
- level monitoring via LT 10 in the glycol tank, which activates reactor trip if the glycol level is too low.

3. Process temperature

- temperature switch TSHH03 in the measuring chain T03, which activates reactor trip if the temperature is too high;
- temperature measuring chain T04, which activates reactor trip if the reaction temperature is too high.

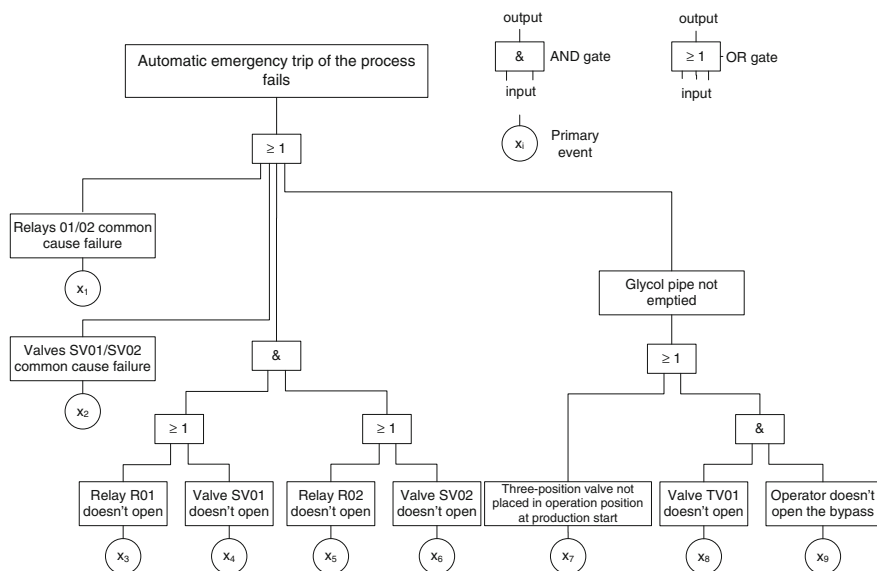


Fig. 9.47 Fault tree for an automatic reactor trip system (without activation)

4. Composition of the nitrating acid according to specification

- periodic sampling and analysis.

The trip is effected by compensating the underpressure (partial vacuum) in the injector by opening the redundant valves SV01 and SV02. In addition control valve TV03 is fully opened. Thus the glycol feed line empties its contents into the glycol tank. The idea behind this measure is to prevent a contact between glycol in the feed line and acid which might penetrate into it. The result would be the formation of nitroglycol with a high probability of exploding because of a lack of the necessary excess of acid.

Fault tree analysis

As seen from the fault tree of Fig. 9.47, where the activation of the reactor trip (denoted by SB in Fig. 9.46) was not included for avoiding too much complexity), the automatic reactor trip can fail for the following reasons:

- both (redundant) valves SV01 and SV02 do not open, because
 - relay R01 does not open (x_3) or
 - valve SV01 does not open (x_4)
 - and
 - relay R02 does not open (x_5) or
 - valve SV02 does not open (x_6)

or

– relays R01/R02 do not open because of a CCF (x_1)

or

– valves SV01/SV02 do not open because of a CCF (x_2)

Furthermore, reactor trip is not successful if the glycol feed line is not emptied, because

- valve TV03 does not open (x_8) or the plant operator does not manually open the bypass of this valve thus violating operating instructions (x_9)

or

- the three-position valve in the feed line was not brought into the position 'operation' when plant operation was started (x_7). In such a case glycol feed takes place through a pipe, which is equipped with a check valve thus impeding the feed line from being emptied in case of reactor trip.

Reliability data

The data of Table 9.25 were used for evaluating the fault tree of Fig. 9.47.

Evaluation of the fault tree

The fault tree has the following minimal cut sets:

$$K_1 = x_1; K_2 = x_2; K_3 = x_7; K_4 = x_3x_5; K_5 = x_8x_9; K_6 = x_4x_5; K_7 = x_3x_6; K_8 = x_4x_6$$

The corresponding unavailabilities are given in Table 9.26.

The total unavailability of the system results from Eq. (9.75) to give

Table 9.25 Data for evaluating the fault tree of Fig. 9.47

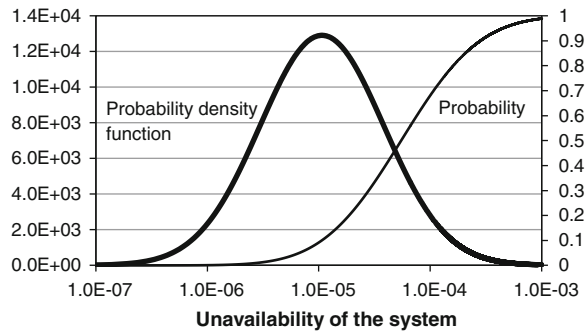
Primary event	Failure rate λ in 10^{-6} h^{-1}	Error factor K_{95}	Intervals between functional tests θ in h	Unavailability u according to Eq. (9.90)
x_1	1.06	3.4	8	4.22×10^{-6}
x_2	3.12	11	8	1.28×10^{-5}
x_3	10.6	3.4	8	4.03×10^{-5}
x_4	31.2	11	8	1.25×10^{-4}
x_5	10.1	3.4	8	4.03×10^{-5}
x_6	31.2	11	8	1.25×10^{-4}
x_7	0.00014*	17.8		0.00014
x_8	1.4	11	4	5.36×10^{-6}
x_9	0.0018*	6.2		0.0018

*probability

Table 9.26 Unavailabilities of the minimal cut sets of the fault tree of Fig. 9.47

Minimal cut set no.	Unavailability
1	4.22×10^{-6}
2	1.28×10^{-5}
3	1.4×10^{-4}
4	1.62×10^{-9}
5	9.65×10^{-9}
6	5.03×10^{-9}
7	5.03×10^{-9}
8	1.56×10^{-8}

Fig. 9.48 Probability distribution and pdf of the unavailability of the reactor trip system



$$E[\Psi(x_1, \dots, x_8)] \approx \sum_{n=1}^8 E(\kappa_n) = 1.57 \times 10^{-4}$$

It can easily be seen that the event x_7 (three-position valve not placed in operation position on start-up) dominates the unavailability with a contribution of 89 %. It represents a good starting point for system improvements.

If the uncertainties of the input data are accounted for, as described in Sect. 9.3.4, we obtain as 5th percentile 6.69×10^{-6} and as 95th percentile 4.49×10^{-4} . The error factor amounts to $K_{95} = 8.2$. The probability distribution and the pdf of the unavailability of the system are shown in Fig. 9.48.

9.8.2 CO₂ Separation in a Rectisol Plant

In the expansion vessel DA of a Rectisol plant (installation for physical gas cleaning), whose flow sheet is shown in Fig. 9.49, CO₂ is separated from methanol saturated with CO₂ by lowering the pressure. The separated CO₂ is fed into the vessel FA. The methanol, which is again saturated because pressure is lower (this implies, of course, a CO₂ content lower than initially) is discharged in a controlled way from DA. The control maintains a filling level of about 40 % in the vessel

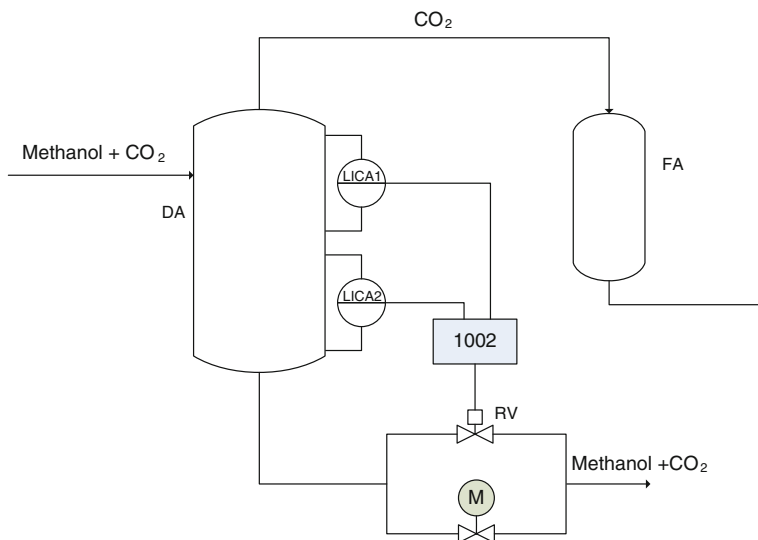


Fig. 9.49 Flow sheet of the expansion vessel of the rectisol plant

DA. Its failure would lead to an introduction of methanol in vessel FA. This is not desirable for operating and safety reasons.

The level control is realized by control valve RV, which is activated by level controllers LICA1 and LICA2, which are redundant (1oo2). They also activate an alarm in the control room if the level is high. According to the operating instructions the operator then has to open the motor valve M by pushing a button. The control valve RV closes if instrument air fails.

The fault tree for the undesired event “filling level too high” is shown in Fig. 9.50. High levels can be initiated by the failure of the activation of control valve RV by LICA1 and LICA2, the failure of the control valve RV itself or the failure of instrument air. Further potential causes are that LICA1 and LICA2 remain in their positions for functional tests after inspection or a CCF of both level measurements. The latter is treated using the Beta Factor Method with $\beta = 0.1$.

The safety system consists of the alarm because of a high filling level and the corresponding instruction to open the motor valve M in the bypass of the methanol outlet by pushing a button. However, the alarm is only useful in case of control valve failure.

Table 9.27 contains the data for quantifying the fault tree of Fig. 9.50.

The fault tree has the following 14 minimal cut sets:

Table 9.27 Data for quantifying the fault tree of Fig. 9.50

Primary-event	Failure rate λ in 10^{-6} h^{-1}	Error factor K_{95}	Time interval between functional tests θ in h	Unavailability u according to Eq. (9.90)
x_1	1.0^*	1	—	—
x_2	2.28^a	3.3	—	—
x_3	22.76^a	3.3	—	—
x_4	$1.78 \times 10^{-4*}$	3.3	—	—
x_5	22.76^a	3.3	—	—
x_6	$1.78 \times 10^{-4*}$	3.3	—	—
x_7	$1.61 \times 10^{-3*a}$	5.0	—	—
x_8	19.8^a	1.7	—	—
x_9	15.2^a	5.0	—	—
x_{10}	19.8	1.7	4,380	4.34×10^{-2}
x_{11}	9.7	1.0	4,380	2.09×10^{-2}
x_{12}	$1.61 \times 10^{-2*}$	5.0	—	—

*probability

^ainitiating event; functional tests of LICA1 and LICA2 (x_7) take place twice a year. The self-announced failure of any one of the two redundant level measurements would be repaired after at the most 16 h

$$K_1 = x_1 x_2 x_{10}; K_2 = x_1 x_7 x_{10}; K_3 = x_1 x_8 x_{10}; K_4 = x_1 x_9 x_{10}; K_5 = x_1 x_2 x_{11};$$

$$K_6 = x_1 x_2 x_{12}; K_7 = x_1 x_7 x_{11}; K_8 = x_1 x_7 x_{12}; K_9 = x_1 x_8 x_{11}; K_{10} = x_1 x_8 x_{12};$$

$$K_{11} = x_1 x_9 x_{11}; K_{12} = x_1 x_9 x_{12}; K_{13} = x_1 x_3 x_4; K_{14} = x_1 x_5 x_6$$

Table 9.28 gives an overview of the initiating events and their contributions to the expected frequency of the undesired event “filling level too high”. The expected frequency of the undesired event, H_j , is obtained by summing the expected values of all minimal cut sets in which the corresponding initiating event appears.

The total expected frequency for “filling level too high” amounts to $H = 0.026 \text{ a}^{-1}$.

Table 9.29 contains the important contributions for reducing the frequency of “filling level too high” which would result if the corresponding component were perfect (failure rate = 0).

An easy way of improving the system consists in making the control valve RV fail in its open position in case of instrument air failure (“fail safe”). This would almost halve the expected frequency of “filling level too high”. If, in addition, the motor valve M is activated by the existing level measurements the expected frequency for “filling level too high” becomes

$$H' = 8.6 \times 10^{-3} \text{ a}^{-1}$$

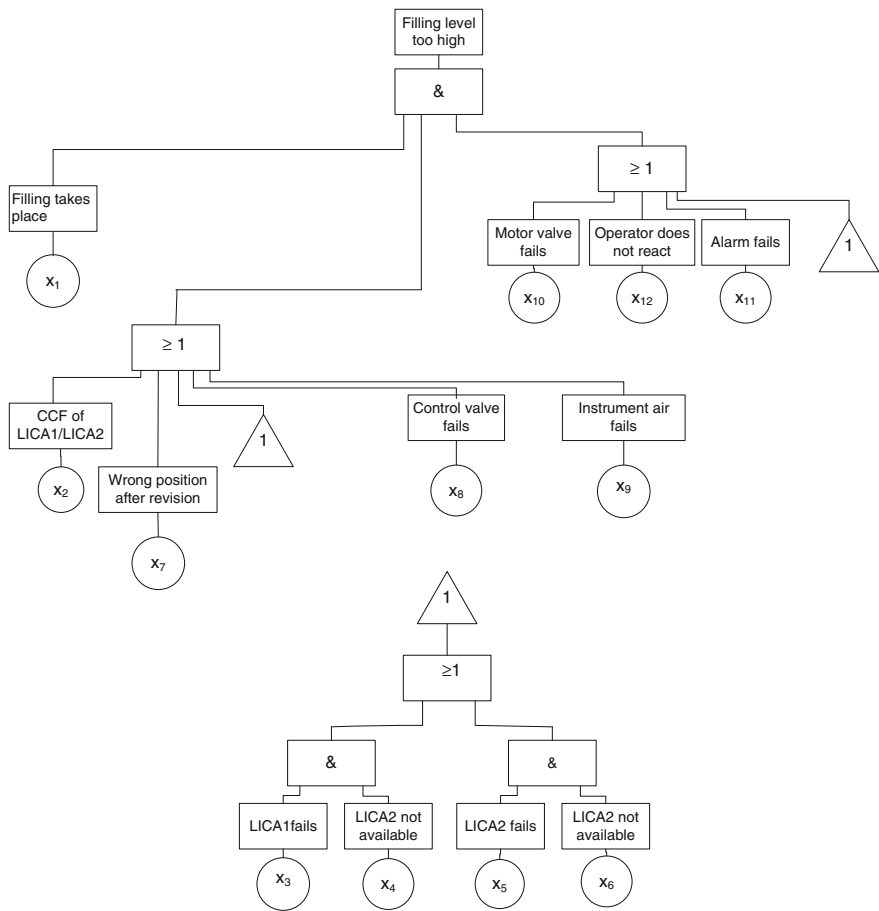


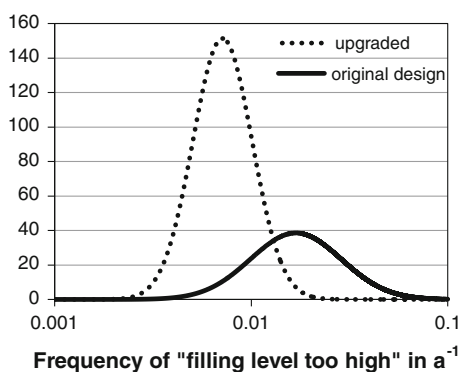
Fig. 9.50 Fault tree for the event “filling level too high” (Note: the failure of the level measurements figures twice; due to the property of idempotence of the binary variables the system is correctly accounted for only once)

Table 9.28 Overview of the numerical results for the undesired event “filling level too high”

Description of the failure (initiating event)	Expected frequency of the initiating event h_j in a^{-1} ($j = 1, \dots, 6$)	Unavailability of the system function	Expected frequency of the undesired event H_j in a^{-1}
GVA LCA1/LCA2	1.99×10^{-2}	7.85×10^{-2}	1.57×10^{-3}
LCA1 fails	1.99×10^{-1}	1.14×10^{-4}	2.27×10^{-5}
LCA2 fails	1.99×10^{-1}	1.14×10^{-4}	2.27×10^{-5}
Control valve fails	1.73×10^{-1}	7.85×10^{-2}	1.36×10^{-2}
Instrument air fails	1.33×10^{-1}	7.85×10^{-2}	1.05×10^{-2}
Wrong position after revision	3.23×10^{-3}	7.85×10^{-2}	2.54×10^{-4}
Total			2.6×10^{-2}

Table 9.29 Important contributions for reducing the expected frequency of “filling level too high”

Primary event	Description	Reduction of the expected frequency to (%)
x_1	Filling takes place	0
x_{10}	Motor valve M fails	46.88
x_8	Control valve RV fails	47.53
x_9	Instrument air fails	59.66
x_{11}	Alarm signal fails	74.94
x_{12}	Operator does not react	80.79
x_2	CCF of LCA1/LCA2	93.96

Fig. 9.51 Probability density functions for event “filling level too high” for the original and upgraded designs

A further reduction of this value can be achieved by upgrading the control valve and motor valve, if necessary by installing another valve in parallel to the existing two.

The upgrading of the activation of the control valve to a two-out-of-three (2oo3) configuration and an automatic activation of the motor valve in the bypass at a level of 80 % planned by the plant operator does not lead to any substantial reduction of the expected frequency of the event “filling level too high”.

Figure 9.51 shows the pdfs for the original and improved designs taking into account the uncertainties of the input data.

9.8.3 Fault Tree Analysis of the Nitrator for the Production of Hexogen (Excerpt from [29])

The possibility and expected frequency of a runaway reaction and hence an explosion of the nitration of hexamine for producing hexogen described in Case study 4.2 is examined below using fault tree analysis.

Fault tree analysis

Only two events are examined in detail here: the failure of the stirrer and the failure of the cooling control. The failure rates have already been converted into unavailabilities using Eq. (9.90) and the pertinent time intervals for functional tests or operational demands. Further details are found in [29].

9.8.3.1 Stirrer Failure

The fault tree for a runaway reaction following stirrer failure is shown in Fig. 9.52. The fault tree is quantified using the failure rates and unavailabilities of Table 9.30.

Table 9.31 shows the minimal cut sets of the fault tree of Fig. 9.52.

System unavailabilities using time-averaged component unavailabilities

The results for the initiating event x_4 are given in Tables 9.32 and 9.33.

The results for the initiating event x_5 are listed in Tables 9.34 and 9.35.

The results for the initiating event x_{11} are listed in Tables 9.36 and 9.37.

All initiating events which contribute to stirrer failure have an expected frequency of occurrence of $0.86 \times 10^{-2} \text{ a}^{-1}$.

9.8.3.2 Failure of Cooling Control

Figure 9.53 shows the fault tree for the failure of cooling control.

The fault trees are quantified using the unavailabilities and failure rates for the initiating events of Table 9.38.

Table 9.39 lists the minimal cut sets of the fault trees of Figs. 9.52 and 9.53.

System unavailabilities using time-averaged component unavailabilities

The results for the initiating event x_7 are listed in Tables 9.40 and 9.41.

The results for the initiating event x_8 are listed in Tables 9.42 and 9.43.

The results for the initiating event x_{10} are listed in Tables 9.44 and 9.45.

The results for the initiating event x_{11} are listed in Tables 9.46 and 9.47.

All initiating events leading to an undesired rise in temperature with an ensuing runaway reaction have an expected frequency of $2.9 \times 10^{-2} \text{ a}^{-1}$.

9.8.3.3 Results of the Complete Analysis

The results calculated in [29] for the contributions of the individual initiating events to the expected explosion frequency of the nitrator are listed in Table 9.48. They lead to a total of $H = 4 \times 10^{-2} \text{ a}^{-1}$.

A closer look at the minimal cut sets in the tables listed above shows that large contributions are made by the initiating events given in Table 9.49.

In order to improve the plant an independent temperature switch for opening the bypass of the coolant control was proposed. It should become effective in case of high reaction temperatures but below the setpoint of temperature switch TSHH2. Thus a device is introduced which is redundant to the operating system. Hence, not every case of high temperature would make it necessary to dump the reactor

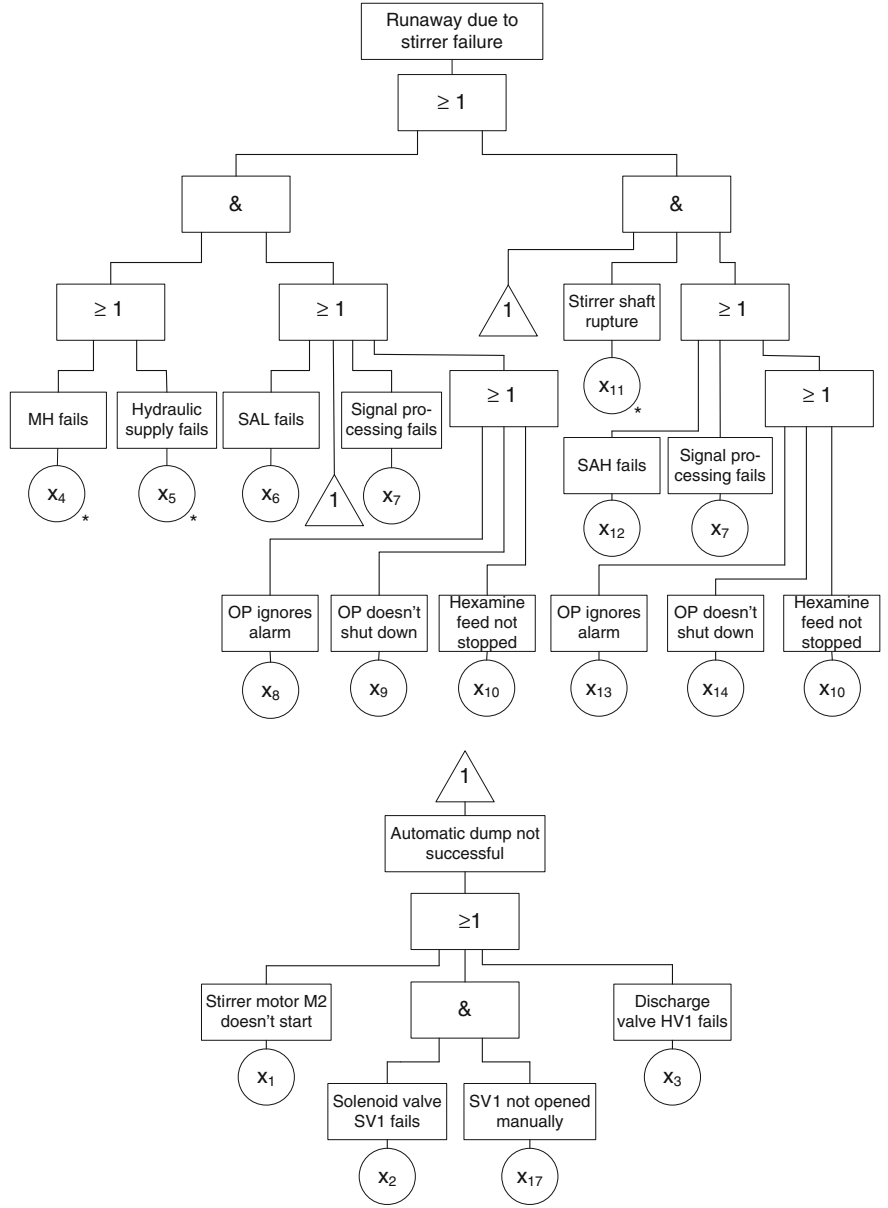


Fig. 9.52 Fault tree for a runaway reaction following stirrer failure and partial fault tree for automatic dump (* initiating event)

contents into the emergency discharge tank. The product would then be saved. This modification reduces the unavailability of the systems required to cope with the initiating events “failure of the transmitter TY1” and “failure of the

Table 9.30 Primary events and unavailabilities for evaluating the fault tree of Fig. 9.52 (* initiating event)

Primary event	Unavailability	Description
x_1	1.814×10^{-3}	Stirrer motor M2 does not start
x_2	2.688×10^{-3}	Solenoid valve SV1 fails
x_3	2.520×10^{-4}	Discharge valve HV1 fails
x_4^a	1.000×10^{-6}	Stirrer motor MH stops running
x_5^a	8.000×10^{-6}	Hydraulic supply fails
x_6	2.051×10^{-3}	Speed alarm “low” SAL fails
x_7	1.599×10^{-3}	Signal processing relays fail
x_8	1.332×10^{-3}	Operator does not notice the alarm
x_9	0.0807	Operator fails, no trip
x_{10}	1.679×10^{-4}	Hexamine feed does not stop
x_{11}^a	2.000×10^{-7}	Shaft or propeller rupture
x_{12}	2.051×10^{-2}	Speed alarm “high” SAH fails
x_{13}	1.332×10^{-3}	Operator does not notice the alarm
x_{14}	0.0807	Operator fails, no trip
x_{15}	1.000	Solenoid valve is not opened manually

^aFailure rate λ in h^{-1} , since initiating event

temperature sensor TE1” from 4.6×10^{-2} to 1.2×10^{-3} . Concurrently the unavailability of the systems coping with the initiating events “control valve TV1 fails” and “controller TIC1 fails” drops from 5×10^{-3} to 1.6×10^{-4} .

In case of events concerning the stirring of the reactor the main contribution stems from “manual activation of reactor discharge”. If the dumping were activated automatically by the alarms SAL1 and SAH1, the unavailability of the systems required for coping with the pertinent initiating events would drop from 0.11 to 2.5×10^{-2} .

The modifications presented reduce the expected frequency of an explosion of the nitrator from

$$H = 4.0 \times 10^{-2} \text{ a}^{-1} \text{ to } H' = 4.1 \times 10^{-3} \text{ a}^{-1}$$

After upgrading the largest contribution to the expected frequency of explosion stems from disturbances related to the stirrer. It amounts to 51 %. The results for the original and upgraded designs including the distribution percentiles are listed in Table 9.50.

The improvement of the system resulting from the proposed modifications is considered as real and not within the region of statistical uncertainty, since the expected value and the percentiles after the improvement all lie below the corresponding values for the original design. This is evident as well from the representation of the pdfs of the original and upgraded designs shown in Fig. 9.55.

Table 9.31 Minimal cut sets of the fault tree of Fig. 9.52

Number	Components		
1	4	6	
2	7	11	
3	5	6	
4	4	7	
5	4	8	
6	1	4	
7	11	12	
8	10	11	
9	1	11	
10	5	7	
11	5	8	
12	1	5	
13	4	9	
14	4	10	
15	3	4	
16	2	4	15
17	11	13	
18	11	14	
19	3	11	
20	2	11	15
21	5	9	
22	5	10	
23	3	5	
24	2	5	15

Table 9.32 Minimal cut sets contributing to the initiating event x_4 and their unavailabilities

Minimal cut set	1	Unavailability	2.05×10^{-2}
Minimal cut set	4	Unavailability	1.60×10^{-3}
Minimal cut set	5	Unavailability	1.33×10^{-3}
Minimal cut set	6	Unavailability	1.81×10^{-3}
Minimal cut set	13	Unavailability	8.07×10^{-2}
Minimal cut set	14	Unavailability	1.68×10^{-4}
Minimal cut set	15	Unavailability	2.52×10^{-4}
Minimal cut set	16	Unavailability	2.69×10^{-9}

Table 9.33 Total result for the initiating event x_4

Initiating event	Annual expected frequency of the initiating event	Unavailability of the system function	Annual expected frequency of the undesired event
x_4	8.76×10^{-3}	0.11	9.32×10^{-4}

Table 9.34 Minimal cut sets contributing to the initiating event x_5 and their unavailabilities

Minimal cut set	3	Unavailability	2.05×10^{-2}
Minimal cut set	10	Unavailability	1.60×10^{-3}
Minimal cut set	11	Unavailability	1.33×10^{-3}
Minimal cut set	12	Unavailability	1.81×10^{-3}
Minimal cut set	21	Unavailability	8.07×10^{-2}
Minimal cut set	22	Unavailability	1.68×10^{-4}
Minimal cut set	23	Unavailability	2.52×10^{-4}
Minimal cut set	24	Unavailability	2.69×10^{-9}

Table 9.35 Total result for the initiating event x_5

Initiating event	Annual expected frequency of the initiating event	Unavailability of the system function	Annual expected frequency of the undesired event
x_5	7.01×10^{-2}	0.11	7.45×10^{-3}

Table 9.36 Minimal cut sets contributing to the initiating event x_{11} and their unavailabilities

Minimal cut set	2	Unavailability	1.60×10^{-3}
Minimal cut set	7	Unavailability	2.05×10^{-2}
Minimal cut set	8	Unavailability	1.66×10^{-4}
Minimal cut set	9	Unavailability	1.81×10^{-3}
Minimal cut set	17	Unavailability	1.33×10^{-3}
Minimal cut set	18	Unavailability	8.01×10^{-2}
Minimal cut set	19	Unavailability	2.52×10^{-4}
Minimal cut set	20	Unavailability	2.69×10^{-9}

Table 9.37 Total result for the initiating event x_{11}

Initiating event	Annual expected frequency of the initiating event	Unavailability of the system function	Annual expected frequency of the undesired event
x_{11}	1.75×10^{-3}	0.11	1.86×10^{-4}

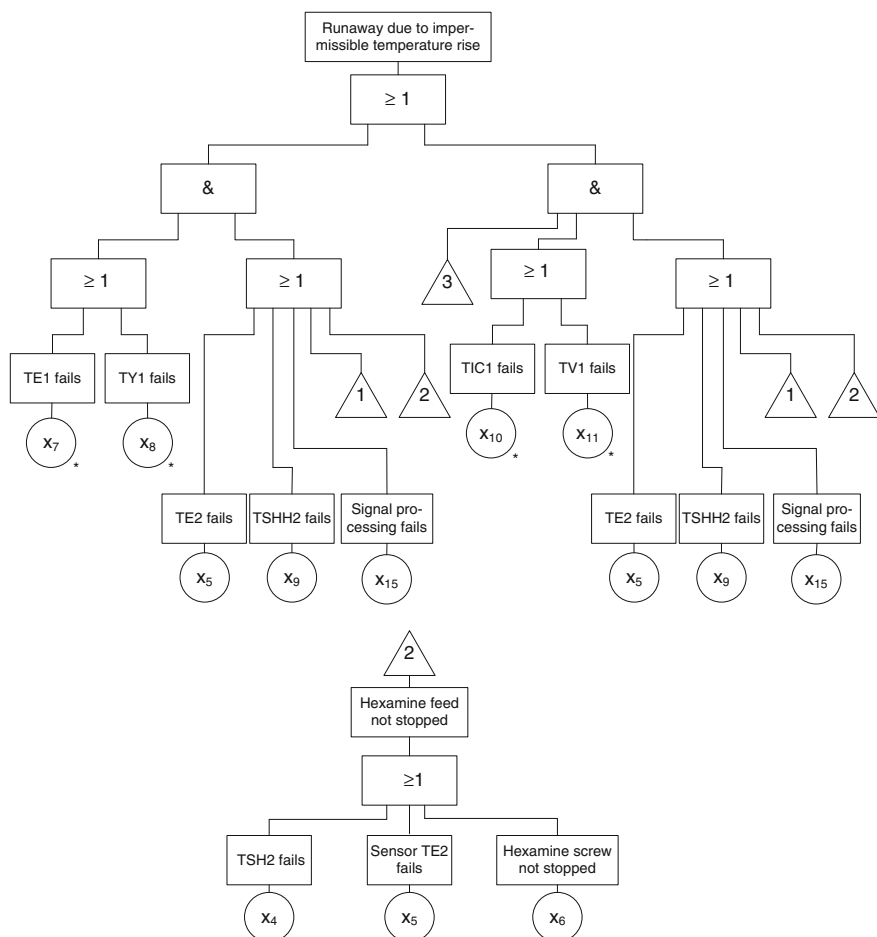


Fig. 9.53 Fault tree for a runaway reaction following impermissible temperature rise due to a failure of cooling control (partial fault tree “1” from Fig. 9.52 and partial fault tree “3” from Fig. 9.54; * initiating event)

9.8.3.4 Conclusions

The investigation has shown how the safety of the system can be improved. At the same time its availability is increased, although this was not the express objective of the analysis. Some of the results were already obtained in the qualitative part of the analysis. The quantification of the fault trees brought further insights and enabled one to identify areas of unbalanced safety measures. The latter are characterized by largely differing contributions of an individual initiating event to the expected frequency of an explosion (vid. Table 9.48). The proposals for

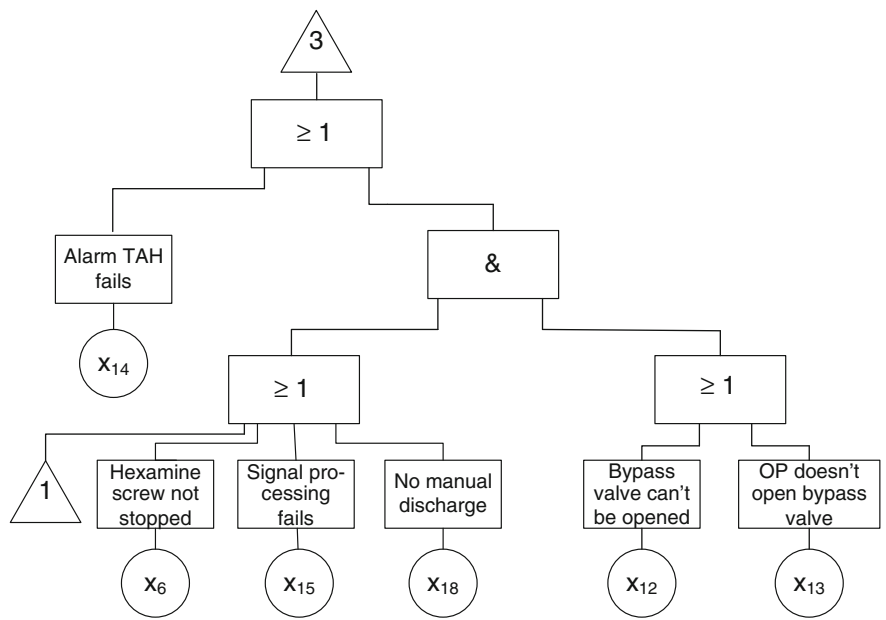


Fig. 9.54 Partial fault tree “3” for the fault tree of Fig. 9.53

Table 9.38 Primary events and unavailabilities for evaluating the fault trees of Figs. 9.53 and 9.54

Primary event	Unavailability	Description
x_1	1.814×10^{-3}	Stirrer motor M2 does not start
x_2	2.688×10^{-3}	Solenoid valve SV1 fails
x_3	2.520×10^{-4}	Discharge valve HV1 fails
x_4	2.017×10^{-2}	Temperature switch TSH2 fails
x_5	2.940×10^{-4}	Sensor TE2 fails
x_6	1.680×10^{-4}	Hexamine feeder screw does not stop
x_7^a	3.500×10^{-6}	Sensor TE1 fails
x_8^a	6.300×10^{-5}	Electric to pneumatic converter TY01 fails
x_9	2.017×10^{-2}	Temperature switch TSHH2 fails
x_{10}^a	4.400×10^{-5}	Temperature controller TIC1 fails
x_{11}^a	2.900×10^{-5}	Control valve TV1 fails
x_{12}	8.400×10^{-5}	Bypass valve cannot be opened
x_{13}	0.807	Operator does not open bypass valve
x_{14}	1.929×10^{-2}	Alarm TAH1 fails
x_{15}	1.599×10^{-3}	Signal processing relays fail
x_{17}	0.807	Discharge valve not opened manually
x_{18}	1.332×10^{-2}	No manual discharge after temperature rise

^aFailure rate λ in h^{-1} , since initiating event

Table 9.39 Minimal cut sets of the fault trees of Figs. 9.52 and 9.53

Number	Components
1	5 7
2	5 10 14
3	5 8
4	7 9
5	7 15
6	1 7
7	4 7
8	5 11 14
9	1 10 14
10	9 10 14
11	10 14 15
12	8 9
13	8 15
14	1 8
15	4 8
16	3 7
17	2 7 17
18	6 7
19	1 11 14
20	9 11 14
21	11 14 15
22	4 10 14
23	3 10 14
24	2 10 14 17
25	3 8
26	2 8 17
27	6 8
28	4 11 14
29	3 11 14
30	2 11 14 17
31	6 10 14
32	6 11 14
33	6 10 12
34	6 11 12
35	5 10 12 18
36	5 11 12 18
37	1 10 12
38	9 10 12 18
39	10 12 15
40	1 11 12
41	9 11 12 18

(continued)

Table 9.39 (continued)

Number	Components
42	11 12 15
43	4 10 12 18
44	4 11 12 18
45	6 10 13
46	6 11 13
47	5 10 13 18
48	5 11 13 18
49	1 10 13
50	9 10 13 18
51	10 13 15
52	1 11 13
53	9 11 13 18
54	11 13 15
55	4 10 13 18
56	3 10 12
57	2 10 12 17
58	4 11 13 18
59	3 11 12
60	2 11 12 17
61	3 10 13
62	2 10 13 17
63	3 11 13
64	2 11 13 17

Table 9.40 Minimal cut sets contributing to the initiating event x_7 and their unavailabilities

Minimal cut set	1	Unavailability	2.94×10^{-4}
Minimal cut set	4	Unavailability	2.02×10^{-2}
Minimal cut set	5	Unavailability	1.60×10^{-3}
Minimal cut set	6	Unavailability	1.81×10^{-3}
Minimal cut set	7	Unavailability	2.02×10^{-2}
Minimal cut set	16	Unavailability	2.52×10^{-4}
Minimal cut set	18	Unavailability	1.68×10^{-4}

Table 9.41 Total result for the initiating event x_7

Initiating event	Annual expected frequency of the initiating event	Unavailability of the system function	Annual expected frequency of the undesired event
x_7	3.07×10^{-2}	4.45×10^{-2}	1.36×10^{-3}

Table 9.42 Minimal cut sets contributing to the initiating event x_8 and their unavailabilities

Minimal cut set	3	Unavailability	2.94×10^{-4}
Minimal cut set	12	Unavailability	2.02×10^{-2}
Minimal cut set	13	Unavailability	1.60×10^{-3}
Minimal cut set	14	Unavailability	1.81×10^{-3}
Minimal cut set	15	Unavailability	2.02×10^{-2}
Minimal cut set	25	Unavailability	2.52×10^{-4}
Minimal cut set	27	Unavailability	1.68×10^{-4}

Table 9.43 Total result for the initiating event x_8

Initiating event	Annual expected frequency of the initiating event	Unavailability of the system function	Annual expected frequency of the undesired event
x_8	0.55	4.45×10^{-2}	2.45×10^{-2}

Table 9.44 Minimal cut sets contributing to the initiating event x_{10} and their unavailabilities

Minimal cut set	2	Unavailability	5.67×10^{-6}
Minimal cut set	9	Unavailability	3.50×10^{-5}
Minimal cut set	10	Unavailability	3.89×10^{-4}
Minimal cut set	11	Unavailability	3.09×10^{-5}
Minimal cut set	22	Unavailability	3.89×10^{-4}
Minimal cut set	23	Unavailability	4.86×10^{-6}
Minimal cut set	31	Unavailability	3.24×10^{-6}
Minimal cut set	33	Unavailability	1.41×10^{-8}
Minimal cut set	35	Unavailability	3.29×10^{-10}
Minimal cut set	37	Unavailability	1.52×10^{-7}
Minimal cut set	38	Unavailability	2.26×10^{-8}
Minimal cut set	39	Unavailability	1.34×10^{-7}
Minimal cut set	43	Unavailability	2.26×10^{-8}
Minimal cut set	45	Unavailability	1.36×10^{-4}
Minimal cut set	47	Unavailability	3.16×10^{-6}
Minimal cut set	49	Unavailability	1.46×10^{-3}
Minimal cut set	50	Unavailability	2.17×10^{-4}
Minimal cut set	51	Unavailability	1.29×10^{-3}
Minimal cut set	55	Unavailability	2.17×10^{-4}
Minimal cut set	56	Unavailability	2.12×10^{-8}
Minimal cut set	61	Unavailability	2.03×10^{-4}

Table 9.45 Total result for the initiating event x_{10}

Initiating event	Annual expected frequency of the initiating event	Unavailability of the system function	Annual expected frequency of the undesired event
x_{10}	0.39	4.39×10^{-3}	1.69×10^{-3}

Table 9.46 Minimal cut sets contributing to the initiating event x_{11} and their unavailabilities

Minimal cut set	8	Unavailability	5.67×10^{-6}
Minimal cut set	19	Unavailability	3.50×10^{-5}
Minimal cut set	20	Unavailability	3.89×10^{-4}
Minimal cut set	21	Unavailability	3.09×10^{-5}
Minimal cut set	28	Unavailability	3.89×10^{-4}
Minimal cut set	29	Unavailability	4.86×10^{-6}
Minimal cut set	32	Unavailability	3.24×10^{-6}
Minimal cut set	34	Unavailability	1.41×10^{-8}
Minimal cut set	36	Unavailability	3.29×10^{-10}
Minimal cut set	40	Unavailability	1.52×10^{-7}
Minimal cut set	41	Unavailability	2.26×10^{-8}
Minimal cut set	42	Unavailability	1.34×10^{-7}
Minimal cut set	44	Unavailability	2.26×10^{-8}
Minimal cut set	46	Unavailability	1.36×10^{-4}
Minimal cut set	48	Unavailability	3.16×10^{-6}
Minimal cut set	52	Unavailability	1.46×10^{-3}
Minimal cut set	53	Unavailability	2.17×10^{-4}
Minimal cut set	54	Unavailability	1.29×10^{-3}
Minimal cut set	58	Unavailability	2.17×10^{-4}
Minimal cut set	59	Unavailability	2.12×10^{-8}
Minimal cut set	63	Unavailability	2.03×10^{-4}

Table 9.47 Total result for the initiating event x_{11}

Initiating event	Annual expected frequency of the initiating event	Unavailability of the system function	Annual expected frequency of the undesired event
11	0.25	4.39×10^{-3}	1.12×10^{-3}

Table 9.48 Contributions of the individual initiating events to the expected frequency of explosion

Description of the failure (initiating event)	Expected frequency of the initiating event h_i in a^{-1}	Unavailability of the system function	Expected frequency of the undesired event H_j in a^{-1}
Mechanical failure of control valve TV1	0.25	4.8×10^{-3}	1.2×10^{-3}
Failure of controller TIC1	0.38	4.8×10^{-3}	1.8×10^{-3}
Coolant supply too small or failed	0.063	5.7×10^{-3}	3.6×10^{-4}
Temperature switch TE1 fails	0.031	4.6×10^{-2}	1.4×10^{-3}
Electric to pneumatic converter TY1 gives a low output signal	0.55	4.6×10^{-2}	2.5×10^{-2}
HNO ₃ supply below lower limit	5.0×10^{-7}	1.0	5.0×10^{-7}
Rupture of stirrer shaft	0.0018	0.11	2.0×10^{-4}
Failure of hydraulic stirrer motor	0.0088	0.11	9.7×10^{-4}
Failure of hydraulic supply	0.071	0.11	7.8×10^{-3}
Coolant ingress into the reactor	0.00085	1.0	8.5×10^{-4}
Total			4.0×10^{-2}

Table 9.49 Initiating events and major contributions to the unavailability of the system function

Initiating event	Main contribution from
“TE1 fails” and “TY1 fails”	TSH2 and TSHH2
“Rupture of stirrer shaft”, “Failure of the hydraulic stirrer motor”, “Failure of the hydraulic supply”	Operator error

Table 9.50 Results for the original and upgraded designs

Frequency of an explosion in a^{-1}	5th percentile	Expected value	95th percentile
Before upgrading	$H_{05} = 8.7 \times 10^{-3}$	$H = 4.0 \times 10^{-2}$	$H_{95} = 0.1$
After upgrading	$H'_{05} = 3.6 \times 10^{-4}$	$H' = 4.1 \times 10^{-3}$	$H'_{95} = 1.3 \times 10^{-2}$

improvement reduce this frequency by an order of magnitude. They can be realized at moderate expenditure.

However, the results should not be regarded as absolute values because there was a lack of reliability data at the time of the analysis. Additionally, quite a

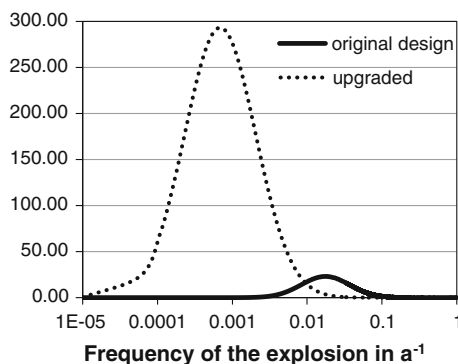


Fig. 9.55 Probability density functions for the event “explosion” for the original and upgraded designs

number of conservative assumptions were made in the analysis. Reliability analyses for process plants should preferably be used for comparing design alternatives given the present state of knowledge. However, a later re-analysis of the plant using several sets of reliability data (among them one evaluated at the site of the plant) confirmed the findings on weak points and the possible improvements [56].

The plant operator, at the same time plant designer, made the automation of the bypass a design rule for reactors. Thus, the analysis does not have to be repeated for every new reactor.

9.8.4 Comparison of the Availabilities of Reactor Trip Systems [57]

The availabilities of an emergency discharge system, an inhibitor system, a pressure relief system and a passive trip system are compared with one another. The pertinent fault tree models are established and quantified.

9.8.4.1 Emergency Discharge System

The emergency discharge or dump system was already described and treated in Sect. 9.8.3. Figure 9.56 shows the corresponding fault tree. The tree was extended beyond the model of the preceding section by the possibility of a leak in the emergency discharge tank and its being empty when dumping is required.

9.8.4.2 Inhibitor System

Figure 9.57 shows the system for injecting an inhibitor into a reactor. The corresponding fault tree is presented in Fig. 9.58. The system mainly consists of the injector vessel containing the inhibitor, the corresponding measuring devices and valves, and a catch tank. In case the temperature is too high temperature switch TSH opens valve AV5 and the inhibitor is injected into the reactor by a pressure blanket inside the injector vessel. Redundantly, pressure switch P1 opens valve

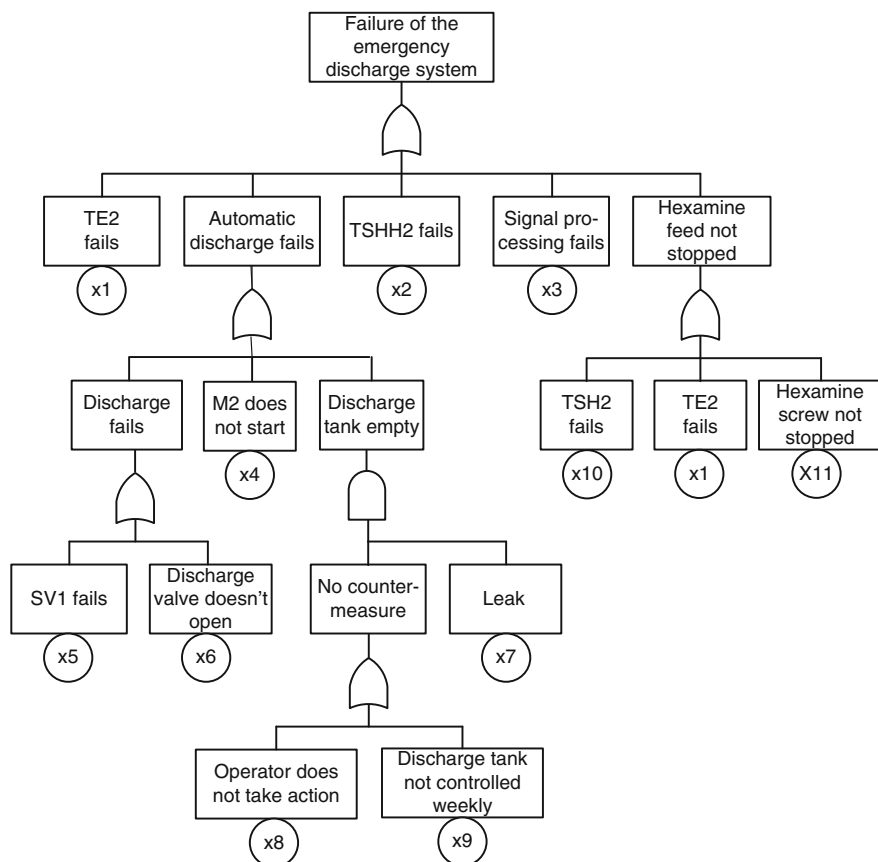


Fig. 9.56 Fault tree for the emergency discharge system of the nitrator for producing hexogen of Fig. 4.11

AV2 due to the pressure increase associated with a rising temperature. The reactor content is then relieved into the catch tank. Sufficient pressure in the injector vessel is ensured by weekly inspections of the pressure sensor P4 and the corresponding operator action, if required.

9.8.4.3 Pressure Relief System

A standard reactor used in the process industry for synthesis reactions is shown in Fig. 9.59. The corresponding fault tree model is presented in Fig. 9.60. Reactants A and B are introduced in controlled quantities into the reactor. A catalyst is continuously supplied and the temperature as well as the pressure increases are measured. The protective trip system consists of the safety valve SV1 and the relief system made up of pressure switch PSHH1, relay I, and pneumatic valve AV1. The “safe place” for relief is considered to be a discharge tank just as that of Fig. 4.11, which is modelled as in Fig. 9.56.

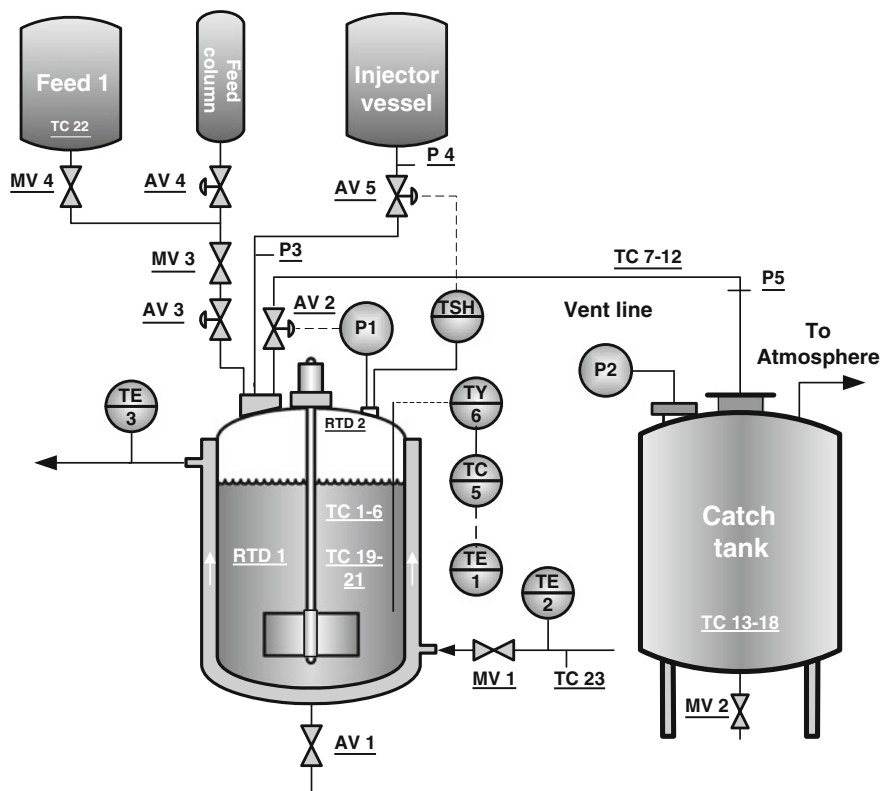


Fig. 9.57 Flow sheet of the inhibitor system

9.8.4.4 Passive Trip System

The design and function of the passive trip system were already explained in Sect. 4.22. The corresponding fault tree is presented in Fig. 9.61.

9.8.4.5 Reliability Data

The reliability data for quantifying the fault trees of Figs. 9.56, 9.58, 9.60 and 9.61 are given in Table 9.51. They stem from [33]. Medians and K_{95} error factors are listed. The probabilities for human error are described by rectangular distributions according to Eq. (C.33) of Appendix C. These were formed on the basis of the data from [52]. The intervals for functional tests are based on information from plant operators. The time-averaged unavailabilities were calculated according to Eq. (9.90).

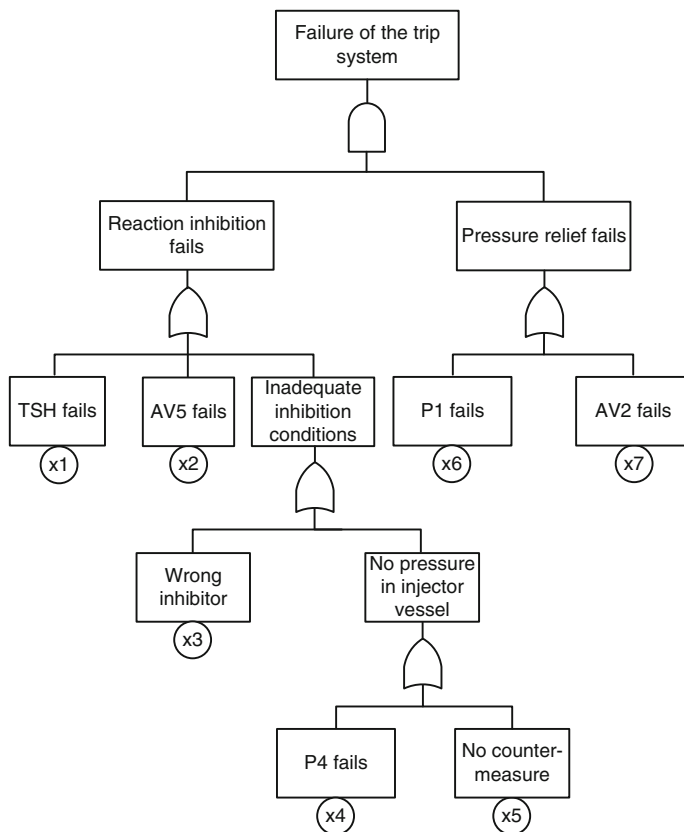


Fig. 9.58 Fault tree for the inhibition trip system of Fig. 9.57

9.8.4.6 Results

The results for the four trip systems are presented in Tables 9.52, 9.53, 9.54 and 9.55.

Table 9.56 contains the parameters of the distributions of the results for the four systems. These are obtained if data uncertainties are accounted for.

9.8.4.7 Discussion of the Results

A closer look at the minimal cut sets of the different systems shows

Emergency discharge system

- Key contributors to the unavailability are the failures of instruments TE2, TSH2, and TSHH2. An introduction of redundant instrumentation would reduce the expected value of the time averaged unavailability of the system to 2.1×10^{-3} .

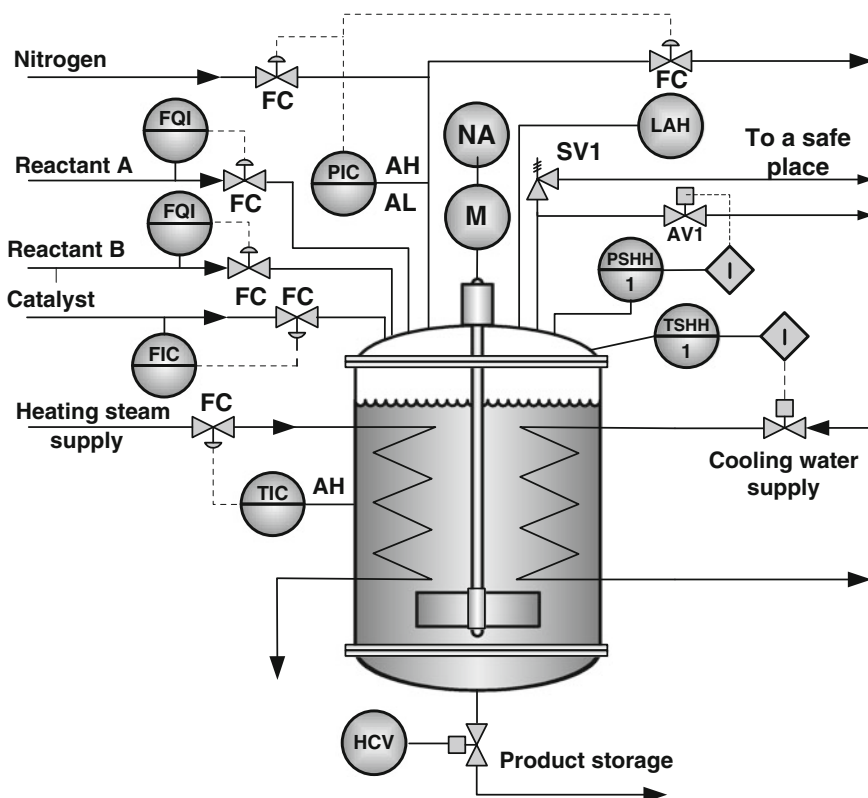


Fig. 9.59 P&I diagram of the reactor with a pressure relief system

Inhibition system

- The most important contributions to its unavailability stem from the minimal cut sets x_1x_6 , x_1x_7 and x_2x_6 , x_2x_7 . Since the system is already redundant, the benefit from further redundancies would most likely be limited by CCFs.

Pressure relief system

- The main contribution to its unavailability stems from the failure of the stirring motor to start. Since the system is already redundant and highly available, the reduction by further redundancies would most likely be limited by CCFs.

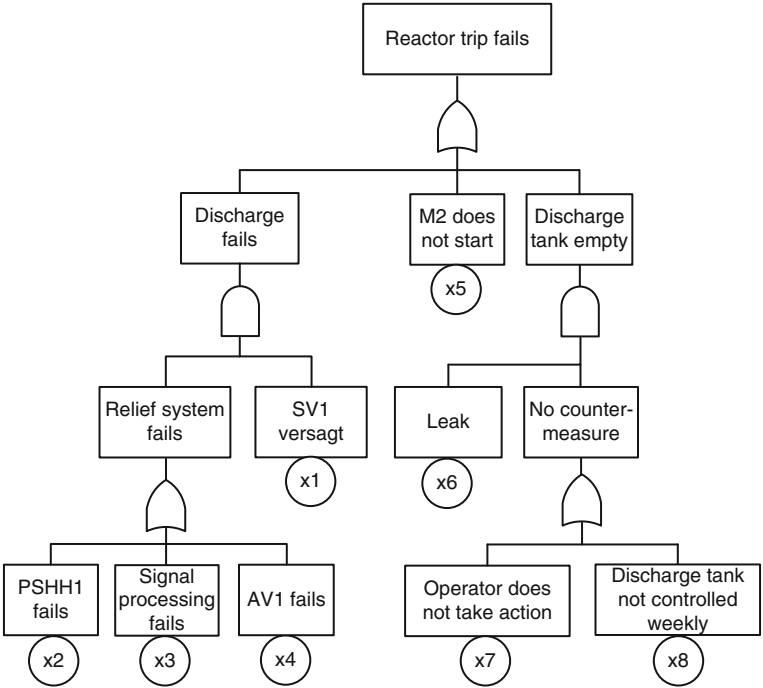


Fig. 9.60 Fault tree for the pressure relief trip system of the reactor of Fig. 9.59

Fig. 9.61 Fault tree for the passive trip system of the reactor of Fig. 4.4

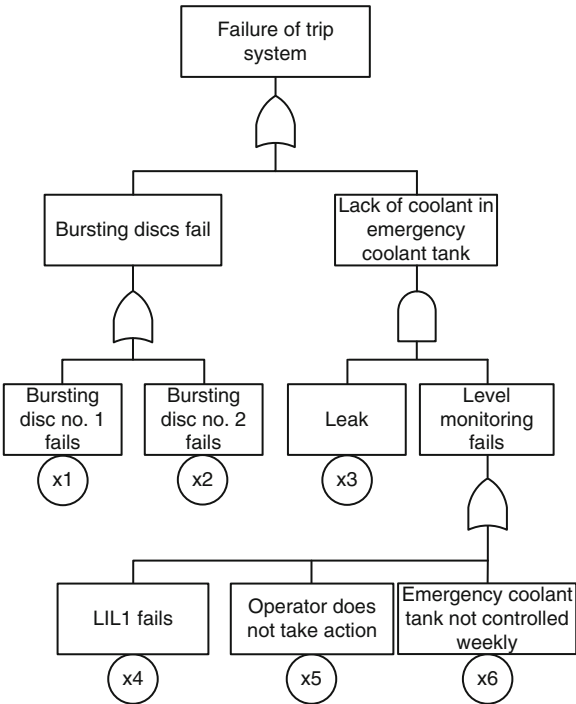


Table 9.51 Reliability data and intervals for functional tests

System	Indicator variable in the fault tree	Component/ Failure mode	Median of the failure rate λ in $10^{-6}/\text{h}$	Error factor K_{95}	Test interval θ in h	Unavailability u
Emergency discharge system	x_1	Temperature sensor TE2 fails	27.8	1.5	720	1.03×10^{-2}
	x_2	Pressure switch fails	0.93	8.4	720	7.73×10^{-4}
	x_3	Signal processing fails	0.30	3.0	720	1.35×10^{-4}
	x_4	Stirrer motor does not start	1.00	3.3	168	1.09×10^{-4}
	x_5	Solenoid valve SV1 fails	1.92	8.4	168	3.72×10^{-4}
	x_6	Discharge valve does not open	17.8	2.2	168	1.68×10^{-3}
	x_7	Leak at discharge tank	1.50	8.4	168	2.91×10^{-4}
	x_8	Operator does not take action	0.05 ^a	0.002 ^b	–	0.026
	x_9	Discharge tank not controlled weekly	0.05 ^a	0.002 ^b	–	0.026
	x_{10}	Temperature switch TSH2 fails	60.4	1.5	720	2.24×10^{-2}
	x_{11}	Hexamine screw not stopped	9.2	1.7	168	8.14×10^{-4}
Inhibitor system	x_1	Temperature switch TSH fails	27.8	1.5	17,520	2.51×10^{-1}
	x_2	Injector valve AV5 fails	17.8	2.2	17,520	1.75×10^{-1}
	x_3	Wrong inhibitor	0.05 ^a	0.002 ^b	–	0.026
	x_4	Pressure switch P4 fails	0.93	8.4	720	7.73×10^{-4}
	x_5	No countermeasure by operator	0.05 ^a	0.002 ^b	–	0.026
	x_6	Pressure switch P1 fails	0.93	8.4	720	7.73×10^{-4}
	x_7	Relief valve AV2 does not open	17.8	2.2	168	1.68×10^{-3}

(continued)

Table 9.51 (continued)

System	Indicator variable in the fault tree	Component/ Failure mode	Median of the failure rate λ in $10^{-6}/\text{h}$	Error factor K_{95}	Test interval θ in h	Unavailability u
Pressure relief system	x_1	Safety valve SV1 does not open	1.13	8.4	17,520	2.28×10^{-2}
	x_2	Pressure switch PSHH1 fails	0.93	8.4	720	7.73×10^{-4}
	x_3	Signal processing fails	0.30	3.0	720	1.35×10^{-4}
	x_4	Relief valve AV1 does not open	17.8	2.2	168	1.68×10^{-3}
	x_5	Stirrer motor does not start	1.00	3.3	168	1.09×10^{-4}
	x_6	Leak at discharge tank	1.5	8.4	168	2.91×10^{-4}
	x_7	No countermeasure by operator	0.05 ^a	0.002 ^b	—	0.026
	x_8	Discharge tank not controlled weekly	0.05 ^a	0.002 ^b	—	0.026
Passive trip system	x_1	Bursting disc no. 1 does not open ^c	0.001	8.4	17,520	2.02×10^{-5}
	x_2	Bursting disc no. 2 does not open ^c	0.001	8.4	17,520	2.02×10^{-5}
	x_3	Leak at the emergency coolant tank	1.5	8.4	168	2.91×10^{-4}
	x_4	Level gauge LIL1 fails	6.7	1.7	168	5.93×10^{-4}
	x_5	No countermeasure by operator	0.05 ^a	0.002 ^b	—	0.026
	x_6	Emergency coolant tank not controlled weekly	0.05 ^a	0.002 ^b	—	0.026

^aupper limit of the probability^blower limit of the probability^ctaken as 0.1 % of the safety valve failure rate, since not opening has not been observed so far, replacement every 2 years

Table 9.52 Minimal cut sets, unavailabilities and system unavailability for the emergency discharge system

Minimal cut set no.	Primary event(s) in the minimal cut set	Unavailability
1	$\kappa_1 = x_1$	1.02×10^{-2}
2	$\kappa_2 = x_2$	2.21×10^{-2}
3	$\kappa_3 = x_3$	1.33×10^{-4}
4	$\kappa_4 = x_4$	1.07×10^{-4}
5	$\kappa_5 = x_5$	3.72×10^{-4}
6	$\kappa_6 = x_7 \cdot x_8$	7.56×10^{-6}
7	$\kappa_7 = x_{10}$	2.21×10^{-2}
8	$\kappa_8 = x_{11}$	8.09×10^{-4}
9	$\kappa_9 = x_6$	1.68×10^{-3}
10	$\kappa_{10} = x_7 \cdot x_9$	7.56×10^{-6}
$E(\Psi) \approx \sum_{i=1}^{10} E(\kappa_i)$		5.75×10^{-2}

Table 9.53 Minimal cut sets, unavailabilities and system unavailability for the reaction inhibition system

Minimal cut set no.	Primary event(s) in the minimal cut set	Unavailability
1	$\kappa_1 = x_1 \cdot x_6$	1.65×10^{-4}
2	$\kappa_2 = x_2 \cdot x_6$	1.21×10^{-4}
3	$\kappa_3 = x_3 \cdot x_6$	2.00×10^{-5}
4	$\kappa_4 = x_1 \cdot x_7$	3.59×10^{-4}
5	$\kappa_5 = x_2 \cdot x_7$	2.62×10^{-4}
6	$\kappa_6 = x_3 \cdot x_7$	4.36×10^{-5}
7	$\kappa_7 = x_4 \cdot x_6$	5.95×10^{-7}
8	$\kappa_8 = x_4 \cdot x_7$	1.29×10^{-6}
9	$\kappa_9 = x_5 \cdot x_6$	2.00×10^{-5}
10	$\kappa_{10} = x_5 \cdot x_7$	4.36×10^{-5}
$E(\Psi) \approx \sum_{i=1}^{10} E(\kappa_i)$		1.04×10^{-2}

Table 9.54 Minimal cut sets, unavailabilities and system unavailability for the pressure relief system

Minimal cut set no.	Primary event(s) in the minimal cut set	Unavailability
1	$\kappa_1 = x_5$	1.07×10^{-4}
2	$\kappa_2 = x_1 \cdot x_2$	1.74×10^{-5}
3	$\kappa_3 = x_6 \cdot x_7$	7.56×10^{-6}
4	$\kappa_4 = x_1 \cdot x_3$	3.00×10^{-6}
5	$\kappa_5 = x_1 \cdot x_4$	3.78×10^{-5}
6	$\kappa_6 = x_6 \cdot x_8$	7.56×10^{-6}
$E(\Psi) \approx \sum_{i=1}^6 E(\kappa_i)$		1.80×10^{-2}

Table 9.55 Minimal cut sets, unavailabilities and system unavailability for the passive trip system

Minimal cut set no.	Primary event(s) in the minimal cut set	Unavailability
1	$\kappa_1 = x_1$	2.02×10^{-5}
2	$\kappa_2 = x_2$	2.02×10^{-5}
3	$\kappa_3 = x_3 \cdot x_4$	1.72×10^{-7}
4	$\kappa_4 = x_3 \cdot x_5$	7.56×10^{-6}
5	$\kappa_5 = x_3 \cdot x_6$	7.56×10^{-6}
$E(\Psi) \approx \sum_{i=1}^5 E(\kappa_i)$		5.58×10^{-5}

Table 9.56 Characteristic parameters of the distributions of the time-averaged unavailabilities for the four trip system obtained with 10, 000,000 Monte Carlo trials

System	5th percentile	Expected value	95th percentile
Emergency discharge system	4.4×10^{-2}	5.4×10^{-2}	7.0×10^{-2}
Inhibitor system	3.5×10^{-4}	1.0×10^{-3}	2.1×10^{-3}
Pressure relief system	4.8×10^{-5}	1.7×10^{-4}	4.1×10^{-4}
Passive trip system	9.1×10^{-6}	5.6×10^{-5}	1.6×10^{-4}

Passive trip system

- Its unavailability is dominated by the failure probability of the bursting discs, which, based on the chosen failure rate and period between replacements, amounts to 2.3×10^{-5} , a values which lies within the range indicated in [20]. If the lower limit given there, i.e. a failure probability of 10^{-5} , were used the time-averaged unavailability of the passive system would drop to 3.5×10^{-5} . The frequency of testing/inspection plays a subordinate role for unavailability. Placing the outlet of the emergency coolant tank above the upper coolant level would make rupture disc no. 2 superfluous and hence further reduce the time-averaged unavailability to 1.8×10^{-5} .

9.8.4.8 Closing Remarks and Conclusions

The choice of the test or inspection intervals has a considerable impact on the unavailabilities of the active trip systems. Hence, it is difficult to make a fair comparison. However, in practice the operator is not free in his choice. For example, the inhibitor and corresponding systems cannot be tested too frequently, because a test involves the loss of the inhibiting substance. The times selected represent a compromise between frequent tests, which lower the unavailability, and operational requirements, which imply avoiding interferences of production and costs caused by tests and inspections.

Overall the passive system shows the lowest time-averaged unavailability and the best technical properties. Its unavailability is dominated by the failure rates assigned to the bursting discs. Test intervals and inspections play a minor role. If the design is made properly, even the most frequent failure mode of bursting discs, i.e. not rupturing exactly at the specified set point, does not affect its effectiveness so that low failure rates are warranted. Hence, the passive system proves to be superior to those involving the necessity of the functioning of active components. This is true especially since it does not require a redundant design in order to reach a high level of availability and will therefore not be affected by potential CCFs.

Which system is to be chosen can only be decided in view of the type of reaction and reactor, just because not every system is effective in any case even if the trip function is successful.

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*There are more things in heaven and earth, Horatio, than are
dreamt of in your philosophy,*

Hamlet, William Shakespeare 1564–1616

After the analyses of the engineered systems were discussed in Chap. 9 and thus the left hand sides of Figs. 8.1 and 8.2 the methods for assessing accident consequences are treated here, i.e. the right hand sides of the figures mentioned. The stochastic nature is a characteristic of the phenomena involved. Consequences of accidents in process plants causing fires, explosions or releases of toxic materials can be described with relatively simple models. However, the results depend on boundary conditions which are not foreseeable, since the moment of occurrence of an accident cannot be foreseen. A factor of influence, which insinuates itself, is the weather. The direction of the wind decides which area in the surroundings of the point of release of a toxic material is affected. Wind speed, stability conditions and possible rain determine the concentration to which people in the affected area are exposed. This means that we cannot predict concrete accident outcomes. We can only indicate a probability for a certain outcome to occur. Therefore the first step is to gain insight into possible accident consequences. This is intended in Fig. 10.1, which is complex but by no means claimed to be complete. In a further step the probabilities for certain outcomes to become true must be determined.

The treatment of accident sequences usually implies a chain of model calculations for different phenomena, for example ‘occurrence of a leak → discharge → pool formation → evaporation → atmospheric dispersion → health effects’. This is already expressed in Fig. 10.1.

Despite the large number of possible sequences, as suggested by Fig. 10.1, modelling a limited number of phenomena is sufficient. In order to assess accident consequences the models are used with different initial and boundary conditions and combined differently. This enables one to simulate a large variety of accident sequences.

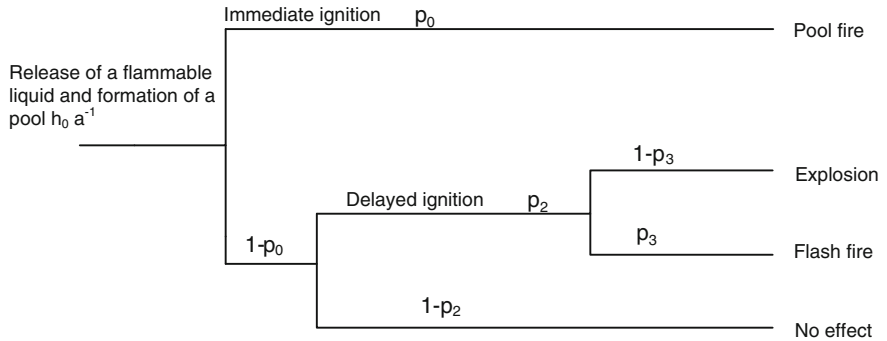


Fig. 10.2 Event tree for an instantaneous or continuous release of a flammable liquid and pool formation

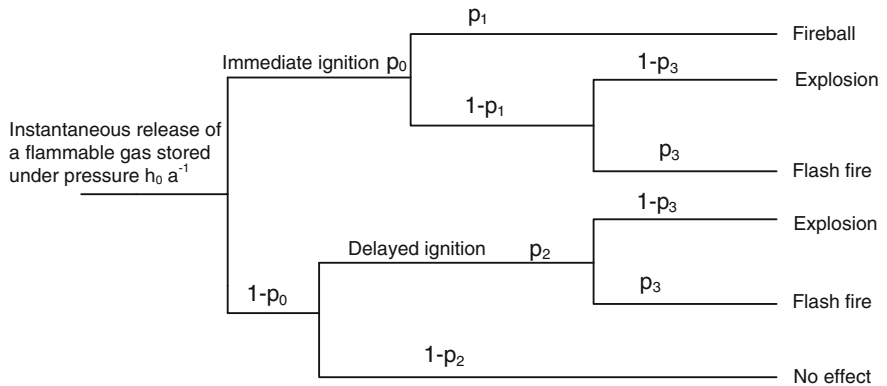


Fig. 10.3 Event tree for the instantaneous release of a flammable gas stored under pressure

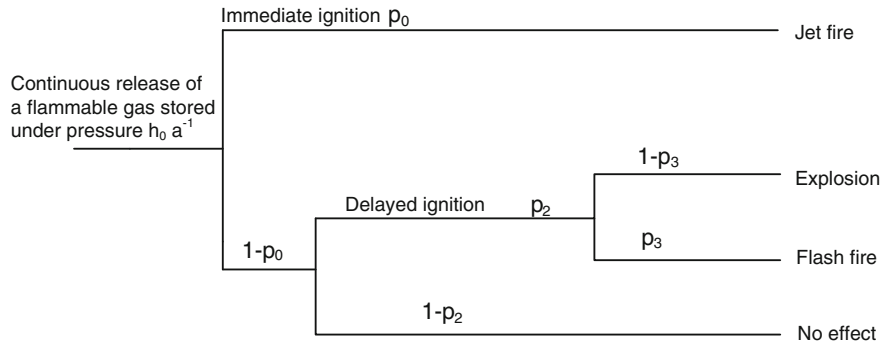


Fig. 10.4 Event tree for the continuous release of a flammable gas stored under pressure

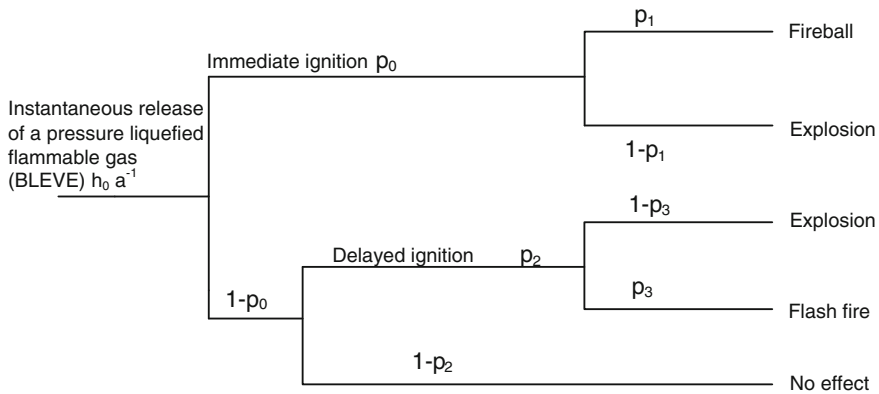


Fig. 10.5 Event tree for the instantaneous release of a flammable gas liquefied under pressure

Reasons for that may be internal fires or explosions or excessive temperature and pressures caused by component malfunctions or operator error.

In addition there is the possibility of so called spontaneous failures (failure without an obvious reason; from the Latin word 'sponte': of one's free will, voluntarily); they might be caused, for example, by hidden flaws in structural materials.

Below the following problems and phenomena are addressed:

- determination of leak sizes and frequencies,
- discharge from pipes and vessels,
- pool formation and evaporation,
- atmospheric dispersion,
- pool fires,
- flash fires,
- fireballs,
- jet fires,
- effects of heat radiation as a function of distance from the source,
- explosions,
- vapour cloud explosions (VCE),
- BLEVE,
- dust explosions,
- missile flight.

Unless an event like a containment-internal explosion or fire is the cause, the release begins with a leak. The cause can be a failure of the containment (loss of containment: LOC) or a planned relief via bursting discs or safety valves, unless they discharge into a receiving vessel. Frequent failure mechanisms and their expected frequencies of occurrence were already addressed in Sect. 8.1.

10.1 Failure of Containment

Some important parameters relating to the loss of containment are the following:

- frequency of occurrence,
- size of the aperture,
- geometry of the aperture,
- location of the aperture (e.g. elevation above ground, orientation),
- time required for leak isolation.

All of these parameters are stochastic and lead to uncertainties of the assessment.

10.1.1 Frequencies of the Occurrence of a Loss of Containment

It is extremely difficult to determine frequencies of occurrence for the loss of containment (leaks and ruptures). These frequencies depend on the size and length of pipes, the number of valves, the design of vessels and other medium containing components (e.g. pump casings). An important part is also played by the number of elbows, flanges, pipe branches, instrumentation ports etc. The properties of the medium involved, the pressures and temperatures just as their variations with time are of relevance, too. The frequency and quality of maintenance should also not be forgotten.

Table 10.1 gives expected frequencies for some classes of ruptures and leaks. Both the frequency and the indication of the size are affected by large uncertainties. If uncertainties are stated the frequencies are represented by parameters of log-normal distributions (vid. Sect. 9.3.4), as often is the case with probabilistic safety analyses.

Depending on whether we deal with a risk-based or a detailed risk study the scope of the failure mechanisms represented by the failure rates must differ. For risk-based analyses the failure rates should represent besides spontaneous failure failures caused by impermissible loads on structural materials following malfunctions or operator errors. Since the latter are explicitly modelled in a detailed risk analysis the failure rates for passive components used there should only represent the spontaneous part. The scope of the failure mechanisms covered is usually not described in sufficient detail and can practically not be determined a posteriori [5].

Example 10.1 Expected frequencies for the occurrence of leaks

A lifetime observation of centrifugal pumps in a process plant resulted in $k = 36$ leaks from casings to the outside during an accumulated time of observation of $t = T_C = 934,984$ h. What are the expected value, the median, and the 5th and 95th percentiles, if a Bayesian evaluation with a non-informative prior pdf is made? The lifetimes are supposed to be exponentially distributed.

Table 10.1 Expected frequencies (mean values) for losses of containment (LOC)

Component and failure mode	h_0 in a^{-1}	K_{95}	Reference
Catastrophic failure ^a of a pressure vessels	10^{-5}	n/a	[2]
Pipe rupture (pressure pipework in a typical refinery, diameter > 15 cm)	5×10^{-3}	n/a	[2]
Pipeline failure per km	4.5×10^{-4}	n/a	[2]
Pipes with a diameter ≤ 5 cm			
• catastrophic rupture per km	8.8×10^{-4}	n/a	[3]
• serious leakage per km	8.8×10^{-3}	n/a	[3]
Pipes with a diameter > 15 cm			
• catastrophic rupture per km	8.8×10^{-5}	n/a	[3]
• serious leakage per km	2.6×10^{-3}	n/a	[3]
Hoses			
• heavily stressed	0.35	n/a	[3]
• lightly stressed	0.035	n/a	[3]
Pressure vessels			
• catastrophic rupture	1×10^{-6}	n/a	[3]
• serious leakage	1×10^{-5}	n/a	[3]
Atmospheric storage tanks			
• catastrophic rupture	6×10^{-6}	n/a	[3]
• serious leakage	1×10^{-4}	n/a	[3]
Refrigerated storage tank(double wall, high integrity)			
• catastrophic rupture from both containments	1×10^{-6}	n/a	[3]
• serious leakage from inner tank	2×10^{-5}	n/a	[3]
Atmospheric tanks			
• leakage to the outside from gaskets, seals	6.6×10^{-2}	1.5	[4]
• leakage to the outside from wall defects or cracks	6.9×10^{-2}	1.4	[4]
Valves			
• leakage from gaskets, seals	0.060	1.2	[4]
• leakage from valve body	0.021	1.3	[4]

^acatastrophic failure or rupture: a rupture such that the entire content and hence the entire hazard potential is released instantaneously, e.g. rupture of an entire vessel; n/a.: no account

Solution

The calculation is based on the procedure described in Sect. 9.3.3.

The expected value is obtained according to Eq. (9.47) giving

$$E = h_0 = \frac{2 \cdot k + 1}{2 \cdot t} = \frac{2 \cdot 36 + 1}{2 \cdot 934,984 \text{ h}} \cdot 8,760 \frac{\text{h}}{\text{a}} = 0.34 \text{ a}^{-1}$$

The 95th percentile is calculated using Eq. (9.48)

$$\bar{h}_0 = \frac{\chi_{2k+1; (1+\gamma)/2}^2}{2 \cdot t} = \frac{\chi_{2 \cdot 36+1; 0.95}^2}{2 \cdot 934,984 \text{ h}} \cdot 8,760 \frac{\text{h}}{\text{a}} = \frac{93.94}{2 \cdot 934,984 \text{ h}} \cdot 8,760 \frac{\text{h}}{\text{a}} = 0.44 \text{ a}^{-1}$$

and the 5th percentile using Eq. (9.49)

$$\underline{h}_0 = \frac{\chi_{2k+1; (1-\gamma)/2}^2}{2 \cdot t} = \frac{\chi_{2 \cdot 36+1; 0.05}^2}{2 \cdot 934,984 \text{ h}} \cdot 8,760 \frac{\text{h}}{\text{a}} = \frac{54.32}{2 \cdot 934,984 \text{ h}} \cdot 8,760 \frac{\text{h}}{\text{a}} = 0.25 \text{ a}^{-1}$$

The median is obtained by setting $\gamma = 0$, i.e.

$$h_{50} = \frac{\chi_{2k+1; (1-\gamma)/2}^2}{2 \cdot t} = \frac{\chi_{2 \cdot 36+1; 0.5}^2}{2 \cdot 934,984 \text{ h}} \cdot 8,760 \frac{\text{h}}{\text{a}} = \frac{72.34}{2 \cdot 934,984 \text{ h}} \cdot 8,760 \frac{\text{h}}{\text{a}} = 0.34 \text{ a}^{-1}$$

The values of the χ^2 distribution can be found in pertinent tables. If these are not used, the percentiles must be determined iteratively. For large arguments, as in the present case, the following approximation is recommended [6]

$$\chi^2 \left(n, \frac{1 \pm \gamma}{2} \right) = n \left[1 - \frac{2}{9n} + z_{1 \pm \frac{\gamma}{2}} \sqrt{\frac{2}{9n}} \right]^3 \quad n > 30$$

In the preceding equation we have

- n : degree of freedom of the χ^2 distribution
- $z_{1 \pm \frac{\gamma}{2}}$: argument of the standard normal distribution corresponding to the degrees of confidence $\frac{1+\gamma}{2}$ resp. $\frac{1-\gamma}{2}$ ($z_{1 \pm \frac{\gamma}{2}} = \pm 1.6449$ for $\gamma = 0.9$)

A practical way of approximating the result by a log-normal distribution is found by equating the median (h_{50}) and the 5th percentile ($\underline{h}_0$) with the corresponding percentiles of the log-normal distribution.

We then have from Eq. (9.52)

$$\mu = -1.0788$$

and from Eq. (9.55)

$$K_{95} = \frac{h_{50}}{\underline{h}_0} = \frac{0.34 \text{ a}^{-1}}{0.25 \text{ a}^{-1}} = 1.36,$$

whence we have from Eq. (9.54)

$$s = \frac{\ln K_{95}}{1.6449} = 0.1870 \quad \square$$

10.1.2 Leak Sizes

Given the difficulty of determining leak sizes and the frequencies of their occurrence these are usually fixed in safety reports (deterministic approach). An important role is played by the leak before break criterion, which implies that a leak of stable size formed before large area leaks in vessels or full cross section ruptures of pipes occur. However, the applicability of this criterion is subject to numerous prerequisites being fulfilled. Details can be found in [7].

For pipes we use

- leak size according to Brötz [8]

$$D_L = 0.11284 \cdot DN \quad DN < 100 \quad (10.1)$$

- leak size according to Strohmeier [9]

$$D_L = 0.02111 \cdot DN^{1.1} \quad (10.2)$$

- leak size according to Moosemiller [10]

$$D_L = \frac{0.00635}{h \cdot DN} \quad (10.3)$$

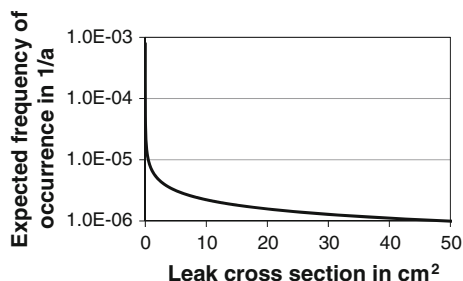
In Eqs. (10.1)–(10.3) D_L denotes the diameter of the leak in mm (a circular leak geometry is assumed) and DN is the nominal diameter (occasionally called nominal bore) of the pipe (approximately equal to the internal diameter in mm). Equation (10.3) is the only one to establish a relationship between leak size and its expected annual frequency of occurrence h . The latter refers to a length of 1 m and must therefore be multiplied by the length of the pipe under consideration. Equation (10.3) is based on evaluations for steel pipes in the process and petrochemical industries.

In [11] pipe leaks are contemplated in the context of determining appropriate distances between industry and urbanisation. A leak cross section of $F_L = 25^2 \cdot \pi/4 \approx 490 \text{ mm}^2$ is used.

A comparison of the different approaches is shown in Table 10.2 taking a pipe with DN 80 as an example.

Table 10.2 Leak cross sections according to the different procedures of calculation [12]

Equation	Leak diameter D_L in mm	Leak cross section F_L in mm ²	Expected annual frequency of occurrence per 1 m pipe length
(10.1)	9.03	64	Not considered
(10.2)	2.62	5.38	Not considered
(10.3)	9.03	64	8.79×10^{-6}
(10.3)	2.62	5.38	3.05×10^{-5}

Fig. 10.6 Relationship between expected annual frequency of occurrence and leak cross section for a 1 m of a pipe with DN80 according to Eq. (10.3)

The relationship between the leak cross section and its annual expected frequency of occurrence is shown in Fig. 10.6.

10.1.3 Geometry of the Aperture

In all cases a circular aperture is assumed. This is not necessarily in line with reality. The contraction of flow on discharge and different degrees of friction depending on the roughness and shape of the leak contours are accounted for by the discharge coefficient μ . Values between 0.595 and 0.62 are used; they increase with increasing smoothness of the leak contours [13].

10.2 Emission from Leaks

In the preceding section several causes for the loss of integrity of containments were described. As a consequence there is a discharge if gas or liquids are contained. Depending on the boundary conditions largely differing types of discharge can result. According to [2] the following situations can be distinguished. It must be recognized, however, that the determination of the discharge situation is affected by uncertainties.

- Type of fluid:
 - gas/vapour
 - liquid
 - liquid–vapour–mixture

- Type of plant:
 - vessel
 - other equipment
 - pipe work
- Type of enclosure:
 - in building
 - in open air
- Height:
 - below ground level
 - at ground level
 - above ground level
- Fluid momentum:
 - low momentum
 - high momentum

The released fluid may be a gas or a vapour, a liquid, a two-phase mixture, a mixture of several components or a fluid in supercritical state (vid. Example 10.19). If the release is from a vessel storing a liquefied gas, liquid is released if the leak is below the liquid level. If the leak is above the level either vapour or a mixture of liquid and vapour is released. For a given difference of pressures across the leak usually higher mass flow rates are reached if a liquid or liquid/vapour mixture is released than in case of a gas or vapour. The equipment from which the release takes place can be a vessel or a heat exchanger, a pump or a pipe. The maximum released quantity depends on the material inventory and the possibility of isolating the leak. The size of the leak may vary between a large portion of the vessel surface and a limited aperture as that of a hole.

The leak can have the shape of

- a sharp edged orifice,
- a conventional pipe branch,
- a rounded nozzle branch, or
- a crack.

The mass flow rate from a rounded nozzle branch is greater than through a conventional pipe branch but it is the latter which is generally used. Further possibilities are leaks from drain and sample points, pressure relief devices, bursting discs, seals and flanges, and pipe ends.

Releases may take place inside buildings or outdoors. This influences the dispersion behaviour. Outdoor releases often remain without grave consequences because of quick dilution of the released materials. A release of the same quantity indoors, however, may have grave consequences because of toxic impacts and the possibility of mixtures with air within the limits of flammability. The elevation of the point of release also influences the dispersion behaviour. A release of a liquid below ground level may remain completely contained. On the other hand, a release of a gas or vapour above ground may lead to a large-scale dispersion.

Furthermore dispersion is influenced by the initial momentum of the released fluid. Gas or vapours released with low initial momentum lead to plume formation. If the initial momentum is high, turbulent jets result. Releases of liquids produce a stream with low initial momentum and a liquid jet, if the momentum is high. In both cases eventually a pool is formed.

10.2.1 Discharge of Liquids from Vessels

The discharge of liquids from a vessel is treated with the equations of Sect. 7.4.2. Two cases are distinguished:

- storage under atmospheric pressure, which is retained during the discharge process,
- storage under imposed pressure.

The elevation of the leak is important, too, just as the driving force for discharge due to gravity results only from the part of the liquid column above the leak

The treatment of discharge is shown in Example 10.2 for the case of a cylindrical vessel. Other geometries, e.g. spherical vessels, are dealt with, for example, in [2]. The procedure applies to materials which are liquid under atmospheric conditions as well as to materials liquefied by lowering their temperature in order to make the ratio of mass to storage volume large.

Example 10.2 Discharge of a liquid from a vessel

A cylindrical vessel with a height of $H = 10$ m and a cross section of $F_Q = 2$ m² is filled to 90 % with petrol, whence we have a column height of $h_0 = 0.9 \times H = 9$ m. A leak with a cross section of $F_L = 0.005$ m² opens at the bottom. How long does the discharge take if

- the liquid column is under atmospheric pressure, or
- if there is a nitrogen blanket which permanently imposes a pressure of $p = 1$ bar above atmospheric, even while the liquid level drops?

Data: $\rho = 730$ kg/m³; discharge coefficient $\mu = 0.62$

Solution

The equations to be applied can in principle be taken over from Sect. 7.4.2. They are slightly modified here, because amongst others they must be time-dependent. The driving force for the discharge depending on the type of storage is provided either by the liquid column or, in addition, the pressure of the nitrogen blanket.

- Discharge velocity

$$c_2(t)^2 = \mu^2 \cdot \left(2 \cdot g \cdot h(t) + \frac{2 \cdot p}{\rho} \right)$$

- Level drop due to liquid loss from the leak

$$h(t) = h_0 - \frac{F_L}{F_Q} \cdot \int_0^t c_2(t') \, dt'$$

If $h(t)$ is inserted in the relation for the discharge velocity, we obtain

$$c_2(t)^2 = \mu^2 \left[2 \cdot g \cdot \left(h_0 - \frac{F_L}{F_Q} \cdot \int_0^t c_2(t') \, dt' \right) + \frac{2 \cdot p}{\rho} \right]$$

Differentiation with respect to t (the rule of Leibniz is applied to the integral) leads to

$$2c_2(t) \cdot c_2'(t) = \mu^2 \cdot 2 \cdot g \cdot \left(-\frac{F_L}{F_Q} \cdot c_2(t) \right)$$

and hence to

$$c_2'(t) = -g \cdot \mu^2 \cdot \frac{F_L}{F_Q}$$

After integration we have

$$c_2(t) = A - g \cdot \mu^2 \cdot \frac{F_L}{F_Q} \cdot t$$

The constant of solution results from the initial condition

$$c_2(0) = A = \mu \cdot \sqrt{2gh_0 + \frac{2 \cdot p}{\rho}}$$

and hence

$$c_2(t) = \mu \cdot \sqrt{2gh_0 + \frac{2 \cdot p}{\rho}} - g \cdot \mu^2 \cdot \frac{F_L}{F_Q} \cdot t$$

When the vessel is empty (point in time t^*), the discharge velocity is equal to 0 and we obtain for the case $p = 0$ (no imposed pressure)

$$0 = \sqrt{2gh_0} - g \cdot \mu \cdot \frac{F_L}{F_Q} \cdot t^*$$

Solving this equation for t^* one obtains

$$t^* = \frac{\sqrt{2gh_0}}{g \cdot \mu \cdot \frac{F_L}{F_Q}} = \frac{\sqrt{2 \cdot 9.81 \frac{m}{s^2} \cdot 9 m}}{9.81 \frac{m}{s^2} \cdot 0.62 \cdot \frac{0.005 m^2}{2 m^2}} = 873.92 s$$

For the case $p \neq 0$ the boundary condition is

$$\begin{aligned} m &= \int_0^{t^*} F_L \cdot \rho \cdot \left(\mu \cdot \sqrt{2gh_0 + \frac{2p}{\rho}} - g\mu^2 \frac{F_L}{F_Q} \cdot t \right) dt \\ &= F_L \cdot \rho \cdot \left(\mu \cdot \sqrt{2gh_0 + \frac{2p}{\rho}} \cdot t^* - g\mu^2 \frac{F_L}{F_Q} \cdot \frac{t^{*2}}{2} \right) \end{aligned}$$

where m is the total mass of petrol in kg (here: $m = 13,140$ kg). The solution of this quadratic equation is

$$\begin{aligned} t^* &= \frac{\sqrt{2gh_0 + \frac{2p}{\rho}}}{g\mu \frac{F_L}{F_Q}} - \sqrt{\left(\frac{\sqrt{2gh_0 + \frac{2p}{\rho}}}{g\mu \frac{F_L}{F_Q}} \right)^2 - \frac{m}{\mu F_L \cdot \rho g\mu \frac{F_L}{2F_Q}}} \\ &= 1,395.96 s - \sqrt{(1,395.96 s)^2 - 763,730.44 s} = 307.40 s \end{aligned}$$

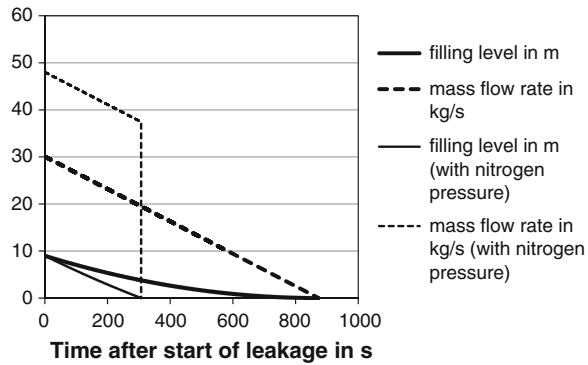
In the preceding equation the negative sign of the square root applies for physical reasons (the discharge time cannot be longer than that for the case without imposed pressure).

The time-dependent mass flow rate from the leak is

$$\dot{m}(t) = F_L \cdot \rho \cdot \left(\mu \cdot \sqrt{2gh_0 + \frac{2p}{\rho}} - g\mu^2 \frac{F_L}{F_Q} \cdot t \right) \quad (10.4)$$

The time-dependent results are shown in Fig. 10.7.

Fig. 10.7 Time-dependent variation of level and mass flow rate from the leak



□

10.2.2 Discharge of a Liquid from a Pipe Leak

Flow resistance has to be accounted for with flow through pipes. It depends on the

- roughness of the internal surface of the pipe,
- number and type of elbows,
- number and type of built-in devices (valves, orifices etc.).

It leads to a pressure drop which can be described by [14]

$$\Delta p = \zeta \cdot a \cdot \frac{\rho \cdot c^2}{2} \quad (10.5)$$

In Eq. (10.5) ζ is the pipe friction factor. It depends, for example on the flow regime (laminar or turbulent), pipe roughness and built-in devices. The factor a is

$$a = \begin{cases} \frac{1}{d_i} & \text{for pipes (l is the length and } d_i \text{ the internal diameter)} \\ 1 & \text{for valves and pipe fittings} \end{cases} \quad (10.6)$$

There are a number of correlations for pipe friction factors [14]. Here we only use the relationship by Moody, which applies to turbulent flow in hydraulically rough pipes. It is

$$\zeta = 0.0055 + 0.15 \cdot \left(\frac{k}{d_i} \right)^{1/3} \quad (10.7)$$

In order to determine the flow regime we need Reynold's number

$$\text{Re} = \frac{c \cdot d_i}{\nu} \quad (10.8)$$

In Eq. (10.8) c denotes the velocity of flow, d_i internal diameter of the pipe and ν the kinematic viscosity of the fluid.

There is turbulence, if $Re > 2,300$ and hydraulic roughness, if $Re \cdot \frac{k}{d_i} > 1,300$.

Below an example for the stationary discharge from a pipe leak is given. Non-stationary problems in which the internal pressure p_1 decreases because of loss of fluid can be treated in analogy to the flow diagram of Fig. 10.9. Then the relationships for gas used there have to be replaced by those for liquids from Example 10.3.

Example 10.3 Discharge from a pipe leak

Petrol flows through a horizontal pipe with DN25 (internal diameter $d_i = 27.2$ mm, cross sectional area $F_R = 5.81 \times 10^{-4} \text{ m}^2$) and a length of 100 m. At a distance of $l = 10$ m downstream a leak with a cross sectional area of $F_L = 7.85 \times 10^{-5} \text{ m}^2$ opens. Upstream of the leak there is a shut-off valve with a friction coefficient $\zeta_h = 0.8$. The built-in devices downstream from the leak are represented by the friction coefficient $\zeta_a = 3$. The roughness of the pipe material is $k = 0.4$ mm and the coefficient of discharge $\mu = 0.62$. The pressure upstream is $p_1 = 2$ bar (it is assumed to be constant despite flow and losses from the leak). The atmospheric pressure is $p_a = 1$ bar.

Two situations are to be treated (vid. Fig. 10.8):

- (a) the end of the pipe is closed, the petrol is only discharged through the leak;
- (b) the petrol flows at the open end of the pipe into a tank which is open to the atmosphere.

Data: $\nu = 0.53 \text{ mm}^2/\text{s}$; $\rho = 730 \text{ kg/m}^3$

Solution

- (a) Using Eq. (10.7) we have

$$\zeta = 0.0055 + 0.15 \cdot \left(\frac{k}{d_i} \right)^{1/3} = 0.0055 + 0.15 \cdot \left(\frac{0.4 \text{ mm}}{27.2 \text{ mm}} \right)^{1/3} = 4.225 \times 10^{-2}$$

Equation (7.5) is used without geodetic difference in elevation. On the other hand the equation must be extended to account for friction losses. The flow resistance is obtained from Eq. (10.5) which gives

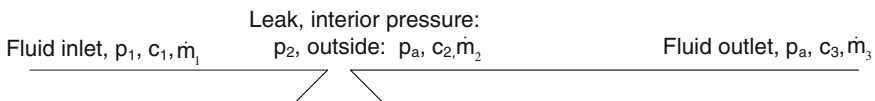


Fig. 10.8 Schematic of pipe and leak

$$\frac{\rho}{2} c_2^2 = \mu^2 \cdot \left[(p_1 - p_a) - \frac{c_1^2 \cdot \rho}{2} \cdot \left(1 + \frac{1}{d_i} \cdot \zeta + \zeta_h \right) \right]$$

Because of continuity of flow we have

$$c_1 = c_2 \cdot \frac{F_L}{F_R}$$

and hence

$$\begin{aligned} c_2 &= \mu \cdot \sqrt{\frac{2 \cdot (p_1 - p_a)}{\rho \cdot \left[1 + \left(\frac{F_L}{F_R} \right)^2 \cdot \left(1 + \frac{1}{d_i} \cdot \zeta + \zeta_h \right) \right]}} \\ &= 0.62 \cdot \sqrt{\frac{2 \cdot (200,000 - 100,000) \text{ Pa}}{730 \frac{\text{kg}}{\text{m}^3} \cdot \left[1 + \left(\frac{7.85 \times 10^{-5} \text{ m}^2}{5.81 \times 10^{-4} \text{ m}^2} \right)^2 \cdot \left(1 + \frac{10 \text{ m}}{0.0272 \text{ m}} \cdot 4.225 \times 10^{-2} + 0.8 \right) \right]}} = 8.94 \frac{\text{m}}{\text{s}} \end{aligned}$$

According to Eq. (10.8) we have $\text{Re} = 458,807.5$, i.e. the condition for turbulent flow is fulfilled just as that for hydraulic roughness, since

$$\text{Re} \cdot \frac{k}{d_i} = 458,807.5 \cdot \frac{0.4 \text{ mm}}{27.2 \text{ mm}} = 6,747.2 > 1,300$$

The discharged mass flow rate is

$$\dot{m} = F_L \cdot \rho \cdot c_2 = 7.85 \times 10^{-5} \text{ m}^2 \cdot 730 \frac{\text{kg}}{\text{m}^3} \cdot 9.72 \frac{\text{m}}{\text{s}} = 0.557 \frac{\text{kg}}{\text{s}}$$

(b) A network has to be treated, where the velocities c_1 to c_3 and the pressure p_2 are unknown. For the velocities we have

$$\begin{aligned} c_1 &= \sqrt{\frac{2 \cdot (p_1 - p_2)}{\rho \cdot \left(1 + \frac{1}{d_i} \cdot \zeta + \zeta_h \right)}} = 2.27 \frac{\text{m}}{\text{s}} \\ c_2 &= \mu \cdot \sqrt{\frac{2 \cdot (p_2 - p_a)}{\rho}} = 8.42 \frac{\text{m}}{\text{s}} \\ c_3 &= \sqrt{\frac{2 \cdot (p_2 - p_a)}{\rho \cdot \left(1 + \frac{100 \text{ m-l}}{d_i} \cdot \zeta + \zeta_a \right)}} = 1.13 \frac{\text{m}}{\text{s}} \end{aligned}$$

The corresponding mass flow rates are

$$\begin{aligned}\dot{m}_1 &= F_R \cdot c_1 \cdot \rho = 0.963 \frac{\text{kg}}{\text{s}} \\ \dot{m}_2 &= F_L \cdot c_2 \cdot \rho = 0.483 \frac{\text{kg}}{\text{s}} \\ \dot{m}_3 &= F_R \cdot c_3 \cdot \rho = 0.480 \frac{\text{kg}}{\text{s}}\end{aligned}$$

Additionally the condition

$$\dot{m}_1 = \dot{m}_2 + \dot{m}_3$$

has to be satisfied. The system of equations is solved iteratively in order to obtain p_2 . This gives $p_2 = 167,372.8$ Pa, which enables one to calculate all the remaining quantities.

If the leak were to open at a distance of $l = 50$ m from the inlet of the pipe, the mass flow rate would be $\dot{m}_2 = 0.294$ kg/s and thus much lower than in the preceding case. Hence, the mass flow rate depends on the location of the leak, which is random. $\square$

10.2.3 Discharge of Gases or Vapours from Vessels

The relationships for the discharge of gases or vapours were derived in Sect. 7.4.3 for the treatment of pressure relief by safety valves and bursting discs. They can also be applied to the discharge through leaks. Gases are stored under pressure in order to accommodate large quantities per unit of volume. This is mostly done, if the total quantity is small. For storing large quantities usually liquefaction or refrigeration are preferred.

Example 10.4 Discharge of ethylene from a vessel

A leak with diameter of 0.1 m (leak cross section area: $7.85 \times 10^{-3} \text{ m}^2$) occurs in a vessel with a volume of $V = 10 \text{ m}^3$. The vessel is filled with $m = 300$ kg of ethylene (boiling point -103.7°C) at a temperature of $T = 290$ K. Determine the mass flow rate $\dot{m}(t)$ as a function of time.

Data: $R = 0.29638$ kJ/(kgK); $\kappa = 1.25$; $\mu = 0.62$, $Z = 1$, atmospheric pressure $p_2 = 100,000$ Pa

Solution

In the first place we check whether the pressure ratio is smaller than critical or not. According to Eq. (7.22) we have

$$w_{\text{crit}} = \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa}{\kappa - 1}} = 0.55$$

The pressure in the vessel is obtained from the equation of state for gases (7.10)

$$p = \frac{m \cdot Z \cdot R \cdot T}{V} = \frac{300 \text{ kg} \cdot 1 \cdot 296.38 \frac{\text{J}}{\text{kgK}} \cdot 290 \text{ K}}{10 \text{ m}^3} = 2,578,506 \text{ Pa}$$

Hence we have

$$w = \frac{100,000 \text{ Pa}}{2,578,506 \text{ Pa}} = 0.0388$$

Since $w < w_{\text{crit}}$, the discharge is critical. Critical discharge ends at a pressure of 1.76 bar. The storage density of the ethylene is

$$\rho_1 = \frac{m}{V} = \frac{300 \text{ kg}}{10 \text{ m}^3} = 30 \frac{\text{kg}}{\text{m}^3}$$

The initial mass flow rate is obtained from Eq. (7.23)

$$\begin{aligned} \dot{m}_{\text{max}} &= \mu \cdot F_L \cdot \left\{ \rho_1 p_1 \kappa \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa + 1}{\kappa - 1}} \right\}^{1/2} \\ &= 0.62 \cdot 7.85 \times 10^{-3} \text{ m}^2 \cdot \left(30 \frac{\text{kg}}{\text{m}^3} \cdot 2,578,506 \text{ Pa} \cdot 1.25 \cdot 0.3464 \right)^{1/2} = 28.17 \frac{\text{kg}}{\text{s}} \end{aligned}$$

The time-dependent mass flow rate is calculated numerically. In doing this the entire process is represented by a sequence of time intervals. Within each of these all quantities are considered as constant. The calculation procedure is shown in the flowchart of Fig. 10.9. Figure 10.10 presents the results.

Fig. 10.9 Computer program flowchart for calculating the time-dependent discharge of gases (i: counter for the time increment; n counter for the iteration for satisfying the equation of state for gases)

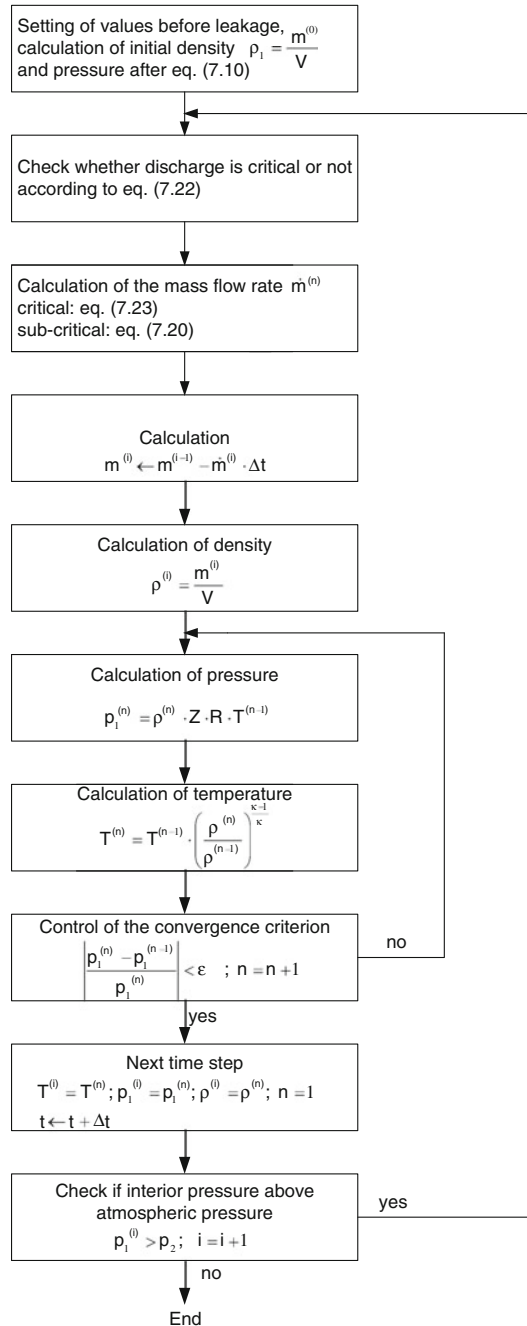
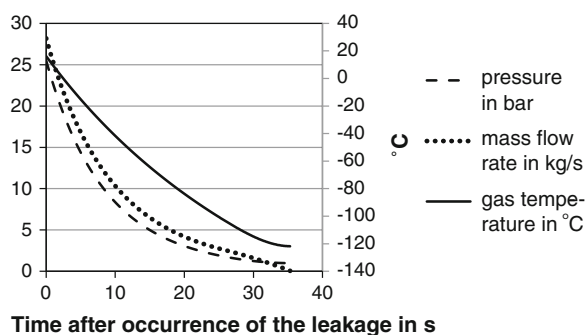


Fig. 10.10 Variation with time of pressure, mass flow rate, and temperature



The temperature drop during depressurization causes icing, a fact to be accounted for in the design of the vessel. The procedure can be applied as well to the discharge from a nozzle. If the leak were to be downstream from a shut-off valve, it could only be isolated, if the design of the valve were to allow its functioning at low temperatures and with icing. □

10.2.4 Discharge of Gases and Vapours from Pipe Leaks

The stationary discharge of gases or vapours from pipe leaks can be treated according to Example 10.3. Instead of the relationships for the velocity and mass flow rate for liquids the corresponding ones for gases of Sect. 7.4.3 have then to be used.

With respect to the non-stationary discharge of a gas or vapour from pipelines the reader is referred to Ref. [2, 15].

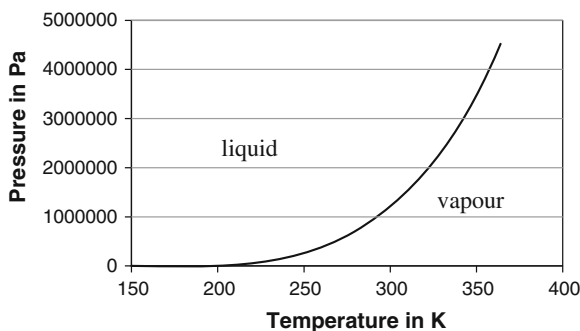
10.2.5 Discharge of a Two-Phase Mixture from Vessels

Releases of superheated liquids have to be considered in safety analyses for process plants. Such liquids vaporize on depressurization, which may occur, for example, following leaks or pressure relief of reactors. It is a difficult issue, which is not yet fully clarified. Most work on two-phase flow concerns mixtures of water and steam, which play an important role for accidents in nuclear reactors. The more complex task of treating flow processes of mixtures of several components and phases, which are characteristic of process plants, still requires intense research.

A basic problem for modelling two-phase flow is whether equilibrium exists between the two phases. This is generally not the case. However, equilibrium is usually assumed because it facilitates the analytical treatment of the problem.

In the lower portion of a vessel containing a superheated liquid we have the liquid phase and in the upper portion the vapour phase. The storage pressure is the vapour

Fig. 10.11 Vapour pressure curve of propylene



pressure corresponding to the storage temperature. The temperature-dependence of the vapour pressure of propylene is shown in Fig. 10.11 as an example.

Depending on the elevation of the leakage point different discharge regimes result. If the leak lies far above the liquid level vapour or gas is discharged; the procedures of Sect. 10.2.3 are then applied. If the leakage point is close to the liquid surface (slightly above or below), two-phase flow must be expected. It is treated according to the procedures of Sect. 7.4.4. If the leakage point is far below the liquid surface, liquid is released. The methods of Sect. 10.2.1 are then applied.

The composition of the fluid released from the leak depends on the liquid swell (bubble formation due to depressurization) and the phase separation (vapour disengagement). Two flow regimes are to be expected. In case of a non-foaming liquid the regime tends to be churn turbulent, whereas with a foaming medium the regime is bubbly. Since the presence of impurities may render a non-foaming liquid foaming, a bubbly regime is usually assumed.

As was mentioned, if the discharge takes place above the liquid surface, but not far enough for pure vapour release, the possibility of two-phase flow exists. Whether this actually takes place or not, can be decided by using the DIERS criterion [16]. This is presented here based on [15]. The following steps are carried out:

1. Determine the discharge rate for gas according to the procedures of Sects. 10.2.3 and 7.4.3 (Assumption: the quality of the discharged fluid is $x_a = 1$, i.e. only vapour)
2. Calculate of the vapour velocity at the surface w_g in m/s

$$w_g = \frac{\dot{m}}{\rho_g \cdot F_Q} \quad (10.9)$$

where F_Q is the liquid surface area in m^2 .

3. Calculate the bubble rise velocity w_b in m/s

$$w_b = \frac{C_{D1} \cdot [g \cdot \sigma \cdot (\rho_l - \rho_g)]^{1/4}}{\sqrt{\rho_l}} \quad (10.10)$$

In Eq. (10.10) we use $C_{D1} = 1.18$ for bubble flow and 1.53 for churn turbulent flow; σ is the surface tension in N/m.

4. Calculate the dimensionless vapour velocity at the liquid surface, which is given by

$$w_{g,r} = \frac{w_g}{w_b} \quad (10.11)$$

5. Calculate the characteristic dimensionless velocity at the surface for bubble flow $w_{g,b}$; for bubble flow $w_{g,r}$ must be larger than $w_{g,b}$, where

$$w_{g,b} = \frac{\phi_g \times (1 - \phi_g)^2}{(1 - \phi_g^3) \times (1 - 1.2 \times \phi_g)} \quad (10.12)$$

6. Calculate the characteristic dimensionless velocity at the surface for churn turbulent flow $w_{g,a}$; for turbulent churn flow $w_{g,r}$ must be larger than $w_{g,a}$, where

$$w_{g,a} = \frac{2 \cdot \phi_g}{1 - 1.5 \cdot \phi_g} \quad (10.13)$$

In Eqs. (10.12) and (10.13) ϕ_g is the volume fraction of vapour in the vessel, which is related to the degree of filling with the liquid phase ϕ_f as follows

$$\phi_g = 1 - \phi_f \quad (10.14)$$

7. Determine the flow regime

$$\begin{array}{ll} w_{g,r} > w_{g,b} & \text{two-phase bubble flow} \\ w_{g,r} > w_{g,a} & \text{two-phase churn turbulent flow} \\ w_{g,r} < w_{g,b} & \text{and } w_{g,r} < w_{g,a} \text{ one-phase vapour flow} \end{array} \quad (10.15)$$

8. If the criterion for one-phase vapour flow is fulfilled, the leak mass flow rate is calculated according to the procedures of Sects. 10.2.3 and 7.4.3. If there is two-phase flow, the mass fraction of vapour at the leak x_a is calculated as follows [17, 18]:

$$x_a = \frac{\frac{\alpha \cdot (1-\alpha) \cdot w_b \cdot F_Q \cdot \rho_g}{\dot{m}_{n,g}} + \frac{\alpha \cdot \rho_g}{(1-\alpha) \cdot \rho_n}}{1 + \frac{\alpha \cdot \rho_g}{(1-\alpha) \cdot \rho_n}} \quad (10.16)$$

for bubble flow and

$$x_a = \frac{\frac{w_b \cdot F_Q \cdot \rho_g}{\dot{m}_{fl,g}} + \frac{\rho_g}{\rho_{fl}}}{\frac{1-\alpha}{2\alpha} + \frac{\rho_g}{\rho_{fl}}} \quad (10.17)$$

for churn turbulent flow.

In Eqs. (10.16) and (10.17) $\dot{m}_{fl,g}$ is the two-phase mass flow rate according to Eqs. (7.30)–(7.32). The volumetric vapour fraction before pressure relief (state “1”) is given by

$$\alpha = \frac{x_1 \cdot v_{g1}}{x_1 \cdot v_{g1} + (1 - x_1) \cdot v_{f1}} \quad (10.18)$$

Equations (10.16) and (10.17) must be solved iteratively, since x_a figures in the relationships for $\dot{m}_{fl,g}$.

9. Determine the leak mass flow rate according to the procedures of Sect. 7.4.4.

The time-dependent mass flow rate for two-phase flow is then calculated in a stepwise procedure in analogy with the flow sheet of Fig. 10.9.

Example 10.5 Determination of the vapour quality of pressure liquefied propylene

A cylindrical vessel with a height of 6 m and a volume of 30 m³ is filled with 60 % of liquid propylene (C₃H₆). The storage temperature is 20 °C. In the vapour space in the upper portion of the vessel (also called freeboard) a leak with a diameter of $d_L = 0.1$ m occurs. Which flow regime is to be expected? How do results change for different degrees of filling (all results should refer to the moment of leak opening)?

Data: Vapour pressure $p_1 = 1.02$ MPa, atmospheric pressure $p_2 = 0.1$ MPa, surface tension $\sigma = 0.0073078$ N/m, $\rho_f = 512.99$ kg/m³, $\rho_g = 21.44$ kg/m³, $\kappa = 1.32$, $\mu = 0.62$

Solution

The calculation requires the steps listed above:

1. Determination of the leak mass flow rate for gas according to the procedures of Sects. 10.2.3 and 7.4.3 (assumption: the quality of the discharged fluid is $x_a = 1$, only vapour)

In the first place it is found out whether the discharge is critical or not. According to Eq. (7.22) we have

$$w_{\text{crit}} = \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa}{\kappa - 1}} = 0.5421$$

With the present data we obtain

$$w = \frac{p_2}{p_1} = \frac{0.1 \text{ MPa}}{1.02 \text{ MPa}} = 0.098$$

Since $w < w_{\text{crit}}$, the discharge is critical and the mass flow rate is calculated according to Eq. (7.23). We obtain

$$\begin{aligned} \dot{m} &= \dot{m}_{\text{max}} = \mu \cdot F_L \cdot \left\{ \rho_1 p_1 \kappa \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa + 1}{\kappa - 1}} \right\}^{1/2} \\ &= 00.62 \cdot \frac{(00.1 \text{ m})^2 \cdot \pi}{4} \cdot \left\{ 21.44 \frac{\text{kg}}{\text{m}^3} \cdot 1,020,000 \text{ Pa} \cdot 1.32 \cdot \left(\frac{2}{1.32 + 1} \right)^{\frac{1.32 + 1}{1.32 - 1}} \right\}^{1/2} = 15.28 \frac{\text{kg}}{\text{s}} \end{aligned}$$

2. Calculation of the vapour velocity at the surface w_g in m/s according to Eq. (10.9)

$$w_g = \frac{\dot{m}}{\rho_g \times F_Q} = \frac{15.28 \frac{\text{kg}}{\text{s}}}{21.44 \frac{\text{kg}}{\text{m}^3} \cdot \frac{30 \text{ m}^3}{6 \text{ m}}} = 0.1425 \frac{\text{m}}{\text{s}}$$

3. Calculation of the bubble rise velocity w_b in m/s according to Eq. (10.10)

$$\begin{aligned} w_b &= \frac{C_{D1} \cdot [g \cdot \sigma \cdot (\rho_{\text{fl}} - \rho_g)]^{1/4}}{\sqrt{\rho_{\text{fl}}}} \\ &= \frac{1.18 \cdot \left[9.81 \frac{\text{m}}{\text{s}^2} \cdot 0.0073078 \frac{\text{N}}{\text{m}} \cdot (512.99 - 21.44) \frac{\text{kg}}{\text{m}^3} \right]^{1/4}}{\sqrt{512.99 \frac{\text{kg}}{\text{m}^3}}} = 0.1269 \frac{\text{m}}{\text{s}} \end{aligned}$$

for bubble flow and $1.53/1.18 \cdot 0.1269 \text{ m/s} = 0.1645 \text{ m/s}$ for churn turbulent flow.

4. The dimensionless vapour velocity at the liquid surface is given by Eq. (10.11)

$$w_{g,r} = \frac{w_g}{w_b} = \begin{cases} \frac{0.1425 \frac{\text{m}}{\text{s}}}{0.1269 \frac{\text{m}}{\text{s}}} = 1.1229 & \text{for bubble flow} \\ \frac{0.1425 \frac{\text{m}}{\text{s}}}{0.1645 \frac{\text{m}}{\text{s}}} = 0.8663 & \text{for churn turbulent flow} \end{cases}$$

5. Calculation of the characteristic dimensionless velocity at the liquid surface for bubble flow $w_{g,b}$ according to Eq. (10.12) gives

$$w_{g,b} = \frac{\phi_g \cdot (1 - \phi_g)^2}{(1 - \phi_g^3) \cdot (1 - 1.2 \cdot \phi_g)} = \frac{0.4 \cdot 0.6^2}{(1 - 0.4^3) \cdot (1 - 1.2 \cdot 0.4)} = 0.2959$$

6. Calculation of the characteristic dimensionless velocity at the liquid surface for churn turbulent flow $w_{g,a}$ according to Eq. (10.13) gives

$$w_{g,a} = \frac{2 \cdot \phi_g}{1 - 1.5 \cdot \phi_g} = \frac{2 \cdot 0.4}{1 - 1.5 \cdot 0.4} = 2$$

7. Determination of the flow regime

$$\begin{array}{ll} w_{g,r} > w_{g,b} & \text{two-phase bubble flow} \\ w_{g,r} > w_{g,a} & \text{two-phase churn turbulent flow} \\ w_{g,r} < w_{g,b} & \text{and } w_{g,r} < w_{g,a} \text{ one-phase vapour flow} \end{array}$$

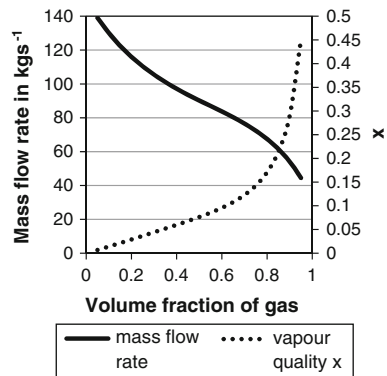
Since $1.1229 > 0.259$, we have two-phase bubble flow.

8. The vapour quality at the leak is calculated by iteratively solving Eq. (10.16) together with Eq. (10.18)

We obtain the quality of the discharging mass flow rate as $x_a = 0.0598$. The mass flow rate results from Eq. (10.16); it amounts to $\dot{m} = 97.16 \frac{\text{kg}}{\text{s}}$.

Figure 10.12 shows the mass flow rate and the vapour quality as functions of the volume fraction α . It is clear that the initial mass flow rate depends strongly on the volume fraction of vapour. This is a stochastic variable, since the vessel is filled and emptied, and the leak occurs at a random point in time.

Fig. 10.12 Mass flow rate and vapour quality at the beginning of release as functions of the volumetric vapour fraction α



10.2.5.1 Liquid Swell After Pressure Relief

Due to the pressure relief vaporization occurs and vapour bubbles are formed inside the liquid column. As a consequence the level rises. The surface of the liquid column then becomes a surface of a mixture of liquid and vapour. Leaks below this surface are treated according to the methods for two-phase flow.

In order to determine the volume fraction of vapour the correlation by Mayinger is used. We then require

- the surface tension of the liquid for boiling conditions, which is given in N/m by

$$\sigma = 6.56 \times 10^{-7} \cdot r \cdot \rho_{\text{fl}} \quad (10.19)$$

In Eq. (10.19) r is the enthalpy of vaporization in J/kg and ρ_{fl} the density of the liquid phase in kg/m³; the numerical coefficient has the unit m.

- the ratio of the kinematic viscosities of the liquid and vapour phases

$$\frac{v_{\text{f}}}{v_{\text{g}}} = \frac{37 \cdot M^{1/6} \cdot \rho_{\text{g}} \cdot (T + 1.47 \cdot T_{\text{s}})}{\rho_{\text{f}}^{7/6} \cdot T^{3/2}} \quad (10.20)$$

In Eq. (10.20) M is the molar mass in g/mol.

Using the abbreviation

$$\sigma' = \sqrt{\frac{\sigma}{g \cdot (\rho_{\text{fl}} - \rho_{\text{g}})}}$$

we obtain the mean volumetric fraction of vapour α in the liquid/vapour mixture as

$$\alpha = 0.73 \cdot \left(\frac{w_{\text{g}}^2}{g \cdot \sigma'} \right)^{0.376} \cdot \left(\frac{\sigma'}{d_{\text{B}}} \right)^{0.176} \cdot \left(\frac{\rho_{\text{fl}}}{\rho_{\text{fl}} - \rho_{\text{g}}} \right)^{-0.585} \cdot \left(\frac{v_{\text{fl}}}{v_{\text{g}}} \right)^{0.256} \quad (10.21)$$

Thus we obtain the (new) volume for the liquid vapour mixture

$$V_{\text{f,g}} = \frac{V}{1 - \alpha} \quad (10.22)$$

which serves to calculate the new filling height for the given vessel geometry.

The volumetric vapour fraction at the surface of the liquid/vapour mixture is given by

$$\alpha_{\text{O}} = \frac{2 \cdot \alpha}{1 - \alpha} \quad (10.23)$$

Assuming a linear relationship the fraction at the vessel bottom is

$$\alpha_B = 2 \cdot \alpha - \alpha_O \quad (10.24)$$

At a leak elevation of z we finally have the vapour fraction

$$\alpha_z = \alpha_B + (\alpha_O - \alpha_B) \cdot \frac{z}{H_{2P}} \quad (10.25)$$

In Eq. (10.25) H_{2P} is the height of the swelled two-phase mixture.

10.2.5.2 Discharge from Vessels Containing a Pressure Liquefied Gas

For calculating the emptying of a vessel an algorithm which accounts for the time dependence of the process is needed. For this purpose a sequence of small time steps, e.g. $\Delta t = 1$ s, is used. Within each of these steps all quantities are assumed to be constant. The changes resulting from discharge and vaporization within a time step are transferred to the subsequent step where again the quantities remain constant. The calculation ends when the pressure inside the vessel equals the outside pressure.

In the first place the mean vapour fraction is calculated according to Sect. 10.2.5.1. If the leak lies above the liquid, respectively liquid/vapour surface, the flow regime and the corresponding mass flow rate are determined according to Sect. 10.2.3. If the leak is below the surface the volumetric vapour fraction is calculated according to Eq. (10.25). The methods of Sect. 7.4 for dealing with two-phase flow are then used.

The temperature is tentatively lowered by a few degrees. The loss of enthalpy of the liquid then serves for vaporization. The volume released is replaced by vapour, as long as there is still liquid and the quantity of vaporized liquid is sufficient. Otherwise this quantity is the upper limit. As a consequence we obtain a new value for the pressure. By iteration the temperature is subsequently modified until the values for pressure and temperature lie on the vapour pressure curve (vid. Fig. 10.4). The latter can be determined from approximate equations [13] or the Clausius-Clapeyron relation [19]. The connection between temperature and pressure is ensured by the equation of state for gases.

Example 10.6 shows some of the results which were obtained with a computer program based on the preceding description.

Example 10.6 Discharge of liquefied propylene from a leak

A cylindrical vessel is filled with propylene (C_3H_6). Its height amounts to 20 m, its diameter to 10 m; 50 % of its volume are filled with liquid propylene, which is stored at a temperature of 20 °C and a pressure of 1,017,000 Pa.

The time-dependent mass flow rates are to be calculated for leaks with a diameter of 10 cm occurring at several different elevations. How do the results change for a leak diameters of 20 cm?

Data: $M = 42.08$, $\rho_f = 513.04 \text{ kg/m}^3$, $\rho_g = 21.44 \text{ kg/m}^3$, $c_f = 2,275 \text{ J/(kg K)}$, $r = 437,737 \text{ J/kg}$, $\kappa = 1.36$, $F_L = 7.85 \times 10^{-3} \text{ m}^2$, $\mu = 0.62$

Solution

Several characteristic parameters are shown in Figs. 10.13, 10.14, 10.15, 10.16, 10.17 and 10.18 for both leak diameters. Results for different leak elevations and a degree of filling of 90 % are presented in Table 10.3.

Fig. 10.13 Variations with time of pressure and temperature for different leak elevations (degree of filling 50 %, leak diameter 0.1 m)

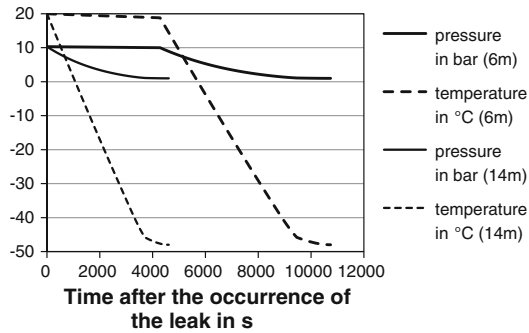


Fig. 10.14 Variations with time of mass flow rate and liquid level for different leak elevations (degree of filling 50 %, leak diameter 0.1 m)

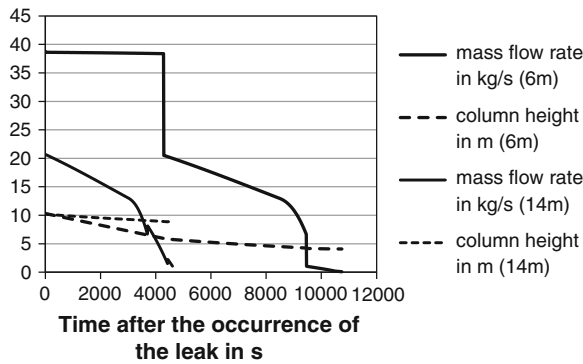


Fig. 10.15 Duration of the release and discharged mass for different leak elevations (degree of filling 50 % (content 417.1 t), leak diameter 0.1 m)

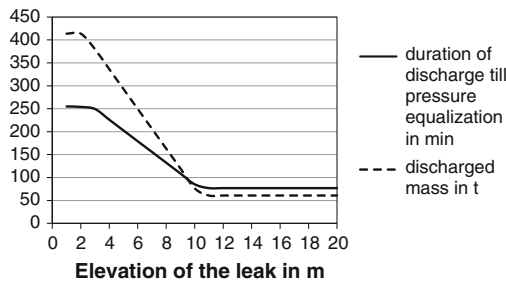


Fig. 10.16 Variations with time of pressure and temperature for different leak elevations (degree of filling 50 %, leak diameter 0.2 m)

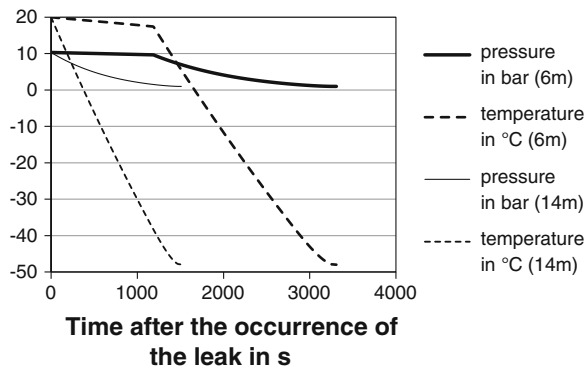


Fig. 10.17 Variations with time of mass flow rate and liquid level for different leak elevations (degree of filling 50 %, leak diameter 0.2 m)

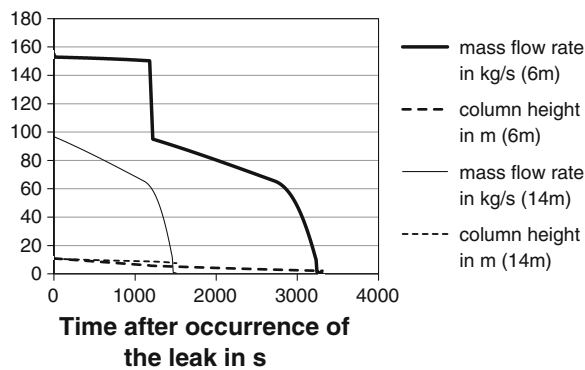


Fig. 10.18 Duration of the release and discharged mass for different leak elevations (degree of filling 50 % (content 417.1 t), leak diameter 0.2 m)

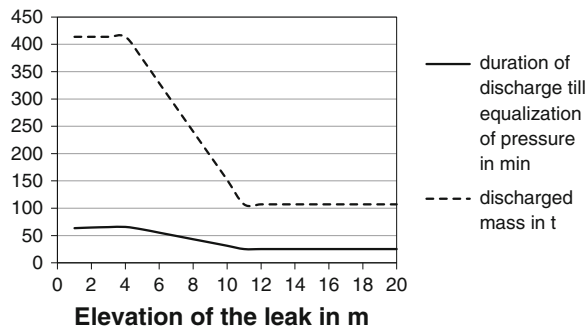


Table 10.3 Characteristic results for a filling height of 90 % (vessel content: 728.1 t) and leaks with a diameter of 0.1 m at different elevations

Elevation in m	8	18.2	20
Discharged mass in kg	469,500	29,920	12,120
Duration of release in min	262.6	25.0	15.4
Maximum height of column in m	18.56	18.56	18.37

The remaining inventory of material vaporizes and is exchanged with the outside air by diffusion. □

10.3 Free Jets

If a gas is released it is subsequently dispersed in the atmosphere. This naturally applies as well to the vapour phase of a two-phase release. If, on the other hand, a liquid is released a pool is formed. This is also true for the liquid phase of a two-phase release. If the materials involved are flammable jet fires or pool fires may occur. These are treated in Sect. 10.6.

The location of the pool to be formed depends on the position and orientation of the leak as well as on the initial momentum of the free jet emanating from the leak. If the pressure difference between the internal pressure of the vessel and the outside pressure is large free jets may reach a length of up to 100 m. Thus they constitute a hazard to their surroundings, e.g. for the staff of the plant.

As far as modelling is concerned the treatment of free jets represents the transition between models, for example from vessel discharge to free jet. It must then be ensured that quantities such as mass flow rate, momentum and enthalpy are conserved (vid. Example 10.7).

The phenomena to be treated are very complex. This leads to modelling uncertainties, which find their expression in the large number of models proposed in the literature. In what follows simple models for treating free jets of liquids, gases and two phases are presented.

10.3.1 Liquids

Free jets of liquids can be treated in a first approximation like the throw of a ball without air resistance, if no substantial vaporization is to be expected (vapour pressure $\ll$ atmospheric pressure). One obtains the path in x-direction (horizontal) for a jet with an initial velocity of v_0 and an angle of α between the jet trajectory and the horizontal line as

$$x(t) = v_0 \cdot \cos(\alpha) \cdot t \quad (10.26)$$

and for the y-direction (vertical)

$$y(t) = l_0 + v_0 \cdot \sin(\alpha) \cdot t - \frac{g}{2} \cdot t^2 \quad (10.27)$$

In Eqs. (10.26) and (10.27) v_0 is the discharge velocity of the jet in m/s, l_0 the elevation of the leak above ground in m; g is the acceleration due to gravity in m/s^2 and t the time since the leak opening in s. Inclusion of the resistance of air and the opening up (divergence) of the jet are treated in [2]. The application of the above equations is illustrated by the following example.

Example 10.7 Free jet of liquid from a vessel leak

The vessel of Example 10.2 is assumed to be supported by columns of length $l_0 = 2$ m. The leak is supposed to occur at a short nozzle at the bottom of the vessel. The following orientations with respect to the horizontal line are analyzed: $\alpha = 20^\circ$, $\alpha = 45^\circ$, $\alpha = 80^\circ$. Determine the impact point of the liquid jet, the moment in time of impact and the corresponding force.

Solution

The initial velocity of the jet is derived from Eq. (10.4)

$$v_0(t') = \frac{\dot{m}(t')}{F_L \cdot \rho} = \mu \cdot \sqrt{2gh_0 + \frac{2\rho}{\rho} - g\mu^2 \frac{F_L}{F_Q} \cdot t'}$$

The time variable is denoted by t' . Liquid issuing at point in time t' from the leak has covered at point in time t the distance

$$x(t, t') = v_0(t') \cdot \cos(\alpha) \cdot (t - t')$$

in the x-direction and

$$y(t, t') = l_0 + v_0(t') \cdot \sin(\alpha) \cdot (t - t') - \frac{g}{2} \cdot (t - t')^2$$

in the y-direction.

With the data of the problem we have for the case without imposed pressure

$$v_0(t') = 8.2388 \frac{\text{m}}{\text{s}} - 0.0094 \frac{\text{m}}{\text{s}^2} \cdot t' \text{ s}$$

Thus we arrive at

$$x(t, t') = \left(8.2388 \frac{\text{m}}{\text{s}} - 0.0094 \frac{\text{m}}{\text{s}^2} \cdot t' \text{ s} \right) \cdot \cos(\alpha) \cdot (t - t') \text{ s}$$

and

$$y(t, t') = 2 \text{ m} + \left(8.2388 \frac{\text{m}}{\text{s}} - 0.0094 \frac{\text{m}}{\text{s}^2} \cdot t' \text{ s} \right) \cdot \sin(\alpha) \cdot (t - t') - \frac{g}{2} \cdot (t - t')^2$$

In case of an imposed pressure of 1 bar one obtains

$$v_0(t') = 13.1603 \frac{\text{m}}{\text{s}} - 0.0094 \frac{\text{m}}{\text{s}^2} \cdot t' \text{ s}$$

The coordinates $x(t, t')$ and $y(t, t')$ are determined in analogy to the above results.

The maximum time of flight and hence the longest flight distance result for the point in time t^* , at which the jet touches the ground, i.e. d.h. $y(t^*, t') = 0$. This gives

$$t^* = t' + \frac{v_0(t') \cdot \sin \alpha}{g} + \sqrt{\frac{2 \cdot l_0}{g} + \left(\frac{v_0(t') \cdot \sin \alpha}{g} \right)^2}$$

In order to determine the force of the jet the following relationship is used

$$F = \rho \cdot F_L \cdot v_0(t') \cdot \sqrt{\dot{x}(t, t')^2 + \dot{y}(t, t')^2}$$

where the dot on top of the quantities denotes the derivative with respect to t , i.e. the velocity. We have

$$\dot{x}(t, t') = \left(8.2388 \frac{\text{m}}{\text{s}} - 0.0094 \frac{\text{m}}{\text{s}^2} \cdot t' \cdot \text{s} \right) \cdot \cos(\alpha)$$

$$\dot{y}(t, t') = \left(8.2388 \frac{\text{m}}{\text{s}} - 0.0094 \frac{\text{m}}{\text{s}^2} \cdot t' \cdot \text{s} \right) \cdot \sin(\alpha) - g \cdot (t - t')$$

If the velocity component in y -direction is equal to 0, the trajectory has reached its highest point. This is true for

$$t^+ = t' + \frac{v_0(t') \cdot \sin \alpha}{g}$$

In Table 10.4 several numerical results are given for vessels without imposed pressure.

Table 10.4 Characteristic parameters of the trajectories of liquid jets for different boundary conditions

t' in s	t^* in s	t^+ in s	$x(t^*, t')$ in m	$y(t^+, t')$ in m	$F(t^*, t')$ in N
$\alpha = 20^\circ$					
0	0.99	0.29	7.66	2.40	311.23
300	300.85	300.19	4.33	2.18	163.82
870	870.64	870.002	0.03	2.00	0.84
$\alpha = 45^\circ$					
0	1.47	0.59	8.56	3.73	311.23
300	301.14	300.39	4.37	2.75	163.82
870	870.64	870.004	0.03	2.00	0.84
$\alpha = 80^\circ$					
0	1.87	0.83	2.68	5.36	311.23
300	301.38	300.54	1.30	3.45	163.82
870	870.64	870.006	0.01	2.00	0.84

The impact force is the same independently of the angle α ; only the components in the x and y directions differ. $\square$

10.3.2 Gases

Models for free jets of gases are treated in detail in [7]. Results of empirical models and solutions of simplified systems of differential equations are presented there and compared with experimental findings.

Gases are usually handled under pressure. On depressurization (vid. Sect. 7.4.3) or on containment failure a momentum jet issues. Owing to entrainment of air from the surroundings the velocity and concentration of the gas in the jet drop with increasing distance from the point of issue. For flammable gases the distances are of interest where concentrations in the jet lie between the lower and upper limits of explosion (vid. Sects. 2.1.1.1 and 2.1.1.2). If a toxic gas is involved the dilution as a function of distance from the point of issue is important. Furthermore the coordinates of the point where the initial momentum is virtually lost mark the place where further transport takes place with the surrounding air. This transport is then treated with the methods of atmospheric dispersion (vid. Sect. 10.5).

In what follows the model of Chen and Rodi [20] is briefly described. It is derived from numerous experimental investigations and applies to vertically upright free jets of gases, which are lighter than air, for a still surrounding atmosphere and subcritical discharge.

In this model several correlations are used. In order to determine which of them applies, Froude's number is needed. It is given by

$$Fr = \frac{v_0}{g \cdot d_0 \cdot \left(\frac{\rho_L}{\rho_0} - 1 \right)} \quad (10.28)$$

The choice of the correlation is based on the following relation

$$K = \frac{z}{d_0 \cdot \sqrt{Fr} \cdot \left(\frac{\rho_0}{\rho_L} \right)^{1/4}} \quad (10.29)$$

The distance-dependent velocity and concentration, $v(z)$ and $c(z)$, are calculated using the following relationships

- if $K < 0.5$ (non-buoyant since the initial momentum dominates the buoyancy forces)

$$v(z) = v_0 \cdot 6.2 \cdot \left(\frac{\rho_0}{\rho_L} \right)^{1/2} \cdot \frac{d_0}{z} \quad (10.30)$$

$$c(z) = c_0 \cdot 5 \cdot \left(\frac{\rho_0}{\rho_L} \right)^{-1/2} \cdot \frac{d_0}{z} \quad (10.31)$$

- if $0.5 \leq K \leq 5$ (transition region)

$$v(z) = \frac{7.26 \cdot v_0}{Fr^{1/10}} \cdot \left(\frac{\rho_0}{\rho_L} \right)^{9/20} \cdot \left(\frac{d_0}{z} \right)^{4/5} \quad (10.32)$$

$$c(z) = 0.44 \cdot c_0 \cdot Fr^{1/8} \cdot \left(\frac{\rho_0}{\rho_L} \right)^{-7/16} \cdot \left(\frac{d_0}{z} \right)^{5/4} \quad (10.33)$$

- if $K > 5$ (buoyant plume)

$$v(z) = \frac{3.5 \cdot v_0}{Fr^{1/3}} \cdot \left(\frac{\rho_0}{\rho_L} \right)^{1/3} \cdot \left(\frac{d_0}{z} \right)^{1/3} \quad (10.34)$$

$$c(z) = 9.35 \cdot c_0 \cdot Fr^{1/3} \cdot \left(\frac{\rho_0}{\rho_L} \right)^{-1/3} \cdot \left(\frac{d_0}{z} \right)^{5/3} \quad (10.35)$$

For heavier-than-air gases the following relationship for the maximum jet length is given

$$l_{\max} = 1.85 \cdot d_0 \cdot \sqrt{|Fr|} \quad (10.36)$$

In Eqs. (10.28) to (10.36) d_0 is the diameter of the aperture in m, v_0 the velocity of release in m/s and $\rho_0/\rho_L = M_L/M_0$ the ratio of the densities of the released gas and air.

Example 10.8 Vertically upright free jet of ethylene from a vessel leak

A vessel with a volume of $V = 10 \text{ m}^3$ has a leak with a diameter of $d_0 = 0.1 \text{ m}$ (cross-sectional area $F_L = 7.85 \times 10^{-3} \text{ m}^2$). It is filled with $m = 20 \text{ kg}$ of ethylene (boiling point -103.7°C) at a temperature of $T = 290 \text{ K}$. Determine the distance at which the jet practically comes to a standstill for the conditions at the beginning of the discharge (wind speed for relatively still air is taken to be 2 m/s [2]).

Data: $R = 0.29638 \text{ kJ/(kgK)}$; $\kappa = 1.25$; $\mu = 0.62$, $Z = 1$, atmospheric pressure $p_2 = 100,000 \text{ Pa}$, molar mass of ethylene $M_E = 28.05 \text{ g/mol}$, molar mass of air $M_L = 28.9964 \text{ g/mol}$

Solution

In the first place it is checked whether the pressure ratio is smaller than critical or not. According to Eq. (7.22) we have

$$w_{\text{crit}} = \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa}{\kappa - 1}} = 0.55$$

The pressure inside the vessel results from the equation of state for gases (7.10)

$$p = \frac{m \cdot Z \cdot R \cdot T}{V} = \frac{20 \text{ kg} \cdot 1 \cdot 296.38 \frac{\text{J}}{\text{kgK}} \cdot 290 \text{ K}}{10 \text{ m}^3} = 171,900.4 \text{ Pa}$$

Thus we have

$$w = \frac{100,000 \text{ Pa}}{171,900.4 \text{ Pa}} = 0.582$$

Since $w > w_{\text{crit}}$, the discharge is subcritical. The initial density of the ethylene is $\rho_1 = \frac{m}{V} = \frac{20 \text{ kg}}{10 \text{ m}^3} = 2 \frac{\text{kg}}{\text{m}^3}$

The initial discharged mass flow rate according to Eq. (7.20) amounts to

$$\begin{aligned} \dot{m} &= \mu \cdot F_L \cdot \left\{ \frac{2 \cdot \kappa}{\kappa - 1} \cdot p_1 \cdot \rho_1 \cdot \left(\frac{p_2}{p_1} \right)^{\frac{2}{\kappa}} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \right] \right\}^{1/2} \\ &= 00.62 \cdot 70.85 \times 10^{-3} \text{ m}^2 \cdot \left(10 \cdot 171,900.4 \text{ Pa} \cdot 2 \frac{\text{kg}}{\text{m}^3} \cdot \left(\frac{100,000 \text{ Pa}}{171,900.4 \text{ Pa}} \right)^{\frac{2}{10.25}} \right. \\ &\quad \left. \left[1 - \left(\frac{100,000 \text{ Pa}}{171,900.4 \text{ Pa}} \right)^{\frac{00.25}{10.25}} \right] \right)^{1/2} = 1.87 \frac{\text{kg}}{\text{s}} \end{aligned}$$

According to Eq. (10.28) Froude's number is

$$\begin{aligned} \text{Fr} &= \frac{v_0}{g \cdot d_0 \cdot \left(\frac{\rho_L}{\rho_0} - 1 \right)} = \frac{\dot{m} \cdot (F_L \cdot \rho_1)^{-1}}{g \cdot d_0 \cdot \left(\frac{M_L}{M_E} - 1 \right)} \\ &= \frac{1.87 \frac{\text{kg}}{\text{s}} \cdot \left(7.85 \times 10^{-3} \text{ m}^2 \cdot 2 \frac{\text{kg}}{\text{m}^3} \right)^{-1}}{9.81 \frac{\text{m}}{\text{s}^2} \cdot 0.1 \text{ m} \cdot \left(\frac{28.9964 \frac{\text{g}}{\text{mol}}}{28.05 \frac{\text{g}}{\text{mol}}} - 1 \right)} = 3,598.6 \end{aligned}$$

where we obtain from the numerator $v_0 = 119.11 \text{ m/s}$ and hence according to Eq. (10.34)

$$\begin{aligned} z^{*1/3} &= \frac{3.5 \cdot v_0 \cdot d_0^{1/3}}{v(z^*) \cdot \text{Fr}^{1/3}} \cdot \left(\frac{\rho_0}{\rho_L} \right)^{1/3} = \frac{3.5 \cdot 119.11 \frac{\text{m}}{\text{s}} \cdot (0.1 \text{ m})^{1/3}}{2 \frac{\text{m}}{\text{s}} \cdot 3,598.6^{1/3}} \cdot \left(\frac{28.9964 \frac{\text{g}}{\text{mol}}}{28.05 \frac{\text{g}}{\text{mol}}} \right)^{1/3} \\ &= 6.38 \text{ m}^{1/3} \end{aligned}$$

Thus we obtain a length of the jet of $z^* = 259.7 \text{ m}$ (jet velocity at z^* : 2 m/s).

Now it can be checked whether the appropriate relationship has been chosen or not by calculating

$$K = \frac{z^*}{d_0 \cdot \sqrt{\text{Fr}} \cdot \left(\frac{\rho_0}{\rho_L}\right)^{1/4}} = \frac{259.7 \text{ m}}{0.1 \text{ m} \cdot \sqrt{3598.6} \left(\frac{28.9964 \frac{\text{g}}{\text{mol}}}{28.05 \frac{\text{g}}{\text{mol}}}\right)^{1/4}} = 42.93$$

Since $K > 5$, the appropriate equation has been chosen and we obtain from Eq. (10.35) that the concentration has dropped to a fraction of

$$\begin{aligned} \frac{c(z^*)}{c_0} &= 9.35 \cdot \text{Fr}^{1/3} \cdot \left(\frac{\rho_0}{\rho_L}\right)^{-1/3} \cdot \left(\frac{d_0}{z^*}\right)^{5/3} \\ &= 9.35 \cdot 3,598.6^{1/3} \cdot \left(\frac{28.9964 \frac{\text{g}}{\text{mol}}}{28.05 \frac{\text{g}}{\text{mol}}}\right)^{-1/3} \cdot \left(\frac{0.1 \text{ m}}{259.7 \text{ m}}\right)^{5/3} \\ &= 2.89 \times 10^{-4} \end{aligned}$$

of its original value.

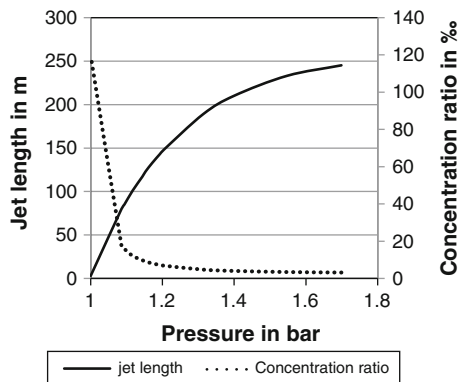
Figure 10.19 shows characteristic parameters of free jets for several initial pressure of release. □

10.3.3 Two-Phase Flow and Flash Vaporization

Leaking liquids may be subcooled or superheated [7]. The temperature of a superheated liquid lies above its vaporization temperature at ambient pressure. For a subcooled liquid the inverse is true.

With subcooled liquids the jet disintegrates into droplets due to aerodynamic forces after a certain distance of flight. Liquid vaporizes from these droplets. They

Fig. 10.19 Jet lengths and concentration ratios between the end of the jet and its point of issue from the vessel at the beginning of discharge for different initial pressures



cool down. The mixture of vapour and air has a mixing temperature which depends on the prevalent temperature of the liquid, the enthalpy of vaporization and the quantity of air sucked into the jet.

Thus, trajectories for the jet droplets result, which may differ. Depending on the elevation of the leak above the ground, the direction of emission, the type of material and the droplet size, the droplets may vaporize before they reach the ground. Droplets which reach the ground form a pool from which further liquid vaporizes in the course of time. Due to these processes droplets are formed which differ in trajectory and extent of vaporization.

If a superheated liquid is released a certain fraction vaporizes on depressurization (flash); the remainder is cooled down because it has to provide the enthalpy of vaporization. The heat balance based on the assumption of adiabatic depressurization is

$$(1 - x) \cdot c_p \cdot (-dT) = \Delta H_v \cdot dx \quad (10.37)$$

In Eq. (10.37) we use

c_p specific heat capacity of the liquid in J/(kgK)

ΔH_v enthalpy of vaporization in J/kg

T temperature in K

x vapour quality in kg/kg

dx respectively dT denote the changes of the corresponding quantities

The fraction of vaporized liquid is obtained by integrating Eq. (10.37). This gives

$$x = 1 - \exp \left[-\frac{c_p}{\Delta H_v} \cdot (T_1 - T_s) \right] \quad (10.38)$$

In Eq. (10.38) we have in addition to the quantities defined above

T_1 temperature of the fluid at the issue of the leak in K

T_s boiling temperature of the fluid in K

Equation (10.38) provides the vapour quality under equilibrium conditions. In practical emission situations part of the liquid is discharged as spray. The droplets then formed receive their enthalpy of vaporization from the surrounding air. In this way the fraction of vaporized liquid is substantially increased. Often one assumes that the fraction of liquid spray is equal to that vaporized by flash vaporization. If the fraction vaporized by flashing is small, about 5 %, one may assume that the quantity vaporized due to spray formation is two or three times that vaporized by flashing.

After the flash vaporization the liquid has its boiling temperature. Vaporization then continues as a process which is chiefly determined by the possibilities of heat

and mass transfer. In this second stage of vaporization the rate of vaporization is limited. It is generally assumed to be less important than the initial flash vaporization, especially as far as the formation of flammable clouds is concerned.

Free jets with incomplete vaporization experience rainout of droplets. This process is treated below using the model by Fauske [21, 22]. According to [7] this model is to be preferred to an alternative also presented there. Fauske's model applies to horizontal jets released at an elevation of s (in m) above the ground.

Starting point is the mass rate flow at the leak. It is calculated as follows

$$G = \mu \cdot \sqrt{2 \cdot [p_1 - p(T_0)]} \cdot \rho_f \quad (10.39)$$

in case it is not taken from discharge calculations (vid. Sect. 10.2).

In Eq. (10.39) G denotes the mass flow rate in $\text{kg}/(\text{s m}^2)$, ρ_f the density of the liquid in kg/m^3 , p_1 the internal pressure and $p(T_0)$ the vapour pressure of the substance at its temperature before release, both in Pa. Equation (10.39) is applicable if $p_1 \gg p(T_0)$, because then the problem can be treated as though only liquid were released.

The discharge velocity results from Eq. (10.39)

$$v_0 = \frac{G}{\rho_f} \quad (10.40)$$

After leaving the aperture the jet disintegrates due to air resistance and vaporization. Assuming that disintegration is caused by the resistance of air we obtain the erosion velocity u_e

$$u_e = 0.08 \cdot \left(\frac{\rho_L}{\rho_f} \right)^{1/2} \cdot v_0 \quad (10.41)$$

The core of the jet fully disintegrates within the interval $[0, t^*]$ with t^* given by

$$t^* = \frac{d_0}{2 \cdot u_e} \quad (10.42)$$

Thus we obtain the flight length until disintegration as

$$L = v_0 \cdot t^* \quad (10.43)$$

Full disintegration before the jet reaches the ground is possible, if

$$t^* < \left(\frac{2 \cdot s}{g} \right)^{1/2} \quad (10.44)$$

applies. In Eq. (10.44) s is the height of fall to the ground.

The entrainment of air during the flight is described by

$$\dot{w}_L = 0.08 \cdot (\rho_L \cdot \rho_f)^{1/2} v_0 \cdot \pi \cdot d_0 \cdot Z \quad (10.45)$$

The jet length Z used in Eq. (10.45) is obtained from

$$\left(\frac{2 \cdot s}{g}\right)^{1/2} = \frac{Z}{v_0} + 0.16 \cdot \left(\frac{\rho_L}{\rho_f}\right)^{1/2} \cdot \frac{Z^2}{d_0 \cdot v_0} \quad (10.46)$$

Air entrainment causes a strong drop of the partial pressure of the released substance and a reduction of the droplet temperature. The liquid droplets are cooled down until the heat flux from the entrained air into the droplets impedes a further temperature drop thus causing a stationary process of vaporization. The corresponding equilibrium temperature T_{KG} can be determined iteratively from

$$\frac{c_{p,L} \cdot (T_L - T_{KG})}{\Delta h_v} = \frac{p(T_{KG}) - p_{H_2O}(T_L) \cdot \frac{\phi}{100}}{p_L - p(T_{KG})} \quad (10.47)$$

In Eq. (10.47) T_L is the temperature of ambient air in K, p_L the atmospheric pressure in Pa, T_{KG} the equilibrium temperature in K, ϕ the relative humidity in %; $p(\dots)$ denote the vapour pressures of the released material and of water in Pa at the respective temperatures.

The fraction which vaporizes because of the drop of the partial pressure is given by

$$x_F = \frac{c_{pl} \cdot (T_0 - T_{KG})}{\Delta h_v} \quad (10.48)$$

where T_0 is the temperature of the substance before release in K. Additionally to the fraction given by Eq. (10.48) heat transfer from the entrained air leads to vaporization, i.e.

$$x_v = 0.32 \cdot \sqrt{\frac{\rho_L}{\rho_f}} \cdot \frac{c_{p,L} \cdot (T_L - T_{KG}) \cdot Z}{\Delta h_v \cdot d_0} \quad (10.49)$$

If formally we obtain $x_F + x_v > 1$, which is possible, this means that all the liquid is vaporized.

Example 10.9 Flash vaporization of propylene

In the context of the calculations for Example 10.6 it was found that for a leak elevation of 1 m and 9,000 s after rupture the released two-phase mixture has the following characteristics: pressure $p_1 = 10.03$ bar, temperature 18.95 °C, vapour quality $x = 1.558 \times 10^{-4}$, mass flow rate 38.75 kg/s.

What is the quality of the vapour after the ensuing flash vaporization?

Data: saturation temperature for 100,000 Pa atmospheric pressure $T_s = 225.17$ K, $\Delta H_v = 439,483$ J/kg, $c_f = 2,275$ J/(kg K)

Solution

According to Eq. (10.38) we obtain

$$\begin{aligned} x &= 1 - \exp \left[-\frac{c_p}{\Delta H_v} \cdot (T_1 - T_s) \right] \\ &= 1 - \exp \left[-\frac{2,275 \frac{\text{J}}{\text{kg K}}}{439,483 \frac{\text{J}}{\text{kg}}} \cdot (292.1 - 225.17) \text{ K} \right] = 0.2928 \end{aligned}$$

This is added to the initial vapour fraction of 1.558×10^{-4} so that 0.293 results. In view of the vaporization by heat transfer due to mixing with the surrounding air (20 °C), which has not been accounted for so far, one may assume that the vapour fraction is even higher. Since propylene is heavier than air the vapour will be dispersed as a dense gas (vid. Sect. 10.5.2). $\square$

Example 10.10 Horizontal free jet according to Fauske's model

In Example 10.6 a calculation was carried out for a leak at the upper edge of the vessel ($s = 20$ m) and a degree of filling of 90 % liquid.

At the moment of the occurrence of leak the vessel content is at a temperature of $T_0 = 292.93$ K. The mass flow rate amounts to $G = 2,910.6$ kg/(m² s) and the vapour quality is $x = 0.23$.

Calculate the characteristic parameters of the free jet according to the model of Fauske.

Data: $M = 42.08$, $\rho_f = 513.04$ kg/m³, $\rho_g = 21.44$ kg/m³, $c_f = 2,275$ J/(kg K), $\Delta H_v = 437,737$ J/kg; $\kappa = 1.36$, $d_0 = 0.1$ m, $p_2 = 100,000$ Pa, $\rho_L = 1.19$ kg/m³, $T_L = 293.15$ K, $c_{pL} = 1,006$ J/(kg K), relative humidity of the air $\varphi = 20$ %

Solution

Equation (10.40) gives the initial velocity of discharge as

$$v_0 = \frac{G}{\rho_f} = \frac{2,910.6 \frac{\text{kg}}{\text{m}^2 \text{s}}}{513.04 \frac{\text{kg}}{\text{m}^3}} = 5.67 \frac{\text{m}}{\text{s}}$$

The erosion velocity is calculated according to Eq. (10.41), which gives

$$u_e = 0.08 \cdot \left(\frac{\rho_L}{\rho_f} \right)^{1/2} \cdot v_0 = 0.08 \cdot \left(\frac{1.19 \frac{\text{kg}}{\text{m}^3}}{513.04 \frac{\text{kg}}{\text{m}^3}} \right)^{1/2} \cdot 5.67 \frac{\text{m}}{\text{s}} = 0.022 \frac{\text{m}}{\text{s}}$$

The time until droplet disintegration results from Eq. (10.42)

$$t^* = \frac{d_0}{2 \cdot u_e} = \frac{0.1 \text{ m}}{2 \cdot 0.022 \frac{\text{m}}{\text{s}}} = 2.27 \text{ s}$$

The flight path until droplet disintegration is calculated using Eq. (10.43), which gives

$$L = v_0 \cdot t^* = 5.67 \frac{\text{m}}{\text{s}} \cdot 2.27 \text{ s} = 12.87 \text{ m}$$

Equation (10.44) serves to check whether the jet fully disintegrates before reaching the ground. It results in

$$t^* < \left(\frac{2 \cdot s}{g} \right)^{1/2} = \left(\frac{2 \cdot 20 \text{ m}}{9.81 \frac{\text{m}}{\text{s}^2}} \right)^{1/2} = 2.02 \text{ s}$$

i.e. the jet does not disintegrate before touching the ground.

From Eq. (10.46) we obtain $Z = 7.32 \text{ m}$

$$\left(\frac{2 \cdot 20 \text{ m}}{9.81 \frac{\text{m}}{\text{s}^2}} \right)^{1/2} = \frac{7.32 \text{ m}}{5.67 \frac{\text{m}}{\text{s}}} + 0.16 \cdot \left(\frac{1.19 \frac{\text{kg}}{\text{m}^3}}{513.04 \frac{\text{kg}}{\text{m}^3}} \right)^{1/2} \cdot \frac{(7.32 \text{ m})^2}{0.1 \text{ m} \cdot 5.67 \frac{\text{m}}{\text{s}}}$$

i.e. droplet disintegration is not totally completed on touching the ground.

The mass flow rate of the entrained air follows from Eq. (10.45)

$$\begin{aligned} \dot{w}_L &= 0.08 \cdot (\rho_L \cdot \rho_f)^{1/2} v_0 \cdot \pi \cdot d_0 \cdot Z \\ &= 0.08 \cdot \left(1.19 \frac{\text{kg}}{\text{m}^3} \cdot 513.04 \frac{\text{kg}}{\text{m}^3} \right)^{1/2} \cdot 5.67 \frac{\text{m}}{\text{s}} \cdot 3.14 \cdot 0.1 \text{ m} \cdot 7.32 \text{ m} = 25.76 \frac{\text{kg}}{\text{s}} \end{aligned}$$

The equilibrium temperature is determined iteratively from Eq. (10.47), which leads to

$$\frac{1,006 \frac{\text{J}}{\text{kg K}} \cdot (293.15 \text{ K} - T_{\text{KG}})}{437,734 \frac{\text{J}}{\text{kg}}} = \frac{p(T_{\text{KG}}) - 2,339.29 \text{ Pa} \cdot \frac{20}{100}}{100,000 \text{ Pa} - p(T_{\text{KG}})}$$

and to $T_{\text{KG}} = 194.57 \text{ K}$, where $(T_{\text{KG}}) = 18,852.4 \text{ Pa}$.

Equation (10.48) provides the vapour fraction

$$x_F = \frac{c_{pf} \cdot (T_0 - T_{KG})}{\Delta h_v} = \frac{2,275 \frac{\text{J}}{\text{kg K}} \cdot (292.93 \text{ K} - 194.6 \text{ K})}{437,737 \frac{\text{J}}{\text{kg}}} = 0.511$$

The vaporized fraction results from Eq. (10.49) as

$$\begin{aligned} x_v &= 0.32 \cdot \sqrt{\frac{\rho_L}{\rho_f} \cdot \frac{c_{p,L} \cdot (T_L - T_{KG}) \cdot Z}{\Delta h_v \cdot d_0}} \\ &= 0.32 \cdot \sqrt{\frac{1.19 \frac{\text{kg}}{\text{m}^3}}{513.04 \frac{\text{kg}}{\text{m}^3}} \cdot \frac{1,006 \frac{\text{J}}{\text{kg K}} \cdot (293.15 \text{ K} - 194.6 \text{ K}) \cdot 7.32 \text{ m}}{437,737 \frac{\text{J}}{\text{kg}} \cdot 0.1 \text{ m}}} = 0.2555 \end{aligned}$$

Thus the total vapour fraction after flash vaporization amounts to $0.23 + 0.511 + 0.2555 = 0.9965$, so that it is assumed for the subsequent dispersion calculation that there is nothing but propylene vapour. $\square$

10.4 Pool Formation and Pool Vaporization

If a liquid is released a pool is formed. Subsequently the liquid vaporizes to produce a plume which is dispersed in the atmosphere. The vaporization process determines the rate of mass transfer from the pool to the plume; it constitutes the source term. In [2] the following situations are distinguished:

- a substance, which is volatile under atmospheric pressure and temperature (e. g. acetone)
- a superheated liquid
 - at ambient temperature and under pressure (pressure liquefied gas, e.g. butane)
 - at high temperature and under pressure (e. g. hot cyclohexane)
- a refrigerated liquefied gas at low temperature and atmospheric pressure (e. g. cold methane)

Releases into bunds (receiving spaces below tanks) and directly onto the ground have to be treated. If the liquid is spilled into a bund the pool geometry and surface are determined by the bund geometry. If the spill is onto the ground, circular geometry of the pool is usually assumed. The pool size then varies with time. The vaporization rate from pools is determined by the following factors:

- mean temperature in the pool, which results from its heat balance,
- surface area of the pool,
- coefficient of mass transfer from the pool to its surroundings.

The heat balance comprises the enthalpy of the spilled liquid, the heat transfer from the ground to the pool, from the air to the pool and heat radiation from the sun or neighbouring warm objects as well as the heat losses by vaporization and heat transfer to the environment from the pool.

This is summarized as follows:

$$c_p \cdot m \cdot \frac{dT}{dt} = -F_Q \cdot (q_v'' - q_B'' - q_L'' - q_S'') + \dot{m}_Z \cdot (h_{f,Z} - h_{f,P}) \quad (10.50)$$

In Eq. (10.50) c_p is the heat capacity of the liquid in J/(kg K), m the mass of liquid contained in the pool in kg, F_Q the surface area of the pool in m^2 , q_v'' the enthalpy loss by vaporization, q_B'' the heat transfer from the ground, q_L'' the convective heat transfer from the air and q_S'' the net radiation gain (pool—environment), all of them in W/m^2 ; $\dot{m}_Z$ finally is the mass flow rate into the pool in kg/s and $h_{f,Z} - h_{f,P}$ the difference of the enthalpy of the spilled liquid and that already present in the pool in J/kg.

The mass balance of the pool is

$$\frac{dm}{dt} = -\dot{m}_V + \dot{m}_Z \quad (10.51)$$

where

$$\dot{m}_V = \frac{F_Q \cdot q_v''}{\Delta H_v} \quad (10.52)$$

The difficulty is to determine the mass and heat transfer for the above equations. The procedures adopted are by no means universal. This is reflected by a large number of models for determining pool sizes and vaporization rates; [23] presents an overview. The most advanced model seems to be GASP [24]. On the one hand it is restricted to treating circular pools, on the other it allows spills on water and land as well as peculiarities of spills of liquefied natural gas (LNG) to be treated.

For solving Eq. (10.52) it is helpful to know that often one of the mechanisms of mass and heat transfer dominates, so that the others may be neglected.

If the vapour pressure of a liquid, p_{sat} , in a pool is lower than ambient pressure, the rate of vaporization is proportional to the difference of the vapour pressure of the liquid and its partial pressure in the surrounding air.

This gives [25]

$$\dot{m}_V = F_Q \cdot \frac{k_m \cdot (p_{\text{sat}}(T) - p_{\text{part}}) \cdot M}{R_m \cdot T} \quad (10.53)$$

Since often $p_{\text{sat}}(T) \gg p_{\text{part}}$, the partial pressure, p_{part} , is frequently neglected in Eq. (10.53).

In order to determine the coefficient of mass transfer in Eq. (10.53) the relationship of MacKay and Matsugu can be used

$$k_m = 0.004435 \cdot u_w^{0.78} \cdot r^{-0.11} \cdot Sc^{-0.67} \quad (10.54)$$

In Eq. (10.54) k_m is the coefficient of mass transfer in m/s, u_w the wind speed at anemometer height (standard: 10 m) in m/s, r the pool radius in m and Sc Schmidt's number, i.e.

$$Sc = \frac{\nu}{D_L} \approx 0.8 \quad (10.55)$$

In Eq. (10.55) ν is the kinematic viscosity of the vapour in m^2/s and D_L the diffusion coefficient of the vapour in air in m^2/s .

The heat input from the surrounding air can be described according to [15] as follows

$$q_L'' = k_L \cdot (T_L - T) \quad (10.56)$$

The coefficient of heat transfer, k_L , is obtained from Nussel's number as follows

$$Nu = 0.037 \cdot Pr^{1/3} \cdot Re^{0.8} \quad (10.57)$$

for $Re > 5 \cdot 10^5$. In Eq. (10.57) we have

$$Nu = \frac{k_L \cdot 2 \cdot r}{\lambda_L} \quad (10.58)$$

and

$$Re = \frac{\rho_L \cdot u_w \cdot 2 \cdot r}{\eta_L} \quad (10.59)$$

as well as

$$Pr = \frac{\eta_L \cdot c_{p,L}}{\lambda_L} \approx 0.786 \quad (10.60)$$

In the preceding equations quantities with the subscript 'L' refer to the surrounding air. In particular we have: $\lambda_L = 0.0257 \text{ W/(m K)}$ and the dynamic viscosity $\eta_L = 1.65 \times 10^{-5} \text{ Ns/m}^2$.

Since in the preceding equations the change of the surface area of the pool by supply from the spill and vaporization does not figure, their application is restricted to pools with fixed geometries (e.g. bunds).

Example 10.11 Vaporization of a petrol pool

A mass of $m_0 = 1,000$ kg petrol at a temperature of $T = 288.15$ K is released instantaneously into a bund with a diameter of 10 m.

What are the initial mass rate of vaporization and its variation and that of its temperature with time?

Note: For simplification only the convective heat transfer from the surrounding air (temperature: 15 °C) is accounted for.

Data: $p_{\text{sat}}(T = 288.15 \text{ K}) = 42,782 \text{ Pa}$, $u_w = 10 \text{ m/s}$, $M = 115 \text{ g/mol}$, $\Delta H_v = 370,135 \text{ J/kg}$, $c_p = 2,195.44 \text{ J/(kg K)}$

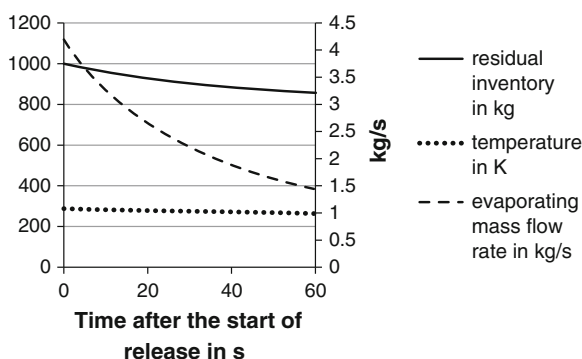
Solution

With the above data and assumptions Eqs. (10.53) and (10.54) provide a stationary rate of vaporization, i.e.

$$\begin{aligned} \dot{m}_v &= F_Q \cdot \frac{0.004435 \cdot u_w^{0.78} \cdot r^{-0.11} \cdot Sc^{-0.67} \cdot M}{R_m} \cdot \frac{p_{\text{sat}}(T)}{T} \\ &= 78.54 \text{ m}^2 \cdot \frac{0.004435 \times 10^{0.78} \cdot 5^{-0.11} \cdot 0.8^{-0.67} \cdot 115 \frac{\text{g}}{\text{mol}} \cdot 42,782 \text{ Pa}}{8.3145 \frac{\text{J}}{\text{mol K}} \cdot 288.15 \text{ K}} = 4,193.1 \frac{\text{g}}{\text{s}} \end{aligned}$$

Figure 10.20 shows the time-dependent variation of the residual inventory of the pool, of its temperature and of the vaporization mass flow rate. In order to obtain these results Eqs. (10.51)–(10.60) were solved numerically.

Fig. 10.20 Residual inventory of the pool, temperature and mass flow rate of vaporization during the first minute after release



Calculations accounting for heat radiation as well as for convective heat transfer give only slightly different results because the vaporization process dominates the variation of temperature. $\square$

If a refrigerated liquefied gas is released, its vaporization is dominated by heat transfer from the ground. We then find the heat flux in W/m^2 as the solution of the equation for heat conduction making the (not entirely true) assumption that the temperature of the pool remains constant

$$q_B''(t) = \left(\frac{\lambda_B \cdot \rho_B \cdot c_B}{\pi} \right)^{1/2} \cdot \frac{T - T_B}{t^{1/2}} = \lambda_B \cdot \frac{T - T_B}{\sqrt{a_B \cdot \pi \cdot t}} \quad (10.61)$$

In Eq. (10.61) λ_B is the coefficient of thermal conductivity of the ground in W/(mK), ρ_B is the density of the ground in kg/m³ and c_B its heat capacity in J/(kg K); $a_B = \lambda_B/(\rho_B c_B)$ is called thermal diffusivity and given in m²/s.

Thus we obtain the vaporization mass flow rate (in kg/s) due to heat input from the ground as

$$\dot{m}_v(t) = \frac{F_Q \cdot q_B''(t)}{\Delta H_v} \quad (10.62)$$

Example 10.12 Vaporization of chlorine from a pool [15]

After the instantaneous release of 65.95 m³ of chlorine onto the ground a circular pool is formed; its initial radius is 9.16 m. The mass of the pool amounts to $m = 102,816.05$ kg.

Initially the temperature of the pool is $T_p = 239.12$ K. It is then warmed up by heat transfer from the ground

Data: temperature of the ground $T_0 = 288.15$ K, coefficient of thermal conductivity $\lambda_B = 2.5$ W/(m K), thermal diffusivity $a_B = 11$ m²/s and a net radiative thermal input from the sun assumed to be 100 W/m², $\Delta H_v = 288,100$ J/kg, heat transfer coefficient air to pool $k_L = 5.26$ W/(m²K)

Solution

For simplicity's sake the ground (earth) is assumed to be a slab infinitely extended in the positive z -direction. The time-dependent equation of heat transfer then is

$$\rho_B \cdot c_B \cdot \frac{\partial T}{\partial t} = \lambda_B \cdot \frac{\partial^2 T}{\partial z^2} \quad (10.63)$$

Use of the abbreviation $\theta = T - T_p$, the thermal diffusivity $a_B = \lambda_B/(\rho_B \cdot c_B)$ and the Laplace transform (denoted by a tilde) converts Eq. (10.63) into

$$\frac{d^2 \tilde{\theta}}{dz^2} - \frac{s}{a_B} \cdot \tilde{\theta} = 0 \quad (10.64)$$

The general solution of Eq. (10.64) is

$$\tilde{\theta} = A \cdot \exp\left(-\sqrt{\frac{s}{a_B}} \cdot z\right) + B \cdot \exp\left(\sqrt{\frac{s}{a_B}} \cdot z\right) \quad (10.65)$$

Since the temperature must remain finite for $z \rightarrow \infty$, B in Eq. (10.65) is set equal to 0. The second boundary condition is $\theta(0, 0) = \theta_0 = T_0 - T_p$, which after being Laplace transformed becomes θ_0/s .

Thus the particular solution of the differential equation is

$$\tilde{\theta} = \frac{\theta_0}{s} \cdot \exp\left(-\sqrt{\frac{s}{a_B}} \cdot z\right) \quad (10.66)$$

Using a table for Laplace transforms the inversion of Eq. (10.66) is found to be

$$\theta(z, t) = \theta_0 \cdot \operatorname{erfc}\left(\frac{z}{2 \cdot \sqrt{a_B \cdot t}}\right) = \theta_0 \cdot \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{z}{2 \cdot \sqrt{a_B \cdot t}}} \exp(-u^2) du\right) \quad (10.67)$$

The heat flux therefore is

$$q_B'' = -\lambda_B \cdot \frac{\partial \theta}{\partial z} = -\lambda_B \cdot \theta_0 \cdot \left[-\frac{1}{\sqrt{\pi \cdot a_B \cdot t}} \cdot \exp\left(-\frac{z}{2 \cdot \sqrt{a_B \cdot t}}\right)\right] \quad (10.68)$$

At the interface between ground and pool ($z = 0$) the heat flux is given by

$$q_B''(t) = \frac{\lambda_B \cdot (T_0 - T_p)}{\sqrt{\pi \cdot a_B \cdot t}} \quad (10.69)$$

Using this result we obtain according to Eq. (10.62), which is extended here by the heat input due to convection from the air and to radiation

$$\begin{aligned} \dot{m}_v(t) &= \frac{F_Q \cdot (q_B''(t) + q_L'' + q_s'')}{\Delta H_v} = \frac{263.60 \text{ m}^2}{288,100 \frac{\text{J}}{\text{kg}}} \\ &\cdot \left(\frac{2.5 \frac{\text{W}}{\text{m} \cdot \text{K}} \cdot (288.15 - 239.12) \text{ K}}{\sqrt{\pi \cdot 11 \frac{\text{m}^2}{\text{s}} \cdot t}} + 257.86 \frac{\text{W}}{\text{m}^2} + 100 \frac{\text{W}}{\text{m}^2} \right) \end{aligned}$$

where we used $q_L'' = k_L \cdot (T_0 - T_p)$.

The time required for vaporizing the total mass of chlorine, t^* , is obtained from

$$\begin{aligned} m \cdot \Delta H_v &= F_Q \cdot \left(\int_0^{t^*} \frac{\lambda_B \cdot (T_0 - T_p)}{\sqrt{\pi \cdot a_B \cdot t}} + q_L'' + q_{ss}'' \right) \\ &= F_Q \cdot \left(\frac{\lambda_B \cdot (T_0 - T_p)}{\sqrt{\pi \cdot a_B}} \cdot t^{*1/2} + (q_L'' + q_{ss}'') \cdot t^* \right) \end{aligned}$$

Inserting the numerical values of the problem in the preceding equation and solving iteratively for t^* , we find that pool is evaporated after $t^* = 89.9$ h.

The time-dependent mass flow rate of the vaporization is shown in Fig. 10.21.

Fig. 10.21 Variation with time of the mass flow rate of vaporization from a pool of refrigerated chlorine with a diameter of 9.16 m

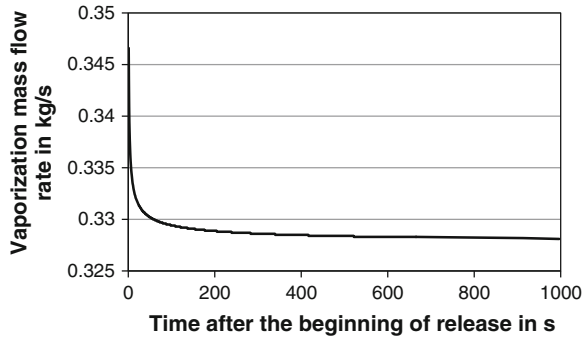
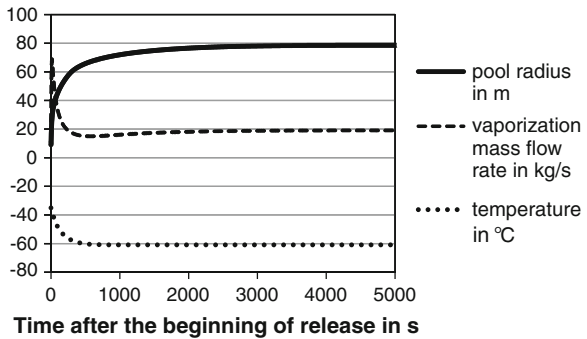


Figure 10.22 was produced with a computer program based on the relationships for the program GASP indicated in [15]. The calculations provide for the spread of the pool and the resulting growth of the area of heat transfer.

The smaller rate of vaporization in the analytical solution of the first case (vid. Fig. 10.21) is due to fact that according to the model assumptions:

- the pool does not cool down so that the corresponding enthalpy difference is not used for vaporization,
- the heat transfer due to convection from the air in the first case is smaller than in the second, because the increase of the temperature difference air/pool is not accounted for in the first case,
- the heat transfer area remains the same in the first case, whilst it grows in the second calculation to about 20,810 m².

Fig. 10.22 Variation with time of the pool radius, the vaporization mass flow rate the and temperature after the release of chlorine



10.5 Atmospheric Dispersion

The way a substance is released or vaporized determines how it is dispersed in the atmosphere. Accordingly the initial and boundary conditions for the dispersion calculation have to be fixed. This constitutes the part of the analytical treatment most affected by uncertainties. We distinguish between releases with large or small initial energy.

If the kinetic energy on release is small mixing of the released material with the surrounding air is relatively slow. On the other hand, if a jet with high kinetic energy is released mixing is fast (vid. Sect. 10.3).

Releases can be instantaneous and last for but a short time ('puff release') or continuous, which then lead to plume formation.

Both types of release are relevant for safety analyses of process plants. Puff or continuous releases of a flammable gas can form a vapour cloud capable of a vapour cloud explosion (VCE). The same consequence may follow releases with high initial kinetic energy. Toxic gases spread analogously. The consequence may then be the formation of gas clouds with lethal concentrations.

The dispersion is passive or airborne if the released material is lighter than air. If it is heavier than air, on the other hand, we are dealing with dense gas dispersion. A combination of both types is possible. For example, refrigerated ammonia is dispersed as a dense gas in the first place. After being warmed up by the surrounding air its dispersion behaviour becomes passive.

Most of the gases used in industry are heavier than air. They spread initially driven by gravity virtually uninfluenced by weather conditions. During the dispersion process the gas cloud mixes with the surrounding air. As a consequence the density of the cloud approaches that of air. The flow processes in the surrounding atmosphere gain importance. Passive or airborne dispersion then results.

Both types of dispersion are generally treated in Germany according to the standards [26, 27] and the accompanying computer code. Despite a certain amount of criticism this will probably remain so in the foreseeable future [28].

In what follows in the first place the airborne and thereafter the dense gas dispersions are treated.

10.5.1 Airborne Dispersion

The airborne dispersion of gas or vapour clouds is strongly influenced by the meteorological conditions at the moment of release and thereafter. In addition the topographic situation in the surroundings of the place of release has an impact. Factors of influence are:

Meteorological factors

(1) Wind

- direction
- speed
 - (a) at the surface
 - (b) above ground
- persistence (characterized by the number of consecutive days with the same wind direction)
- turbulence

(2) stability

- vertical temperature decrease (“lapse rate”)
- inversion

Topographical factors

- (1) ground slope
- (2) surface roughness
- (3) buildings and other obstructions

10.5.1.1 Wind

The wind is an important factor of influence on the dispersion. The wind direction is defined as the direction from which the wind blows. Informations on the wind directions at a specific site are given in the form of a windrose. This is a polar diagram, where the length of the sections of the spokes is proportional to the observed frequencies of wind direction and speed.

The wind speed varies with height. This variation is described by [26]

$$u(z) = u(z_A) \cdot \left(\frac{z}{z_A} \right)^m \quad (10.70)$$

In Eq. (10.70) $u(z)$ is the wind speed at height z and z_A is a reference height (anemometer height: $z_A = 10$ m). In [26] the following values for the exponent m are recommended depending on the weather conditions

- $m = 0.2$ unstable temperature layers
- $m = 0.28$ neutral temperature layers
- $m = 0.37$ stable temperature layers

Usually the mean value of the wind speed between the reference height z_A and the effective source height (height of emission, possible with an increment added in case of strong buoyancy of the released gas) is used for calculations. Integrating

Eq. (10.70) between 0 and h and dividing by h we obtain the average wind speed between height h and the ground

$$\bar{u} = \frac{u(z_A)}{m+1} \cdot \left(\frac{h}{z_A} \right)^m \quad (10.71)$$

Of course, local variations of wind directions and speeds can occur (both quantities are random variables). They are not reflected by the mean values but can influence the dispersion behaviour.

Turbulence is a further characteristic of the wind. In the context of dispersion calculations wind fluctuations with a frequency >2 per hour are considered [2]. The important fluctuations lie in the region $0.01\text{--}1\text{ s}^{-1}$. The main factors that determine turbulence are the gradient of the wind speed, the roughness of the terrain, and the temperature differences between the ground and the air. A measure for the turbulence is given by the standard deviation σ_{xyz} of the wind fluctuations over a certain interval of time (often one hour). Its value depends on the following factors:

- horizontal distance between the point of release and the reference point,
- stability conditions,
- wind speed,
- surface roughness,
- elevation of the source,
- averaging time.

With increasing distance between the point of release and the reference point the standard deviation increases. It is often described by the following power law [29].

$$\sigma = A \cdot x^a \quad (10.72)$$

The factor of proportionality A and the exponent a in Eq. (10.72) are derived from experimental results.

With increasing stability the standard deviations (in x -, y -, and z -direction) decrease. In a cloudless night with low wind speeds stability is greatest. Thus the standard deviations are small. On a cloudless summer afternoon with weak winds stability is smallest. The condition is unstable and the standard deviations are particularly large.

Furthermore the standard deviation depends on the wind speed. Extreme stabilities or instabilities only occur at low wind speeds. At high wind speeds stability is always neutral with intermediate values for the standard deviation.

Large surface roughness, i.e. above forests or urban areas, causes an additional dilution of gas clouds. This is accounted for by increasing the standard deviation.

10.5.1.2 Stability

The stability of the atmosphere is essentially the extent to which it allows vertical motion by suppressing or assisting turbulence. It is a function of the forces of wind shear and the vertical temperature gradient. Generally it is described in terms of the latter. Two important elements of stability are the vertical temperature decrease (“lapse rate”) and inversion.

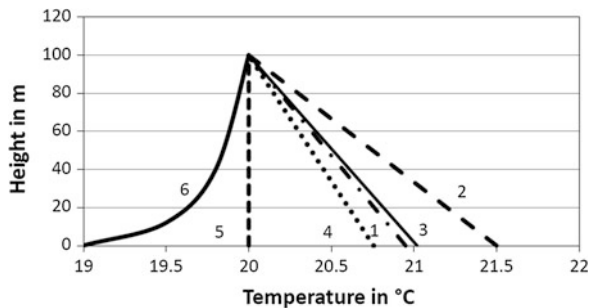
If a parcel of air is carried upwards in the atmosphere it encounters regions of lower surrounding pressure. Because of this it expands and cools. If the air were dry and the process adiabatic, the temperature decrease would be about 1 °C per 100 m of increase in height. Yet, this is idealized. Figure 10.23 shows the temperature variations with height for several realistic situations. In Fig. 10.23 curve (1) shows the behaviour for a dry adiabatic condition, curve (2) that for a superadiabatic condition. The latter results from strong solar radiation or the passing of cold air over warm surfaces, which enhances convection and instability. Curve (3) shows the neutral situation, which occurs with clouded sky and moderate to strong wind speed. Curve (4) refers to the subadiabatic condition, which enhances stability. Curve (5) describes an isothermal situation with a very stable condition. Finally, curve (6) shows an inversion condition, which reduces the turbulent exchange and suppresses vertical convection thus strongly favouring stability.

There are regions in the atmosphere where the turbulent transport in the vertical direction becomes so small that one can speak of a layer which cannot be penetrated by released materials, an inversion lid, (inversion weather condition). The inversion layers are characterized by extreme temperature increases with height. Such layers can occur at any height.

One group of inversion lids preferably occurs near ground level. It results from nocturnal cooling of the earth’s surface in cloudless nights with little wind (‘radiation night’) or a strong warming of the earth’s surface on a cloudless summer midmorning with weak wind.

With a cloudless weather condition with little wind a temperature inversion occurs over night, i.e. the temperature increases in upward direction starting from the surface of the earth (cooling area). At the boundary of the inversion the temperature increase is especially large, an inversion lid has formed. This is formed in the first place at the ground and then rises over night to 100–200 m.

Fig. 10.23 Vertical temperature profiles and lapse rates for (1) dry adiabatic condition; (2) superadiabatic condition; (3) neutral condition; (4) subadiabatic condition; (5) isothermal condition; (6) inversion condition (after [2])



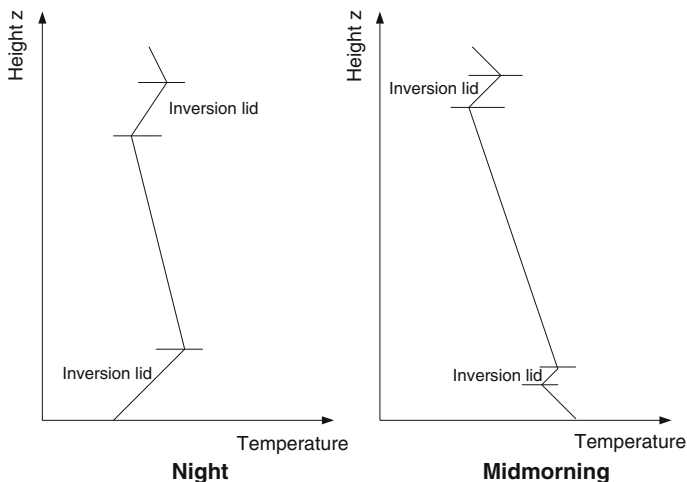


Fig. 10.24 Temperature changes with height during day and by night for cloudless weather conditions with weak winds and movements of the inversion lids (according to [29])

During the day this inversion lid is destroyed from below by the surface of the earth which then acts as a heater. In the upper part the inversion layer still remains. Below an ever increasing layer is created where the temperature decreases “normally” with height. The upper boundary of this layer respectively the lower boundary of the risen residual inversion constitutes a lid against the vertical movement of hazardous materials.

Another group of inversion lids is produced by parcels of air subsiding from heights in high pressure weather conditions. This type of inversion has no importance for released hazardous materials because its boundary rarely lies below 300 m. Figure 10.24 illustrate the situations described.

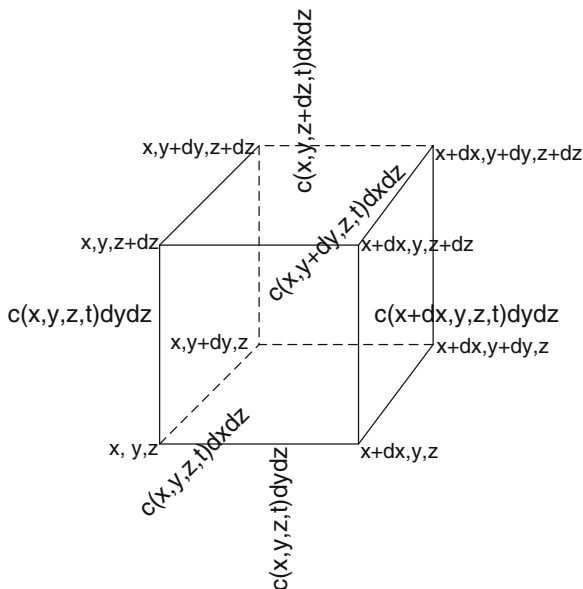
If a release occurs above an inversion lid the ground concentration is equal to zero. Toxic effects would then not have to be contemplated. However, flammable clouds may be formed in such a case, if the properties of the released material allow this to happen.

Hazardous materials accumulate below the inversion lid. This process cannot be represented directly by the Gaussian model used in [26]. However, one assumes that the released substances are reflected by both the inversion lid and the surface of the earth. Thereby this type dispersion can be modelled all the same by introducing so-called “virtual sources” into the Gaussian model.

10.5.1.3 Modelling

In what follows the fundamentals of the Gaussian model and its solution for several specific situations are presented. We consider the control volume shown in Fig. 10.25 through which a mixture of released gas and air is supposed to flow.

Fig. 10.25 Control volume for deriving the equations for airborne dispersion



The time-dependent variation of the concentration of a hazardous material $\frac{dc}{dt}$ within the control volume is equal to the change of concentration due to transport with the wind (advection) and a superimposed diffusion process.

- Advection term (u : velocity component in the x -direction in m/s; v : velocity component in the y -direction in m/s and w : velocity component in the z -direction in m/s; c : concentration in kg/m^3)

Net mass flow rate in kg/s as the difference between the outflowing and inflowing mass flow densities

$$\begin{aligned}
 \text{x-direction: } & c(x+dx, y, z, t) \cdot u \, dy \, dz - c(x, y, z, t) \cdot u \, dy \, dz \\
 \text{y-direction: } & c(x, y+dy, z, t) \cdot v \, dx \, dz - c(x, y, z, t) \cdot v \, dx \, dz \\
 \text{z-direction: } & c(x, y, z+dz, t) \cdot w \, dx \, dy - c(x, y, z, t) \cdot w \, dx \, dy
 \end{aligned} \tag{10.73}$$

By Taylor expansion and truncation after the second term Eq. (10.73) becomes

$$\begin{aligned}
 \text{x-direction: } & c(x+dx, y, z, t) \cdot u \, dy \, dz = c(x, y, z, t) \cdot u \, dy \, dz + \frac{\partial c(t, x, y, z)}{\partial x} \cdot u \cdot dx \, dy \, dz \\
 \text{y-direction: } & c(x, y+dy, z, t) \cdot v \, dx \, dz = c(x, y, z, t) \cdot v \, dx \, dz + \frac{\partial c(t, x, y, z)}{\partial y} \cdot v \cdot dx \, dy \, dz \\
 \text{z-direction: } & c(x, y, z+dz, t) \cdot w \, dx \, dy = c(x, y, z, t) \cdot w \, dx \, dy + \frac{\partial c(t, x, y, z)}{\partial z} \cdot w \cdot dx \, dy \, dz
 \end{aligned} \tag{10.74}$$

Combining Eqs. Gl. (10.73) and (10.74) we obtain the advection term

$$\frac{\partial c(t, x, y, z)}{\partial x} \cdot u \cdot dx dy dz + \frac{\partial c(t, x, y, z)}{\partial y} \cdot v \cdot dx dy dz + \frac{\partial c(t, x, y, z)}{\partial z} \cdot w \cdot dx dy dz \quad (10.75)$$

Using Taylor's expansion in an analogous way we obtain the diffusion term (j_x : mass flux in x-direction in $\text{kg}/(\text{m}^2\text{s})$; (j_y : mass flux in y-direction in $\text{kg}/(\text{m}^2\text{s})$; (j_z : mass flux in z-direction in $\text{kg}/(\text{m}^2\text{s})$)

$$\begin{aligned} \text{x-direction: } j_x(x + dx, y, z, t) dy dz - j_x(x, y, z, t) dy dz &= \frac{\partial j_x(t, x, y, z)}{\partial x} dx dy dz \\ \text{y-direction: } j_y(x, y + dy, z, t) dx dz - j_y(x, y, z, t) dx dz &= \frac{\partial j_y(t, x, y, z)}{\partial y} dx dy dz \\ \text{z-direction: } j_z(x, y, z + dz, t) dx dy - j_z(x, y, z, t) dx dy &= \frac{\partial j_z(t, x, y, z)}{\partial z} dx dy dz \end{aligned} \quad (10.76)$$

In order to establish a relationship between the mass flux and the concentration Fick's law is used. It states that the diffusion mass flux is proportional to the negative concentration gradient. The pertinent constants of proportionality are K_x , K_y and K_z , the so-called eddy coefficients. One obtains

$$j_x = -K_x \frac{\partial c}{\partial x} \quad (10.77)$$

$$j_y = -K_y \frac{\partial c}{\partial y} \quad (10.78)$$

$$j_z = -K_z \frac{\partial c}{\partial z} \quad (10.79)$$

We assume isotropic turbulence, i.e. $K_x = K_y = K_z = K$, and that materials are neither created inside nor lost from the control volume. Then the combination of the preceding equations leads to a description of the time-dependent variation of the concentration in the control volume. It is written omitting for simplicity's sake the independent variables t, x, y, z

$$\frac{\partial c}{\partial t} = -\frac{\partial c}{\partial x} \cdot u - \frac{\partial c}{\partial y} \cdot v - \frac{\partial c}{\partial z} \cdot w + K \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \quad (10.80)$$

In order to solve Eq. (10.80) one normally assumes that the wind blows only in one direction, so that $v = w = 0$ and the equation is simplified accordingly.

Furthermore spherical symmetry is postulated and the additional assumption is made that $u = 0$ holds, which will be relaxed again afterwards.

If written in spherical symmetry, since $r^2 = x^2 + y^2 + z^2$, and observing the above assumptions, Eq. (10.80) gives

$$\frac{\partial c}{\partial t} = K \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c}{\partial r} \right) \quad (10.81)$$

Thus, only the diffusion term remains. After applying the Laplace transformation we obtain

$$s \cdot \tilde{c} = K \left(\frac{\partial^2 \tilde{c}}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial \tilde{c}}{\partial r} \right) \quad (10.82)$$

since $c(t = 0, r > 0) = 0$. In Eq. (10.82) s is the Laplace variable and the tilde denotes the transformed quantities.

The solution of Eq. (10.82) is found by setting

$$\tilde{c}(r) = A \cdot \frac{\exp(-\alpha r)}{r} \quad (10.83)$$

If we insert Eq. (10.83) in Eq. (10.82) we obtain the equation for determining the parameter α , i.e.

$$K \cdot \alpha^2 \cdot A \cdot \frac{\exp(-\alpha r)}{r} = \frac{s \cdot A \cdot \exp(-\alpha r)}{r} \quad (10.84)$$

with the solution

$$\alpha^2 = \frac{s}{K} \quad (10.85)$$

From Eq. (10.85) we obtain

$$\alpha = \pm \sqrt{\frac{s}{K}}$$

Thus we have the general solution

$$\tilde{c}(r) = A \cdot \frac{\exp\left(-\sqrt{\frac{s}{K}} \cdot r\right)}{r} + B \cdot \frac{\exp\left(+\sqrt{\frac{s}{K}} \cdot r\right)}{r} \quad (10.86)$$

Since the concentration has to remain finite for $r \rightarrow \infty$, only the first term on the right hand side of Eq. (10.86) is retained, i.e. $B = 0$. After inverting the Laplace transform we have

$$c(t, r) = A \cdot \frac{\exp\left(-\frac{r^2}{4Kt}\right)}{2 \cdot \sqrt{\pi K} \cdot t^{3/2}} \quad (10.87)$$

The constant A results from the condition that

$$\int_0^\infty 4\pi r^2 \cdot c(t, r) dr = Q \quad (10.88)$$

must hold, where Q is the total quantity released in kg. This converts Eq. (10.87) into

$$c(t, r) = \frac{Q}{8 \cdot (\pi K t)^{3/2}} \cdot \exp\left(-\frac{r^2}{4Kt}\right) \quad (10.89)$$

If r^2 is expressed in terms of cartesian coordinates, we obtain

$$c(t, x, y, z) = \frac{Q}{8 \cdot (\pi K t)^{3/2}} \cdot \exp\left(-\frac{x^2 + y^2 + z^2}{4Kt}\right) \quad (10.90)$$

Equation (10.90) can be extended to account for the wind. For wind speed $u \neq 0$, we have

$$c(t, x, y, z) = \frac{Q}{8 \cdot (\pi K t)^{3/2}} \cdot \exp\left(-\frac{(x - ut)^2 + y^2 + z^2}{4Kt}\right) \quad (10.91)$$

Equation (10.91) is quite general if we make the x-axis point in the direction of the wind.

The K-model of Eq. (10.81) is a substantial simplification, because it is based on the assumption that the eddy coefficient and the wind speeds are constants. In addition, many of the parameters of influence on atmospheric dispersion presented above cannot be accounted for. This motivated numerous further developments. If the following relationship between the eddy coefficient and the atmospheric standard deviation is used

$$\sigma^2(t) = 2 \cdot K \cdot t \quad (10.92)$$

Equation (10.91) becomes

$$c(t, x, y, z) = \frac{Q}{(2\pi)^{3/2} \sigma^3(t)} \cdot \exp\left(-\frac{(x - ut)^2 + y^2 + z^2}{2\sigma^2(t)}\right) \quad (10.93)$$

Table 10.5 Assignment of the roughness length z_0 to different types of terrain (from [26])

z_0 [m]	Description of the terrain
0.02	Extremely smooth: homogeneous extremely flat terrain (neither buildings nor trees or bushes in the broader surroundings) and open water
0.2	Smooth: homogeneous flat terrain; only occasional buildings or trees in the broader surroundings
0.5	Little rough: relatively even terrain; only few buildings and little vegetation in the broader surroundings
0.8	Moderately rough: uneven terrain; villages respectively small forest areas in the broader surroundings
1.2	Very rough: urban and forest areas

Note z must not be smaller than z_0

If the release is close to the ground, the concentration is doubled, since the released gases can only fill a hemisphere. We then have

$$c(t, x, y, z) = \frac{2 \cdot Q}{(2\pi)^{3/2} \sigma^3(t)} \cdot \exp\left(-\frac{(x - ut)^2 + y^2 + z^2}{2\sigma^2(t)}\right) \quad (10.94)$$

If the assumption of isotropy is removed, σ is decomposed into three components, i.e.

$$\sigma^3(t) = \sigma_x(t) \cdot \sigma_y(t) \cdot \sigma_z(t) \quad (10.95)$$

The σ -values are the standard deviations of the concentration in the direction of the wind, at a right angle from the wind direction and vertically upwards. They can easier be determined experimentally than the eddy coefficient K . The standard deviations depend on the atmospheric conditions and the distance from the source in the direction of the wind. In [26] relationships are given for them which depend on the weather condition (stable, neutral, unstable), the velocity of the wind and the surface roughness z_0 (vid. Table 10.5). Separate values for σ_x and σ_z are provided; for σ_y the same value as for σ_x is used. For distances < 100 m the standard deviations are not verified. That is why results in that range have to be treated with caution. The integration of further factors of influence in the dispersion process is described in [26].

Example 10.13 Stationary emissions

A source close to the ground continuously emits $\dot{Q} = 10$ kg/s of nitrogen. To which concentration is a person at a distance of 200 m exposed, if there is no wind.

Data: $K = 4$ m²/s; elevation of the mouth of the person 1.7 m.

Solution

A stationary source implies that the mass emitted by the source has to flow per unit of time through any surface at distance r , i.e.

$$4 \cdot \pi \cdot r^2 \cdot K \cdot \frac{dc}{dr} = \dot{Q} \quad (10.96)$$

The concentration has to remain finite everywhere. Therefore the boundary condition for Eq. (10.96) is

$$\lim_{r \rightarrow \infty} c(r, t) = 0 \quad (10.97)$$

Separation of the variables in Eq. (10.96) leads to

$$dc = \frac{\dot{Q}}{4 \cdot K \cdot \pi \cdot r^2} dr \quad (10.98)$$

After integration of Eq. (10.98) we obtain

$$\int_r^\infty dc = \int_r^\infty \frac{\dot{Q}}{4 \cdot K \cdot \pi \cdot r^2} dr \quad (10.99)$$

with the solution

$$\begin{aligned} c(r) &= \frac{\dot{Q}}{4 \cdot K \cdot \pi \cdot r} \text{ and hence} \\ c(x, y, z) &= \frac{\dot{Q}}{4 \cdot K \cdot \pi \cdot \sqrt{x^2 + y^2 + z^2}} \end{aligned} \quad (10.100)$$

The distance from the source at the height of the mouth of the person amounts to

$$r = \sqrt{(1.7 \text{ m})^2 + (200 \text{ m})^2} = 200.007 \text{ m}$$

Inserting the numerical values in Eq. (10.100) and observing that the source strength is multiplied by a factor of 2, because the release is close to the ground, we have

$$c(200.007 \text{ m}) = \frac{2 \times 10 \frac{\text{kg}}{\text{s}}}{4 \cdot 4 \frac{\text{m}^2}{\text{s}} \cdot 3.14 \cdot 200.007} = 1.99 \times 10^{-3} \frac{\text{kg}}{\text{m}^3}$$

□

Example 10.14 Effects of a puff release of carbon monoxide

By accident 80 kg of carbon monoxide are released instantaneously close to the ground. A person stands for $t^* = 20 \text{ min}$ at a distance of $x_1 = 100 \text{ m}$ from the

point of release. Determine whether this person is exposed to a dose of $D = 0.09$ kgs/m³, which constitutes a health hazard, or not. The wind speed is $u = 2$ m/s, the standard deviation $\sigma = 30$ m. Both quantities remain constant during the time period contemplated.

Solution

Starting point is Eq. (10.94), where in this case $y = z = 0$

$$D = \frac{2 \cdot Q}{2\pi\sigma^2} \cdot \int_0^{t^*} \frac{1}{(2\pi)^{1/2}\sigma} \cdot \exp\left(-\frac{(x_1 - ut)^2}{2\sigma^2}\right) dt \quad (10.101)$$

By substituting

$$\alpha = \frac{x_1 - ut}{\sigma}, \quad \left(\frac{d\alpha}{dt} = -\frac{u}{\sigma}\right)$$

we obtain

$$\begin{aligned} D &= -\frac{Q}{\pi\sigma^2 u} \cdot \int_{x_1/\sigma}^{\frac{x_1 - ut^*}{\sigma}} \frac{1}{(2\pi)^{1/2}} \cdot \exp\left(-\frac{\alpha^2}{2}\right) d\alpha \\ &= \frac{Q}{\pi\sigma^2 u} \cdot \left[\phi\left(\frac{x_1}{\sigma}\right) - \phi\left(\frac{x_1 - ut^*}{\sigma}\right) \right] \end{aligned} \quad (10.102)$$

In Eq. (10.102) ϕ is the standard normal distribution

$$D = 1.415 \times 10^{-2} \text{ kgs/m}^3 \cdot [\underbrace{\phi(3.33)}_{\approx 0.99} - \underbrace{\phi(-76.7)}_{\approx 0}]$$

Thus the dose amounts to 0.014 kgs/m³ which is below 0.09 kgs/m³. The relationship (10.102) shows that higher wind speeds lead to smaller doses. □

Example 10.15 Application of the computer program accompanying the VDI guideline on atmospheric dispersion [26]

The Example 10.14 is re-evaluated with the computer program accompanying [26]. In order to obtain a conservative result different weather conditions, described by so-called dispersion classes, are addressed. The most pessimistic result is then chosen as the adequate solution.

Program input is subject to certain limitations. For example, the wind speed at anemometer height cannot lie below 1 m/s, the smallest possible surface roughness is characterized by $z_0 = 0.02$ m (vid. Table 10.5) and the source must lie at least 0.5 m above the ground.

*Solution**Dispersion class 2 (neutral conditions)*

This class is characterized by neutral conditions without inversion. The cloud passes about 220 s after its release above the exposed person. The dose amounts to 0.037 kgs/m^3 .

Dispersion class 1 (stable with inversion)

This class is characterized by stable conditions with an inversion lid at a height of 20 m. The cloud passes about 150 s after its release above the exposed person. The dose amounts to 0.093 kgs/m^3 .

Dispersion class 2 (neutral with inversion)

This class is characterized by neutral conditions with an inversion lid at a height of 20 m. The cloud passes about 170 s after its release above the exposed person. The dose amounts to 0.047 kgs/m^3 .

Dispersion class 3 (unstable with inversion)

This class is characterized by unstable conditions with an inversion lid at a height of 20 m. The cloud passes about 230 s after its release above the exposed person. The dose amounts to 0.035 kgs/m^3 .

Thus the most unfavourable situation is given by dispersion class 1, which is characterized by stable conditions and inversion. In this case the limit value of 0.09 kgs/m^3 would be exceeded.

If the calculation is carried out with a wind speed of 10 m/s at anemometer height of 10 m/s, a difference results only for the neutral conditions of class 2, since inversion conditions are incompatible with higher wind speeds. Therefore in case of inversion wind speed is always set automatically to 1 m/s independently of the input value.

For the conditions of class 2 one then obtains a dose of $1.11 \times 10^{-3} \text{ kgs/m}^3$; the cloud passes over the person within about 30 s. Thus the impact is smaller than that for lower wind speeds.

It is evident that the results strongly depend on the stochastic parameter “weather”.

□

10.5.2 Dense Gas Dispersion

There are cases in which the dispersion of a gas cloud is influenced by the fact that the density of the gas-air mixture differs from that of air. Such differences can result from differences in molar masses or from temperature differences between the air and the released gas. However, these differences only have an impact if the concentration of the gas is large enough.

Many of the gases with relevance for accidents like hydrocarbons, chlorine, ammonia and oxygen can form clouds which are heavier than air. Whether a gas behaves as a dense gas or not depends on the following factors:

- molecular weight of the gas,
- gas temperature,
- presence of liquid spray,
- temperature and humidity of the surrounding air.

In [27] the following criteria are used to decide whether a gas is treated as dense or not:

- relative excess of density at the point of release $(\rho_0 - \rho_a)/\rho_a > 0.16$, where ρ_a denotes the density of the surrounding air (recommended value: 1.2 kg/m^3) and ρ_0 the density of the released gas;
- at the same time the released volume V_0 has to satisfy $V_0 > 0.1 \text{ m}^3$ in case of a puff release respectively the volumetric flow rate $\dot{V}_0$ has to comply with $\dot{V}_0 > 10^{-3} \text{ m}^3/\text{s}$ in case of a continuous release.

A dense gas cloud behaves differently from a cloud of neutral density. It is not only dispersed in the direction of the wind, but also against this direction. It is flatter than a cloud of neutral density and the mechanism of mixing with the surrounding air is different.

In its initial phase a dense gas cloud spreads less in the vertical direction than a cloud of neutral density. Yet, the belief that a dense gas cloud therefore migrates further than one of neutral density is not correct. The different mechanism of mixing with air leads to faster spreading especially under stable weather conditions. In the long run the density of a dense gas cloud becomes practically neutral due to mixing with air. A phase of passive dispersion, whose modelling was explained in the preceding section, ensues.

The model for dense gas dispersion in [27] is based on experimental results and similitude relations. It is to be preferred to the simple model presented in the next paragraph.

In general one can state that the modelling of both airborne and dense gas dispersion comprises numerous problems which are still to be solved. This is particularly true for near field and if obstacles like buildings or industrial structures must be accounted for, which is the usual situation for releases from process plants.

10.5.2.1 Modelling

In what follows the simple model of Van Ulden [2, 30] is described. It gives an impression of the mechanisms of dense gas dispersion. In any case the model according to [27] should be preferred for practical applications.

The original mixture of gas and air, which results from a puff release, is supposed to have cylindrical shape. Usually a ratio of diameter to height of 1 is assumed.

The change of the cloud radius with time is expressed in terms of the velocity u_f , i.e.

$$\frac{dr}{dt} = c \cdot \sqrt{g \cdot h \cdot \frac{\rho - \rho_a}{\rho_a}} = u_f \quad (10.103)$$

In Eq. (10.103) different values for c are given depending on the author. However, a value of $c = 1$ seems to be appropriate in view of a comparison with experiments.

For the volume of the cloud we have

$$V = \pi \cdot r^2 \cdot h \quad (10.104)$$

where the initial state is given by

$$V_0 = \pi \cdot r_0^2 \cdot h_0 \quad (10.105)$$

The subscript “0” in Eq. (10.105) denotes the conditions immediately after release.

During spreading the volume of the cloud increases because its movement causes air from the surroundings to be entrained and integrated in the cloud. Two mechanisms are considered:

- entrainment of air at the edges,
- entrainment of air at the top.

Both are influenced by the turbulence of the atmosphere and the density difference between the cloud and the surrounding air $\rho - \rho_a$.

The time-dependent change of the volume of the cloud is then described by

$$\frac{dV}{dt} = \pi \cdot r^2 \cdot w_e + 2 \cdot \pi \cdot r \cdot h \cdot u_e \quad (10.106)$$

The first term on the right hand side of Eq. (10.106) represents the entrainment at the top of the cylindrical cloud and the second the entrainment at the edge; w_e and u_e are the entrainment velocities in m/s.

We find in [31]

$$u_e = \alpha^* \quad (10.107)$$

and

$$w_e = \frac{\alpha' \cdot u_1}{\text{Ri}} \text{ if } w_e = u_1 \quad (10.108)$$

In Eq. (10.108) Ri is Richardson's number and u_1 the longitudinal turbulence velocity, which is proportional to the friction velocity u^* . The following relationships apply

$$\frac{u_l}{u^*} = \begin{cases} 3.0 & \text{for stable conditions} \\ 2.4 & \text{for neutral conditions} \\ 1.6 & \text{for very unstable conditions} \end{cases} \quad (10.109)$$

and

$$Ri = \frac{g \cdot l_s \cdot \Delta \rho}{u_l^2 \cdot \rho_a} \quad (10.110)$$

In Eq. (10.110) we use

$$l_s = 5.88 \cdot h^{0.48} \quad (10.111)$$

According to [31] we have

$$\frac{u^*}{u} = 0.04\text{--}0.22 \text{ depending on the weather condition and the surface roughness,} \quad (10.112)$$

where u is the mean velocity of the wind in m/s ist. For an open and flat terrain a value of 0.1 is appropriate for the ratio u^*/u of Eq. (10.112).

On the basis of evaluations of the Maple Sands experiments the values of Table 10.6 are given for the remaining constants [31].

An important effect not accounted for in the above model is the heat transfer from the surrounding air to the released gas. This is particularly important for gases from a refrigerated storage or if a gas cools on release due to expansion.

Example 10.16 Puff release of chlorine

1,000 kg of chlorine, which are stored at 15 °C and 100,000 Pa are released instantaneously and dispersed in an open flat terrain. There is virtually no wind ($u = 1$ m/s). What is the distance for the transition from dense gas to airborne dispersion, if the weather conditions are stable, neutral or very unstable?

The results are to be compared with those of the computer program accompanying [27].

Table 10.6 Values of the model coefficients from [31] based on the evaluation of dispersion experiments at Maple Sands

Parameter	Possible range	Recommended (best) value
Gravitational slumping constant c	0.5–2.0	1
Edge entrainment coefficient α^*	0.5–1.1	0.9
Top entrainment coefficient α'	0.5–1.5	0.8
Criterion for the transition to passive dispersion $\rho - \rho_a$	10^{-2} – 10^{-3}	10^{-3}

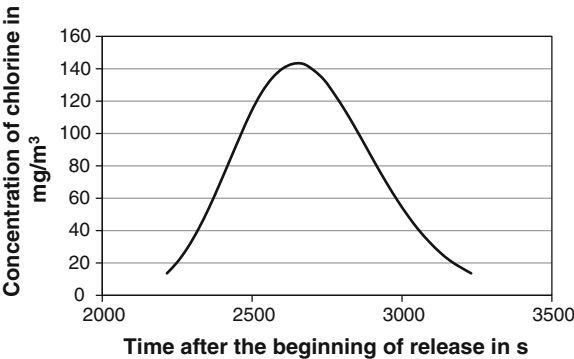
Solution

Equations (10.103) and (10.106) are solved using the Runge-Kutta method. The required coefficients are determined from the remaining relationships indicated above. The parameters are chosen on the basis of the information from Table 10.6, the results of the dispersion calculations are presented in Table 10.7 and Fig. 10.26.

Table 10.7 Results of the dispersion calculations for a puff release of chlorine

Atmospheric condition	Distance of the transition to airborne dispersion in m	Time until transition to airborne dispersion in s
Stable	76.1	80.1
Neutral	89.8	112.6
very unstable	121.5	206.3
<i>Evaluation with the computer program according to [27]</i>		
Average dispersion situation	249.5	44.5
Unfavourable dispersion situation	381.1	61.7

Fig. 10.26 Variation with time of the concentration at a reference point 300 m away from the point of release for the unfavourable dispersion situation (stable condition, inversion lid at a height of 20 m) (calculated with the computer program according to [27])



The differences of the results underline the modelling uncertainties still existent in dense gas dispersion. □

10.5.3 Impact of Atmospheric Dispersion

If the released and dispersed materials are flammable, the dispersion calculation can serve to find out which part of the cloud lies within the limits of explosion and can therefore burn or explode. This is shown in Example 10.17. If the material is toxic it affects the health of people, as described in Sect. 2.6. The effects can then be calculated using a probit relation. This is shown in Example 10.18.

The formation of large clouds of flammable substances is an important problem in safety analyses for process plants. As already mentioned such clouds can be formed following instantaneous or continuous releases of flashing and/or vaporizing substances.

The treatment of dispersion is based here on Eq. (10.94), which reads for spherical symmetry and constant σ as follows

$$c(r) = \frac{2 \cdot Q}{(2\pi)^{3/2} \sigma^3} \cdot \exp\left(-\frac{r^2}{2\sigma^2}\right) \quad (10.113)$$

The mass of flammable gas between the radii r_1 and r_2 is obtained as

$$W = \int_{r_1}^{r_2} 2\pi r^2 c(r) dr \quad (10.114)$$

If we integrate Eq. (10.114) between $r_1 = 0$ and $r_2 \rightarrow \infty$, we obtain the entire quantity which has been released, i.e. $W = Q$. Furthermore, the maximum concentration is found for $r = 0$, i.e.

$$c_{\max} = \frac{2 \cdot Q}{(2\pi)^{3/2} \sigma^3} \quad (10.115)$$

The maximum hazard from a flammable material results if the concentration in the centre of the cloud is equal to the upper explosion limit (UEL) (vid. Sects. 2.1.1.1 and 2.1.1.2), i.e. there is no region within the cloud where the mixture is too rich. We then have

$$c_{\max} = \text{UEL} \quad (10.116)$$

Analogously one arrives at the radius at which the lower explosion limit (LEL) is reached, r_u , from Eq. (10.113)

$$r_u = \left(2 \cdot \sigma^2 \cdot \ln \frac{\text{UEL}}{\text{LEL}}\right)^{1/2} \quad (10.117)$$

The mass of gas within the limits of explosion W^* is calculated as

$$W^* = \int_0^{r_u} 2 \cdot \pi \cdot r \cdot c_{\max} \cdot \exp\left(-\frac{1}{2} \cdot \frac{r^2}{\sigma^2}\right) dr \quad (10.118)$$

Example 10.17 Flammable portion of a methane cloud

An accident causes a puff release of 1,000 kg of methane. The release can be considered as a point source. The pertinent LEL is 4.4vol% and the UEL 17vol% (vid. Table 2.1). The standard deviation amounts to $\sigma = 30$ m.

How much methane-air mixture within the explosion limits is contained in the cloud?

Solution

Based on Eq. (10.118) we obtain

$$r_u = \left[2 \cdot 30^2 \cdot \ln \frac{17}{4.4} \right]^{0.5} = 49.32 \text{ m}$$

In order to solve the Eq. (10.118) in part analytically it is rewritten as follows

$$W^* = \int_0^{r_u} \frac{2 \cdot Q}{\sigma^2} \cdot r^2 \left[\frac{1}{\sigma(2\pi)^{1/2}} \cdot \exp \left(-\frac{1}{2} \cdot \frac{r^2}{\sigma^2} \right) \right] dr$$

Integration by parts then gives

$$\begin{aligned} W^* &= \frac{2 \cdot Q}{\sigma^2} \cdot \left\{ -\frac{\sigma}{(2\pi)^{1/2}} \cdot \left[r \cdot \exp \left(-\frac{1}{2} \cdot \frac{r^2}{\sigma^2} \right) \right]_0^{r_u} + \sigma^2 \cdot \left[\phi \left(\frac{r_u}{\sigma} \right) - \phi(0) \right] \right\} \\ &= \frac{2 \cdot 1000 \text{ kg}}{(30 \text{ m})^2} \cdot \left\{ -\frac{30 \text{ m}}{2.5066} \cdot 49.32 \text{ m} \cdot \exp \left(-\frac{1}{2} \cdot \frac{(49.32 \text{ m})^2}{(30 \text{ m})^2} \right) + (30 \text{ m})^2 \cdot \left[\phi \left(\frac{49.32 \text{ m}}{30 \text{ m}} \right) - \phi(0) \right] \right\} \\ &= 560.0 \text{ kg} \end{aligned}$$

In the above equation ϕ denotes the standard normal distribution. In valuating the result one should observe, however, that turbulences due to the initial momentum and the influence of the wind can lead to a different result. Therefore one often assumes conservatively that the entire released mass takes part in the combustion process.

□

Example 10.18 Health impact of chlorine exposure

The time-dependent concentration of exposure to chlorine of the Example 10.16 (vid. Fig. 10.26) at a distance of 300 m can be represented by the following equation:

$$c(t) = 96.73 \text{ ppm} \cdot \exp \left[-\frac{(t - 44.208)^2 \text{ min}^2}{22.905 \text{ min}^2} \right]$$

Calculate the probability of death due to chlorine exposure.

Solution

The probit relation for determining the probability of death is given, for example, by Eq. (B.7a)

$$Y = -17.1 + 1.69 \cdot \ln \left(\int_0^t C(t')^{2.75} \cdot dt' \right) \quad (\text{B.7a})$$

Since the time-dependent concentration very quickly tends towards zero (the cloud passes quickly) the upper limit of integration may be set equal to $t = \infty$ without substantially affecting the result. We then obtain

$$\begin{aligned} Y &= -17.1 + 1.69 \cdot \ln \left(\int_0^{\infty} 96.73^{2.75} \cdot \exp \left[-\frac{2.75 \cdot (t' - 44.208)^2}{22.905} \right] \cdot dt' \right) \\ &= -17.1 + 1.69 \cdot \ln \left(1,476,258.343 \cdot \frac{1}{\sqrt{2 \cdot \pi \cdot \sigma}} \int_0^{\infty} \exp \left[-\frac{(t' - \bar{t})^2}{2 \cdot \sigma^2} \right] \cdot dt' \right) \end{aligned}$$

where $\bar{t} = 44.208$ min and $\sigma = 2.0407$ min.

The integral in the preceding expression is the normal distribution. Therefore we have

$$Y = -17.1 + 1.69 \cdot \ln \left(1,476,258.343 \cdot \left[\underset{=1}{\phi(\infty)} - \underset{=\phi(-21.66) \approx 0}{\phi\left(\frac{-\bar{t}}{\sigma}\right)} \right] \right) = 6.9065$$

The probability of death then is

$$P_{\text{death}} = \phi(Y - 5) = \phi(1.9065) = 0.97$$

Table 10.8 presents the solutions obtained by using the different probit relations for chlorine listed in the Appendix B.

Table 10.8 Probabilities of death following exposure to chlorine calculated with different probit relations

Equation	P _{death}
B7a	0.97
B7b	0.9999
B7c	10 ⁻⁶
B7d	1.7 × 10 ⁻³

The extremely large differences show that blind trust in the results of the probit calculations is not adequate. They should be underpinned by comparisons with

other data. For example, in the present case the ERPG-3 value for chlorine (vid. Table 2.26) is exceeded only during 14 min. This insinuates that the results of Eqs. (B.7a) and (B.7b) may be slightly too conservative.

□

Example 10.19 Discharge of supercritical ammonia and subsequent dispersion

Ammonia is employed in a process for NH_3 synthesis at $p_1 = 221$ bar and $T_1 = 573.15$ K. A leak of cross sectional area $F_L = 490 \text{ mm}^2$ opens, but can be isolated after 10 min. The jet emanating from the leak is supposed to have a length of 30 m in the horizontal direction. At which maximum distance from the point of release do we reach a maximum concentration of 150 ppm (ERPG-2 value, vid. Table 2.35)?

The atmospheric dispersion is to be calculated using the following conditions: anemometric wind speed 3 m/s, neutral conditions, $z_0 = 1.2$ from Table 10.5, elevation of the mouth of a potentially affected person $z = 1.8$ m.

Data: molar mass $M = 17.03$ g/mol, critical temperature $T_c = 405.65$ K, critical pressure $p_c = 11,300,000$ Pa, acentric factor $\omega = 0.2526$, universal gas constant $R_m = 8.314$ J/(mol K), discharge coefficient $\mu = 0.62$.

Solution

The condition of the ammonia is supercritical. Its density is calculated according to the equation of state of Peng and Robinson (cf. [13]), which is given by

$$p = \frac{R_m \cdot T}{v_m - b} - \frac{a \cdot \alpha}{v_m \cdot (v_m + b)}$$

where

$$a = 0.457235 \cdot \frac{(R_m \cdot T_c)^2}{p_c}$$

$$b = 0.077796 \cdot \frac{R_m \cdot T_c}{p_c}$$

and

$$\alpha = \left[1 + (0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2) \cdot \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2$$

The above equations have to be solved iteratively for the molar volume v_m . Using the above data we obtain

$$a = 0.4602 \quad b = 2.3219 \times 10^{-5} \quad \alpha = 0.7380$$

and

$$22,100,000 = 30,664,449.4231 - 8,564,449.4231$$

whence we have the initial molar volume $v_m = 1.7862 \times 10^{-4} \text{ m}^3/\text{mol}$. This gives an initial fluid density of

$$\rho_1 = \frac{M}{v_m} = \frac{17.03 \frac{\text{g}}{\text{mol}}}{1.7862 \times 10^{-4} \frac{\text{m}^3}{\text{mol}} \cdot 1,000 \frac{\text{g}}{\text{kg}}} = 95.34 \frac{\text{kg}}{\text{m}^3}$$

The expansion process is assumed to be isentropic. The entropy amounts to

$$s = 173.68 \text{ J}/(\text{mol K})$$

In calculating this iteratively, the following relationship for the standard entropy s^0 in J/(mol K) was used:

$$s^0 = a \cdot \ln t + b \cdot t + c \cdot \frac{t^2}{2} + d \cdot \frac{t^3}{3} - \frac{e}{2 \cdot t^2} + g$$

where we have $t = T/1,000$ and for $298 \text{ K} \leq T \leq 1,400 \text{ K}$: $a = 19.99563$, $b = 49.77119$, $c = -15.37599$, $d = 1.921168$, $e = 0.189174$, $g = 203.8591$ [32].

The adaptation to different pressures results from

$$s = s^0 - R_m \cdot \ln \frac{p}{p_a}$$

Hence we obtain for the initial state ($T_1 = 573.15 \text{ K}$, $p_1 = 221 \text{ bar}$)

$$s = s^0 - R_m \cdot \ln \frac{p_1}{p_a} = 218.56 \frac{\text{J}}{\text{mol K}} - 8.314 \frac{\text{J}}{\text{mol K}} \cdot \ln 221 = 173.68 \frac{\text{J}}{\text{mol K}}$$

The maximum of the discharge mass flow rate is calculated in a stepwise fashion, since the mass flow rate is limited by the speed of sound (critical discharge). We use

$$\begin{aligned} \dot{m}_{\max} &= \mu \cdot F_L \cdot \rho_c \cdot \sqrt{2 \cdot (h_c - h_1)} = \mu \cdot F_L \cdot \rho_c \cdot \sqrt{2 \cdot \int_1^c v \cdot dp} \\ &\approx \mu \cdot F_L \cdot \rho_c \cdot \sqrt{2 \cdot \sum_{(i)} v_i \cdot \Delta p} \end{aligned}$$

In the above relation Eq. (7.11) served to calculate the emission velocity; h_1 and h_c are the enthalpies for the initial state and for critical flow conditions, respectively, and $v = v_m/M$.

The maximum flow rate is determined taking pressure steps $p^{(1)} = p_1$, $p^{(2)} = p_1 - \Delta p$, $p^{(3)} = p_1 - \Delta p$, ..., $p_2 = p_1 - \Delta p \cdot (p_1 - p_2)/\Delta p$, where Δp is the step size (e.g. $\Delta p = 1$ Pa), and searching the maximum according to

$$\dot{m}_{\max} = \max_{i=1, \dots, (p_1-p_a)/\Delta p} \left(\mu \cdot F_L \cdot \rho_i \cdot \sqrt{2 \cdot \sum_{(i)} v_i \cdot \Delta p} \right)$$

The Peng-Robinson equation of state is used there to determine v_i and $\rho_i = 1/v_i$ and the entropy equation for calculating the temperature corresponding to the pressure of every step $p^{(i)}$. This gives $\dot{m}_{\max} = 9.2 \frac{\text{kg}}{\text{s}}$ at critical flow conditions characterized by a temperature of 240.1 °C, a pressure of 124.1 bar, and the corresponding speed of sound of 500.7 m/s.

If the procedure for ideal gases of Sect. 10.2.3 were used, a maximum mass flow rate of $\dot{m}'_{\max} = 10.0 \frac{\text{kg}}{\text{s}}$ would result.

Thus a total quantity of $m = \dot{m}_{\max} \cdot 600 \text{ s} = 9.2 \frac{\text{kg}}{\text{s}} \cdot 600 \text{ s} = 5,520 \text{ kg}$ of ammonia is released.

The dispersion calculation is performed using the computer program accompanying [26, 27], which gives a concentration of 150 ppm for a maximum distance from the source of $425 \text{ m} + 30 \text{ m} = 455 \text{ m}$ in the direction of the jet.

□

10.6 Fires and Explosions

10.6.1 Pool Fires

If a flammable liquid is released it may either vaporize (vid. Sect. 10.4) or catch fire thus causing a so-called pool fire. Depending on the type of material and the quantity released conditional probabilities (the condition is the release) for the occurrence of a fire of up to 0.7 are advanced [33].

The calculation of the formation of a pool and of the effects of the fire is done in several steps. The presentation here largely follows the procedures described in [15]. An overview and a description of more advanced models are found in [34, 35].

10.6.1.1 Pool Dimensions

In the first place the diameter of the pool is determined. It is assumed to be of circular shape. If a different geometry, e.g. a rectangular bund, has to be treated, a circle of the same area is used.

Two cases have to be distinguished:

- (1) a bund determines the geometry, e.g. in a hall. This results in

$$d = \sqrt{\frac{4 \cdot F}{\pi}} \quad (10.119)$$

In Eq. (10.119) d denotes the diameter in m and F the area of the bund in m^2 . After the bottom is wet, the supply of further liquid, for example from containers failing because of being heated, only makes the level rise. This rise is counteracted by a drop of the level caused by the evaporation and combustion of the liquid, i.e.

$$\frac{d\delta}{dt} = -\frac{m''}{\rho} + \frac{\dot{V}}{F} \quad (10.120)$$

In Eq. (10.120) δ is the depth (liquid level height) of the pool in m, m'' is the mass burning rate in $\text{kg}/(\text{m}^2 \text{ s})$ of the material involved, ρ its density in kg/m^3 , $\dot{V}$ the released volumetric flow m^3/s and F the cross sectional area of the pool in m^2 .

- (2) The pool spreads without obstacles on the ground, as would happen outdoors or if the bund were absent or generously dimensioned. Then the radius of the pool, which is considered to be of circular shape, too, varies according to the following differential equation

$$\frac{dr}{dt} = \frac{\dot{m} - \pi \cdot r^2 \cdot m''}{2 \cdot \pi \cdot r \cdot \rho \cdot \delta} \quad (10.121)$$

In Eq. (10.121) r is the radius of the pool in m, $\dot{m}$ the mass flow rate into the pool, e.g. from a vessel, in kg/s , and δ the depth of the pool in m, for which a value has to be assumed, e.g. 2 cm. The mass burning rate m'' depends on the material and the radius of the pool, i.e.

$$m'' = m_{\infty} \cdot [1 - \exp(-2 \cdot r \cdot k \cdot \beta)] \quad (10.122)$$

In Eq. (10.122) m_{∞} denotes the mass burning rate for a pool of infinite diameter in $\text{kg}/(\text{m}^2 \text{ s})$, k is the absorption extinction coefficient of the flame in m^{-1} and β the mean beam length corrector. In case of petrol we have, for example, $m_{\infty} = 0.055 \text{ kg}/(\text{m}^2 \text{ s})$, $k = 2$ and $\beta = 1.05$.

In order to determine $\dot{m}$ in Eq. (10.121) the procedures of Sects. 10.2.1 and 10.2.2 are used.

10.6.1.2 Flame Dimensions

The flame is treated as a cylinder. This requires the characteristic wind speed to be calculated in the first place, i.e.

$$u_c = \left(g \cdot m'' \cdot 2 \cdot \frac{r}{\rho_L} \right)^{1/3} \quad (10.123)$$

In Eq. (10.123) g denotes the acceleration due to gravity, r the pool radius in m, m'' the mass burning rate in $\text{kg}/(\text{m}^2 \text{ s})$ and ρ_L the density of air ($1.2 \text{ kg}/\text{m}^3$).

Furthermore we need the scaled wind speed

$$u^* = \frac{u_w}{u_c} \quad (10.124)$$

In Eq. (10.124) u_w is the wind speed in m/s.

The flame length L is obtained from relationships for L_1 (cf. [15]) or for wind speeds tending towards 0 from L_2 [36]. Equation (10.126) is to be used as well for very small wind speeds, whose magnitude is, however, not specified. Therefore we assume 0.3 m/s here.

$$L_1 = \frac{2 \cdot r \cdot 55}{u^{*0.21}} \cdot \left(\frac{m''}{\rho_L \cdot \sqrt{2 \cdot g \cdot r}} \right)^{0.67} \quad \text{if } u_w > 0.3 \text{ m/s} \quad (10.125)$$

$$L_2 = 2 \cdot r \cdot 42 \cdot \left(\frac{m''}{\rho_L \cdot \sqrt{2 \cdot g \cdot r}} \right)^{0.61} \quad \text{if } u_w \leq 0.3 \text{ m/s} \quad (10.126)$$

L is normally equal to L_1 ; if with $u_w \leq 0.3 \text{ m/s}$ L_1 is $> L_2$, instead of $L = L_1$ $L = L_2$ is used.

In order to calculate the flame tilt with respect to the vertical line, which is caused by cross-wind, Froude's and Reynolds' numbers are needed in the first place, i.e.

$$\text{Fr} = \frac{u_w^2}{2 \cdot r \cdot g} \quad (10.127)$$

and

$$\text{Re} = \frac{2 \cdot r \cdot u_w}{\nu} \quad (10.128)$$

In Eq. (10.128) ν denotes the kinematic viscosity of air ($1.38 \times 10^{-5} \text{ m}^2/\text{s}$).

The flame tilt angle between the vertical line and the vertical flame axis, θ in degrees, then results iteratively from

$$\theta = \arctan(\cos(\theta) \cdot \text{Fr}^{0.333} \cdot \text{Re}^{0.117} \cdot 0.666) \quad (10.129)$$

10.6.1.3 Surface Emissive Power

The surface emissive power (SEP) for a cylindrical flame is calculated as follows

$$q''_{\max} = f_s \cdot m'' \cdot \frac{\Delta H_c}{1 + \frac{2L}{r}} \quad (10.130)$$

In Eq. (10.130) $q''_{\max}$ is the maximum surface emissive power of a flame without soot production in W/m^2 , f_s the fraction of the combustion energy radiated from the flame ($f_s = 0.4$ is considered to be a conservative value), and L the flame length, which is either equal to L_1 according to Eq. (10.125) or equal to L_2 according to Eq. (10.126) (see above); r is the pool radius in m. In addition we need the surface emissive power of soot

$$q''_{\text{soot}} = 20,000 \text{ W/m}^2 \quad (10.131)$$

Both equations are combined to give

$$q''_{\text{act}} = (1 - \zeta) \cdot q''_{\max} + \zeta \cdot q''_{\text{soot}} \quad (10.132)$$

In Eq. (10.132) q''_{act} is the actual surface emissive power in W/m^2 and ζ empirical fraction of the flame surface covered by soot. For oil products $\zeta = 0.8$ is an appropriate value.

10.6.1.4 Heat Flux at a Distance from the Source

Equation (10.132) refers to the surface of the flame. In order to assess the impact of a flame, the heat flux as a function of the distance between the flame and the point of reference (position of the receiver) has to be calculated. In doing this two effects have to be taken into account:

- (1) The reduction of the heat flux due to the geometries of the emitting and receiving bodies and their distance from each other. It is described by the view factor $f_{\text{ab}}(x)$, which represents the ratio between the received and the emitted power per unit area.
- (2) The atmospheric transmissivity for radiation, which amongst others depends on the humidity of the air; it is described by the coefficient of transmissivity $\tau_a(x)$.

Thus we obtain the heat flux at a distance x from the source

$$q''(x) = q''_{\text{act}} \cdot f_{\text{ab}}(x) \cdot \tau_a(x) \quad (10.133)$$

In Eq. (10.133) x is the distance between the centre of the flame and the point of reference in m, f_{ab} the view factor (in the present case for a tilted cylinder) and τ_a

the coefficient of atmospheric transmissivity; f_{ab} is obtained according to [36] (the indications in [15] contain errors) from

$$\begin{aligned} \pi F_v = & \frac{\arccos \theta}{b - \arcsin \theta} \cdot \frac{a^2 + (b+1)^2 - 2b(1 + a \sin \theta)}{\sqrt{AB}} \cdot \arctan \left(\sqrt{\frac{A}{B}} \sqrt{\frac{b-1}{b+1}} \right) \\ & + \frac{\cos \theta}{\sqrt{C}} \cdot \left[\arctan \left(\frac{ab - (b^2 - 1) \sin \theta}{\sqrt{b^2 - 1} \sqrt{C}} \right) + \arctan \left(\frac{(b^2 - 1) \sin \theta}{\sqrt{b^2 - 1} \sqrt{C}} \right) \right] \\ & - \frac{\arccos \theta}{b - \arcsin \theta} \cdot \arctan \left(\sqrt{\frac{b-1}{b+1}} \right) \end{aligned} \quad (10.134)$$

$$\begin{aligned} \pi F_h = & \arctan \left(\sqrt{\frac{b+1}{b-1}} \right) - \frac{a^2 + (b+1)^2 - 2(b+1 + ab \sin \theta)}{\sqrt{AB}} \cdot \arctan \left(\sqrt{\frac{A}{B}} \sqrt{\frac{b-1}{b+1}} \right) \\ & + \frac{\sin \theta}{\sqrt{C}} \cdot \left[\arctan \left(\frac{ab - (b^2 - 1) \sin \theta}{\sqrt{b^2 - 1} \sqrt{C}} \right) + \arctan \left(\frac{\sqrt{b^2 - 1} \sin \theta}{\sqrt{C}} \right) \right] \end{aligned}$$

$$a = \frac{L}{r}; \quad b = \frac{x}{r}; \quad A = a^2 + (b+1)^2 - 2a(b+1) \sin \theta$$

$$B = a^2 + (b-1)^2 - 2a(b-1) \sin \theta \text{ and } C = 1 + (b^2 - 1)(\cos \theta)^2$$

where

$$f_{ab} = \sqrt{F_v^2 + F_h^2} \quad (10.135)$$

holds.

According to [37] we can use as coefficient of atmospheric transmissivity

$$\tau_a(x) = 0.4343 \cdot \ln \left(14.1 \cdot \varphi^{-0.108} \cdot (x - r)^{-0.13} \right) \quad (10.136)$$

In Eq. (10.136) φ is the relative humidity of the air in % and x the distance between the centre of the flame, which has radius r , in m, and the receiver. The equation is valid for relative humidities ≥ 20 %. It shows that absorption in air increases for higher humidities.

Example 10.20 Fire in a petrol filling station

Filling stations for petrol often have volumetric flow rates of 1,000 l/h. If the petrol is spilled on the ground (e.g. because of an operator error), a pool is formed. Immediate ignition is assumed.

Calculate the time-dependent radius of the pool, the heat flux of the fire at a distance of 10 m from the pool centre at the time of maximum pool size and the conditional probability of death for a person exposed to the fire for $t_{ex} = 10$ min at that distance.

Assumption: the mass burning rate for a pool of infinite size is used, which for petrol amounts to $m_{\infty} = 0.055 \text{ kg}/(\text{m}^2 \text{ s})$.

Data: $\rho = 740.38 \text{ kg}/\text{m}^3$; $m'' = m_{\infty}$; $\delta = 0.02 \text{ m}$; $\dot{m} = 0.2057 \text{ kg}/\text{s}$; wind speed at anemometer height $u(z_A) = 3 \text{ m}/\text{s}$; $\Delta H_c = 45,000,000 \text{ J}/\text{kg}$

Solution

Starting point is Eq. (10.121), which reads after the variables have been separated as follows

$$dt = \frac{2 \cdot \pi \cdot r \cdot \rho \cdot \delta}{\dot{m} - \pi \cdot r^2 \cdot m''} \cdot dr$$

After integration we have

$$t + A = -\frac{\rho \cdot \delta}{m''} \cdot \ln (\dot{m} - \pi \cdot r^2 \cdot m'')$$

The initial condition is $r = 0$ at point in time $t = 0$, so that one obtains the particular solution

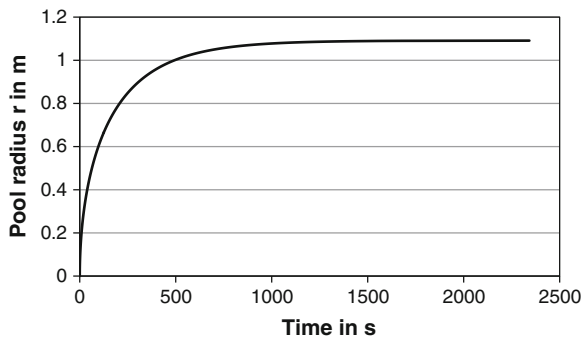
$$t = \frac{\rho \cdot \delta}{m''} \cdot \ln \frac{\dot{m}}{\dot{m} - \pi \cdot r^2 \cdot m''}$$

The maximum radius of the pool, $r_{\max}$, is obtained by setting the left hand side of Eq. (10.121) equal to zero. Thus we have

$$r_{\max} = \sqrt{\frac{\dot{m}}{\pi \cdot m''}} = \sqrt{\frac{0.2057 \frac{\text{kg}}{\text{s}}}{\pi \cdot 0.055 \frac{\text{kg}}{\text{m}^2 \text{s}}}} = 1.091 \text{ m}$$

By inserting this value into the preceding equation the corresponding time is found to be $t_{\max} = 2,342.8 \text{ s}$. After that the situation becomes stationary and the following calculations refer to that situation. Figure 10.27 shows the variation of the pool radius as a function of time based on the above solution of Eq. (10.121).

Fig. 10.27 Variation with time of the pool radius r



Flame dimensions

According to Eq. (100.23) we obtain for the radius of the stationary pool ($r = 1.091$ m)

$$u_c = \left(g \cdot m'' \cdot 2 \cdot \frac{r}{\rho_L} \right)^{1/3} = \left(9.81 \frac{\text{m}}{\text{s}^2} \cdot 0.055 \frac{\text{kg}}{\text{m}^2 \text{s}} \cdot 2 \cdot \frac{1.091 \text{ m}}{1.2 \frac{\text{kg}}{\text{m}^3}} \right)^{1/3} = 0.9937 \frac{\text{m}}{\text{s}}$$

and according to Eq. (100.24)

$$u^* = \frac{u_w}{u_c} = \frac{1.9 \frac{\text{m}}{\text{s}}}{0.9937 \frac{\text{m}}{\text{s}}} = 1.912 \frac{\text{m}}{\text{s}}$$

where u_w was determined by using Eq. (10.71) for neutral conditions and $h = L_1 = 4.75$ m

$$u_w = \frac{u(z_A)}{m+1} \left(\frac{h}{z_A} \right)^m = \frac{3 \frac{\text{m}}{\text{s}}}{1.28} \left(\frac{4.75 \text{ m}}{10 \text{ m}} \right)^{0.28} = 1.9 \frac{\text{m}}{\text{s}}$$

As flame length we obtain based on Eq. (10.125)

$$\begin{aligned} L_1 &= \frac{2 \cdot r \cdot 55}{u^{*0.21}} \cdot \left(\frac{m''}{\rho_L \cdot \sqrt{2 \cdot g \cdot r}} \right)^{0.67} \\ &= \frac{2 \cdot 1.091 \text{ m} \cdot 55}{\left(1.912 \frac{\text{m}}{\text{s}} \right)^{0.21}} \cdot \left(\frac{0.055 \frac{\text{kg}}{\text{m}^2 \text{s}}}{1.2 \frac{\text{kg}}{\text{m}^3} \cdot \sqrt{2 \cdot 9.81 \frac{\text{m}}{\text{s}^2} \cdot 1.091 \text{ m}}} \right)^{0.67} = 4.75 \text{ m} \end{aligned}$$

The tilt of the flame axis with respect to the vertical line, θ , is determined according to Eqs. (10.127)–(10.129):

$$\begin{aligned} \text{Fr} &= \frac{u_w^2}{2 \cdot r \cdot g} = \frac{\left(1.9 \frac{\text{m}}{\text{s}} \right)^2}{2 \cdot 1.091 \text{ m} \cdot 9.81 \frac{\text{m}}{\text{s}^2}} = 0.1686 \\ \text{Re} &= \frac{2 \cdot r \cdot u_w}{\nu} = \frac{2 \cdot 1.091 \text{ m} \cdot 1.9 \frac{\text{m}}{\text{s}}}{1.38 \times 10^{-5} \frac{\text{m}^2}{\text{s}}} = 300,420.29 \end{aligned}$$

The flame tilt, θ in degrees, then follows iteratively from Eq. (10.129)

$$\theta = \arctan(\cos(\theta) \cdot \text{Fr}^{0.333} \cdot \text{Re}^{0.117} \cdot 0.666) = \arctan(\cos(\theta) \cdot 1.6103) = \arctan 1.0894$$

as $\theta = 47.43^\circ$.

Specific emissive power

The specific emissive power (SEP) is calculated according to Eqs. (10.130) to Gl. (10.132), which give

$$q''_{\max} = f_s \cdot m'' \cdot \frac{\Delta H_c}{1 + \frac{2L}{r}} = 0.4 \cdot 0.055 \frac{\text{kg}}{\text{m}^2 \text{ s}} \cdot \frac{45,000,000 \frac{\text{J}}{\text{kg}}}{1 + \frac{2 \cdot 4.7 \text{ m}}{1.091 \text{ m}}} = 102,953.96 \frac{\text{W}}{\text{m}^2}$$

$$q''_{\text{act}} = (1 - \zeta) \cdot q''_{\max} + \zeta \cdot q''_{\text{soot}} = (1 - 0.8) \cdot 102,953.96 \frac{\text{W}}{\text{m}^2} + 0.8 \cdot 20,000 \frac{\text{W}}{\text{m}^2} = 36,590.8 \frac{\text{W}}{\text{m}^2}$$

Heat flux at a distance of $x = 10 \text{ m}$ from the source

The view factor is determined according to Eqs. (10.134) and (10.135)

$$F_v = 0.1345 + 0.01538 - 0.1092 = 0.04068$$

$$F_H = -0.00619 + 0.01718 = 0.01099$$

$$f_{\text{ab}} = \sqrt{F_v^2 + F_H^2} = \sqrt{0.04068^2 + 0.01099^2} = 0.04214$$

The transmissivity of the air is obtained according to Eq. (10.136) for a relative humidity of $\varphi = 20 \%$

$$\tau_a(x) = 0.4343 \cdot \ln \left(14.1 \cdot \varphi^{-0.108} \cdot (x - r)^{-0.13} \right)$$

$$= 0.4343 \cdot \ln \left(14.1 \cdot 20^{-0.108} \cdot (10 \text{ m} - 1.091 \text{ m})^{-0.13} \right) = 0.8852$$

Hence, the heat flux at $x = 10 \text{ m}$ according to Eq. (10.133) amounts to

$$q''(10 \text{ m}) = q''_{\text{act}} \cdot f_{\text{ab}}(10 \text{ m}) \cdot \tau_a(10 \text{ m}) = 36,590.8 \frac{\text{W}}{\text{m}^2} \cdot 0.04214 \cdot 0.8852$$

$$= 1,364.92 \frac{\text{W}}{\text{m}^2}$$

The probit value for the (improbable) case of a person remaining for ten minutes at a distance of $x = 10 \text{ m}$ according to Eq. (B.29) is

$$Y = -14.9 + 2.56 \cdot \ln \left(q''^{1.3333} \times 10^{-4} \cdot t_{\text{ex}} \right)$$

$$= -14.9 + 2.56 \cdot \ln \left(1,364.92^{1.3333} \times 10^{-4} \cdot 600 \text{ s} \right) = 2.54$$

The corresponding probability of death is obtained according to Eq. (2.56) as

$$\phi(Y - 5) = 6.9 \times 10^{-3}$$

This probability would become even smaller if the release of petrol were to be shut off at an early stage or the ignition of the pool were prevented by timely covering it with foam. $\square$

10.6.2 Gases

If a flammable gas is released, a fire or an explosion may occur. Fires and explosions can take place inside the containment (vessels, pipework etc.) of a process plant and after release (vid. Fig. 10.1). The former are the subject of the analysis of the engineered systems of the plant, the latter the concern of accident consequence calculations. In the former case the expected frequency of the undesired events ‘fire’ and ‘explosion’ must be determined, the reasons for their occurrence and possible countermeasures as well as potential consequences such as the flight of fragments (vid. Sect. 10.9) and the possibility of impacts on other parts of the plant. In the latter case the consequences are considered. Mainly these are treated below.

Released flammable gases may either burn without pressure buildup (flash fire, vapour cloud fire, fireball) or explode producing pressure waves. They can ignite instantaneously, with some delay or not at all. Figure 10.3 shows an event tree presenting several possibilities of future developments (scenarios) after the instantaneous release of a flammable gas.

In addition to the event paths shown in Fig. 10.3 the possibility exists that the cloud drifts a certain distance, before ignition occurs (cf. [2]). This path is not pursued further here.

10.6.2.1 Flash or Vapour Cloud Fires and Fireballs

If a flammable gas or vapour is released and there is sufficient time for a cloud to be formed before ignition, a flash fire, a fireball or no fire at all may result. This is supported by experimental findings from [38]. At least six out of ten vapour cloud experiments led to a fireball. Furthermore, an explosion may occur (vid. Sects. 2.1, 1.9 and 10.6.3), if the following conditions are fulfilled [37]:

- partial confinement and/or obstacles exist,
- the release has high initial energy (jet),
- the cloud grows in an explosion-like manner,
- ignition energy is high.

Hence, an explosion is not to be expected if none of these conditions is fulfilled. Instead a flash fire or a fireball will occur. The delimitation in the literature is not crisp and this is true also for observed events. A fireball is usually expected in connection with a BLEVE (vid. Sect. 10.7).

Flash fire

A flash or vapour cloud fire is defined in [37] as “the combustion of a flammable gas or vapour and air mixture in which the flame propagates through that mixture in a manner such that negligible or no damaging overpressure is generated”. There are few models for treating flash fires. The objective of a model is to determine the heat radiation as a function of distance from the surface of the cloud. Whilst it may safely be assumed that a person inside the cloud dies, the amount of

damage to persons outside the cloud depends on factors such as SEP and distance. Hence, the calculation for determining the consequences consists essentially of a dispersion calculation (vid. Sect. 10.5) which provides the cloud dimensions.

In [39] three models are mentioned. It is emphasized there that their application is limited to sources with low initial momentum, that there is little or no validation and no agreement on how to calculate flame length and velocity.

In what follows the semi-empirical approach of Raj and Emmons is presented based on [2, 37].

The model accounts for the velocity of the flame, as it sweeps through the cloud. It is assumed that during combustion a turbulent flame front moves at constant speed into the unburnt portion of the cloud. This speed is approximately proportional to the wind speed. Furthermore, it is assumed that with high gas concentrations a big flame is formed at the edge of the unburnt cloud.

The flame length is determined by

$$L = 20 \cdot d \cdot \left(\frac{S^2}{d \cdot g} \cdot \left(\frac{\rho_0}{\rho_L} \right)^2 \cdot \frac{w \cdot r^2}{(1-w)^3} \right)^{1/3} \quad (10.137)$$

The flame speed S in Eq. (10.137) is calculated as

$$S = 2.3 \cdot u_w \quad (10.138)$$

In Eq. (10.138) u_w denotes the wind speed in ms^{-1} ist. The ratio of the densities of fuel and air is given by

$$\left(\frac{\rho_0}{\rho_L} \right)^2 = \left[\frac{(1-\phi) \cdot M_L + \phi \cdot M_B}{M_L} \right]^2 \quad (10.139)$$

The stoichiometric fuel/air mass ratio, r , is calculated from the stoichiometric fuel volume ratio, ϕ_{st} , and the molar masses of air, M_L , and of the fuel, M_B .

$$r = \frac{(1 - \phi_{\text{st}}) \cdot M_L}{\phi_{\text{st}} \cdot M_B} \quad (10.140)$$

Finally w is determined from the actual fuel/air volumetric ratio, ϕ , the stoichiometric fuel volume ratio, ϕ_{st} , and the constant pressure expansion ratio for stoichiometric combustion α

$$w = \begin{cases} \frac{\phi - \phi_{\text{st}}}{\alpha \cdot (1 - \phi_{\text{st}})} & \text{für } \phi > \phi_{\text{st}} \\ 0 & \text{für } \phi \leq \phi_{\text{st}} \end{cases} \quad (10.141)$$

The expansion ratio α is typically 8 for hydrocarbons.

In order to determine the impact on the surroundings the surface emissive power of the fire has to be known. According to [37] $q''_{\text{act}} = 173 \text{ kW/m}^2$ is an appropriate value.

The duration of the fire results from

$$t_d = \frac{D}{S} \quad (10.142)$$

In Eq. (10.142) D denotes the cloud diameter in m and S the flame speed according to Eq. (10.138). Cloud size and its part within the explosion limits can be determined from dispersion calculations.

If the cloud is a plume, the flame shape can be approximated by a flat plane of constant cross section consuming the plume in a lengthwise direction [37]. The time-dependent variation of flame width, W , is then given by

$$W = 2 \cdot \sqrt{R^2 - (R - S \cdot t)^2} \quad (10.143)$$

During time t_d W increases from 0 to $2 \cdot R$ and again drops to 0.

View factor

In the preceding model the gas cloud is considered to be a cylinder. The fire is modelled by a flat plane firefront which moves at speed S towards the target (e.g. a person). This means that the distance between fire and target, x , is a function of time, i.e.

$$x = l + \frac{D}{2} - S \cdot t \quad (10.144)$$

In Eq. (10.144) l is the distance on the ground between the centre of the cloud and the target, and D the diameter of the cloud, both in m.

In order to determine the view factor we need d , the height of the cloud, which ideally stems from a dispersion calculation, and the flame width. The latter is divided into two halves, i.e. $b = W/2$, in order to calculate contributions from both sides from the normal on the flame surface. This leads to the view factor [37]

$$F_h = \frac{1}{2\pi} \cdot \left[\arctan\left(\frac{1}{x_r}\right) - A \cdot x_r \cdot \arctan(A) \right] \quad (10.145)$$

$$F_v = \frac{1}{2\pi} \cdot \left[h_r \cdot A \cdot \arctan(A) + \left(\frac{B}{h_r}\right) \cdot \arctan(B) \right] \quad (10.146)$$

where we used

$$h_r = \frac{L}{b}; \quad x_r = \frac{x}{b}; \quad A = (h_r^2 + x_r^2)^{-1/2} \quad \text{and} \quad B = h_r \cdot (1 + x_r^2)^{-1/2} \quad (10.147)$$

Thus we have

$$f_{hv} = \sqrt{F_v^2 + F_h^2} \quad (10.148)$$

In order to account for the contributions from both sides we obtain

$$f_{ab} = 2 \cdot f_{hv} \quad (10.149)$$

The heat flux at a distance of x from the source is then obtained by using Eq. (10.133), where in Eq. (10.136) $r = 0$ and x according to Eq. (10.144) are used.

Example 10.21 Flash fire

Following the release of $m = 2,000$ kg of propylene a gas cloud with $\phi = 20$ vol% of propylene is formed. Its height amounts to $d = 2$ m. There are no factors present which enhance an explosion (see above) so that a flash fire occurs. Calculate the heat flux for $t = 5$ s at $l = 120$ m distance from the point of release and the health impact on a person standing there assuming that the heat flux calculated for $t = 5$ s prevails while the fire lasts ($t_{ex} = t_d$).

Data: $M_B = 42.08$ g/mol, $M_L = 28.96$ g/mol, $\rho_{C_3H_6} = 1.81$ kg/m³, $u_w = 2$ m/s, $\varphi = 20$ %

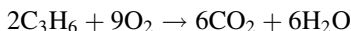
Solution

Determination of the cloud diameter D

$$D = \sqrt{\frac{m \cdot 4}{\rho \cdot \pi \cdot d \cdot \phi}} = \sqrt{\frac{2,000 \text{ kg} \cdot 4}{1.81 \frac{\text{kg}}{\text{m}^3} \cdot 3.1416 \cdot 2 \text{ m} \cdot 0.2}} = 59.31 \text{ m}$$

Determination of the stoichiometric fuel volume ratio, ϕ_{st} , and other parameters

The reaction equation for stoichiometric combustion is



From this we obtain, assuming that air contains 21 % of oxygen,

$$\phi_{st} = \frac{2 \cdot 0.21}{9} = 0.0467$$

For w we have according to Eq. (10.141)

$$w = \frac{\phi - \phi_{st}}{\alpha \cdot (1 - \phi_{st})} = \frac{0.2 - 0.0467}{8 \cdot (1 - 0.0467)} = 0.0201$$

and for the stoichiometric fuel/air mass ratio, r , according to Eq. (10.140)

$$r = \frac{(1 - \phi_{st}) \cdot M_L}{\phi_{st} \cdot M_B} = \frac{(1 - 0.0467) \cdot 28.96 \frac{\text{g}}{\text{mol}}}{0.0467 \cdot 42.08 \frac{\text{g}}{\text{mol}}} = 14.0487$$

The ratio of densities is calculated according to Eq. (10.139)

$$\left(\frac{\rho_0}{\rho_L}\right)^2 = \left[\frac{(1 - \phi) \cdot M_L + \phi \cdot M_B}{M_L}\right]^2 = \left[\frac{(1 - 0.2) \cdot 28.96 \frac{\text{g}}{\text{mol}} + 0.2 \cdot 42.08 \frac{\text{g}}{\text{mol}}}{28.96 \frac{\text{g}}{\text{mol}}}\right]^2 = 1.1894$$

The flame speed is obtained from Eq. (10.442)

$$S = 2.3 \cdot u_w = 2.3 \cdot 2 \frac{\text{m}}{\text{s}} = 46 \frac{\text{m}}{\text{s}}$$

and the flame length L from Eq. (10.137)

$$\begin{aligned} L &= 20 \cdot d \cdot \left(\frac{S^2}{d \cdot g} \cdot \left(\frac{\rho_0}{\rho_L} \right)^2 \cdot \frac{w \cdot r^2}{(1 - w)^3} \right)^{1/3} \\ &= 20 \cdot 2 \text{ m} \cdot \left(\frac{(4.6 \frac{\text{m}}{\text{s}})^2}{2 \text{ m} \cdot 9.81 \frac{\text{m}}{\text{s}^2}} \cdot 1.1894 \cdot \frac{0.0201 \cdot 14.0487^2}{(1 - 0.0201)^3} \right)^{1/3} = 70.21 \text{ m} \end{aligned}$$

The duration of the fire is calculated according to Eq. (10.142), which gives

$$t_d = \frac{D}{S} = \frac{59.31 \text{ m}}{4.6 \frac{\text{m}}{\text{s}}} = 12.9 \text{ s}$$

The flame width results from Eq. (10.143) as

$$W = 2 \cdot \sqrt{R^2 - (R - S \cdot t)^2} = 2 \cdot \sqrt{(29.66 \text{ m})^2 - \left(29.66 \text{ m} - 4.6 \frac{\text{m}}{\text{s}} \cdot t\right)^2}$$

The distance between the flame and the target is calculated from Eq. (10.144), which gives

$$x = 1 + \frac{D}{2} - S \cdot t = 120 \text{ m} + 29.66 \text{ m} - 4.6 \frac{\text{m}}{\text{s}} \cdot t$$

By way of example the view factor and the transmissivity of air are calculated below for $t = 5 \text{ s}$.

The above equations give

$$W(5 \text{ s}) = 57.81 \text{ m}$$

$$x(5 \text{ s}) = 126.66 \text{ m}$$

Thus the abbreviations of Eq. (10.147) become

$$\begin{aligned} h_r &= \frac{L}{b} = \frac{70.21 \text{ m}}{28.91 \text{ m}} = 2.4286 \\ x_r &= \frac{x}{b} = \frac{126.66 \text{ m}}{28.91 \text{ m}} = 4.3812 \\ A &= (h_r^2 + x_r^2)^{-1/2} = (2.4286^2 + 4.3812^2)^{-1/2} = 0.1996 \\ B &= h_r \cdot (1 + x_r^2)^{-1/2} = 2.4286 \cdot (1 + 4.3812^2)^{-1/2} = 0.5404 \end{aligned}$$

and according to Eqs. (10.145) and (10.146)

$$\begin{aligned} F_h &= \frac{1}{2\pi} \cdot \left[\arctan\left(\frac{1}{x_r}\right) - A \cdot x_r \cdot \arctan(A) \right] \cdot 2 \\ &= 0.1592 \cdot (0.2244 - 0.1996 \cdot 4.3812 \cdot 0.1970) = 8.2985 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} F_v &= \frac{1}{2\pi} \cdot \left[h_r \cdot A \cdot \arctan(A) + \left(\frac{B}{h_r}\right) \cdot \arctan(B) \right] \cdot 2 \\ &= 0.1592 \cdot (2.4286 \cdot 0.1996 \cdot 0.1997 + 0.2225 \cdot 0.4954) = 3.2960 \times 10^{-2} \end{aligned}$$

According to Eq. (10.148) we have

$$f_{hv} = \sqrt{F_v^2 + F_h^2} = \sqrt{(8.2985 \times 10^{-3})^2 + (3.2960 \times 10^{-2})^2} = 3.3989 \times 10^{-2}$$

and according to Eq. (10.149)

$$f_{ab} = 2 \cdot f_{hv} = 2 \cdot 3.3989 \times 10^{-2} = 6.7977 \times 10^{-2}$$

The transmissivity of air is obtained from Eq. (10.136), which gives

$$\begin{aligned} \tau_a(x) &= 0.4343 \cdot \ln \left(14.1 \cdot \varphi^{-0.108} \cdot (x - r)^{-0.13} \right) \\ &= 0.4343 \cdot \ln \left(14.1 \cdot 20^{-0.108} \cdot 126.66^{-0.13} \right) = 0.7354 \end{aligned}$$

The heat flux is calculated with Eq. (10.133), which gives

$$q''(x) = q''_{act} \cdot f_{ab}(x) \cdot \tau_a(x) = 173,000 \frac{\text{W}}{\text{m}^2} \cdot 6.7977 \times 10^{-2} \cdot 0.7354 = 8,648.32 \frac{\text{W}}{\text{m}^2}$$

The probability of death due to exposure is calculated, making the untrue assumption that the values for $t = 5$ s apply to the entire duration of the fire, as follows

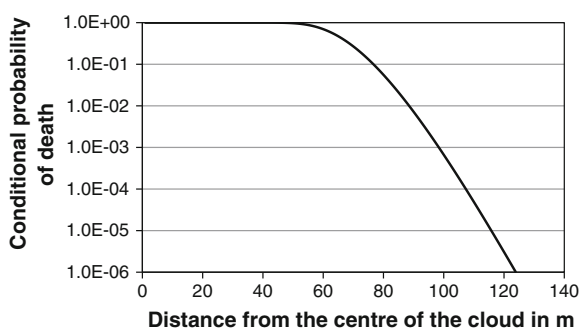
$$\begin{aligned} Y &= -14.9 + 2.56 \cdot \ln(q''^{1.3333} \times 10^{-4} \cdot t_{\text{ex}}) \\ &= -14.9 + 2.56 \cdot \ln(8,648.32^{1.3333} \times 10^{-4} \cdot 12.9 \text{ s}) = -0.9897 \end{aligned}$$

The probability according to Eq. (2.55) is

$$\phi(Y - 5) = 1.1 \times 10^{-9}$$

Figure 10.28 is based on calculations which take into account the time variation of heat radiation due to the movement of the flame front between $-D/2$ and $D/2$ during the duration of fire, t_d .

Fig. 10.28 Conditional probability of death as function of the distance of the target (receiver) from the centre of the gas cloud



□

Fireball

A fireball is understood to be “a burning fuel-air cloud whose energy is emitted primarily in the form of radiant heat. The inner core of the cloud consists almost completely of fuel, whereas the outer layer (where ignition first occurs) consists of a flammable fuel-air mixture. As the buoyancy forces of hot gases increase, the burning cloud tends to rise, expand, and assume a spherical shape” [37]. According to [2] there are several situations for a fireball to occur

- spontaneous vessel failure;
- failure of a vessel due to fire loads;
- ignition of a release on a liquefied gas pipeline;
- instantaneous vaporization of hot oil forming a flammable vapour.

Often a fireball follows a BLEVE (‘Boiling Liquid Vapor Cloud Explosion’) (vid. Sect. 10.7), which may occur, for example, if a vessel containing pressure liquefied gas fails.

An important parameter for determining the damage caused by a fireball is its specific surface emissive power ('SEP'), at least if the object to be protected is not inside the ball and hence directly exposed. The model used here is the solid flame model. According to [39] the result of the calculation strongly depends on how the SEP is defined and measured. In [2] a low value of 141 kW/m^2 and a maximum value of 450 kW/m^2 are quoted; [37] indicates a range from 320 kW/m^2 to 350 kW/m^2 . In view of these values the use of a value of $q''_{\text{act}} = 350 \text{ kW/m}^2$ for the SEP is recommended.

The majority of models for treating fireballs is based on correlations for its diameter and duration [2, 40]. More fundamental models are discussed in [2] and the application of methods of computational fluid dynamics ('CFD') to fireballs is treated, for example, in [41].

One uses for the diameter

$$D = k_1 \cdot m^{n_1} \quad (10.150)$$

In Eq. (10.150) D is the diameter of the fireball in m, k_1 is a constant and n_1 an exponent; m is the mass of hydrocarbons in kg, contained in the fireball.

For the duration of the fireball, t_d (in s), one uses

$$t_d = k_2 \cdot m^{n_2} \quad (10.151)$$

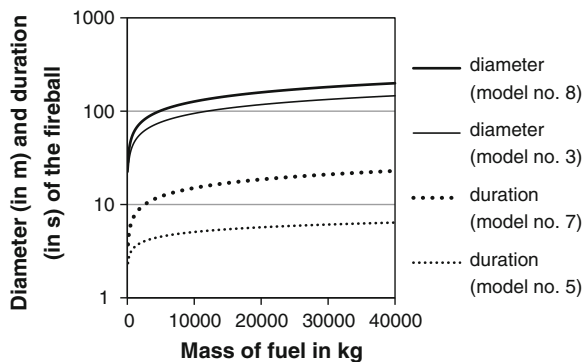
Constants and exponents for the Eqs. (10.150) and (10.151) for several materials and models are listed in Table 10.9. Extreme values for the diameter and the duration of the fireball, which result from a comparison of calculations with the nine sets of constants from Table 10.9, are shown in Fig. 10.29.

According to the investigation [42], where the model results were compared amongst others with experiments by British Gas and BAM as well as observations in Mexico City and Los Alfaques, the model by Shield [43] is to be preferred. However, it is stated that the empirical model according to CCPS [33] gives conservative results. That is why it is used here.

Table 10.9 Coefficients for Eqs. (10.150) and (10.151) (after [2])

Model	k_1	n_1	k_2	n_2	Material
1	5.55	0.333	—	—	Propane
2	6.36	0.325	2.57	0.167	Hydrocarbons
3	5.25	0.314	1.07	0.181	n-Pentane
4	5.80	0.333	0.45	0.333	Hydrocarbons
5	5.88	0.333	1.09	0.167	Propane
6	5.72	0.333	0.45	0.333	Butane
7	5.33	0.327	0.923	0.303	Hydrocarbons
8	6.48	0.325	0.852	0.26	LPG
9	5.50	0.333	0.38	0.333	Hydrocarbons

Fig. 10.29 Extreme values for diameter and duration of a fireball as a function of fuel mass with indication of the respective model from Table 10.9



For the diameter of the fireball the constants of no. 4 of Table 10.9 are used. In calculating the duration we distinguish between

$M \leq 30,000$ kg (constants of no. 4 from Table 10.9)

$M > 30,000$ kg (constants of no. 2 from Table 10.9)

View factor

Fireballs are modelled as spheres radiating onto a plane receiver. Assuming that the fireball has not yet lifted from the ground the following view factors are obtained

$$F_h = \frac{(D/2)^3}{[x^2 + (D/2)^2]^{3/2}} \quad (10.152)$$

$$F_v = \frac{x \cdot (D/2)^2}{[x^2 + (D/2)^2]^{3/2}} \quad (10.153)$$

$$f_{ab} = \sqrt{F_v^2 + F_h^2} \quad (10.154)$$

The heat flux density at a distance of x from the source is obtained from Eq. (10.133) using $r = D/2$ in Eq. (10.136).

Example 10.22 Fireball after a release of propane

A release of $m = 10,000$ kg of propane occurs. What is size of the fireball and for how long does it exist? What are the heat flux and the conditional probability of death at a distance of $x = 150$ m, if the relative humidities of the air amount to $\varphi = 20\%$ respectively 50% ?

Solution

The diameter is determined from Eq. (10.150). We have

$$D = k_1 \cdot m^{n_1} = 5.8 \cdot 10,000^{1/3} = 124.96 \text{ m}$$

The duration of the fireball is obtained from Eq. (10.151), which gives

$$t_d = k_2 \cdot m^{n_2} = 0.45 \cdot 10,000^{1/3} = 9.69 \text{ s}$$

The heat flux follows from Eq. (10.133) together with Eqs. (10.152)–(10.154) and (10.136)

$$\begin{aligned} F_h &= \frac{(D/2)^3}{[x^2 + (D/2)^2]^{3/2}} = \frac{(124.96 \text{ m}/2)^3}{[(150 \text{ m})^2 + (124.96 \text{ m}/2)^2]^{3/2}} = 0.05685 \\ F_v &= \frac{x \cdot (D/2)^2}{[x^2 + (D/2)^2]^{3/2}} = \frac{150 \text{ m} \cdot (124.96 \text{ m}/2)^2}{[(150 \text{ m})^2 + (124.96 \text{ m}/2)^2]^{3/2}} = 0.1365 \\ f_{ab} &= \sqrt{F_v^2 + F_h^2} = \sqrt{0.1365^2 + 0.05685^2} = 0.1479 \end{aligned}$$

Equation (10.136) gives for the transmissivity of air (relative humidity 20 %)

$$\begin{aligned} \tau_a(x) &= 0.4343 \cdot \ln \left(14.1 \cdot \varphi^{-0.108} \cdot (x - r)^{-0.13} \right) \\ &= 0.4343 \cdot \ln \left(14.1 \cdot 20^{-0.108} \cdot (150 - 62.68)^{-0.13} \right) \\ &= 0.7562 \text{ and for a relative humidity of 50 \% } \tau_a(x) = 0.7133 \end{aligned}$$

Thus we obtain the heat fluxes at the target as

$$\begin{aligned} q''(x) &= q''_{\text{act}} \cdot f_{ab}(x) \cdot \tau_a(x) = 350,000 \frac{\text{W}}{\text{m}^2} \cdot 0.1479 \cdot 0.7562 \\ &= 39,144.7 \frac{\text{W}}{\text{m}^2} \text{ for a relative humidity of 20 \%} \\ q''(x) &= q''_{\text{act}} \cdot f_{ab}(x) \cdot \tau_a(x) = 350,000 \frac{\text{W}}{\text{m}^2} \cdot 0.1479 \cdot 0.7133 \\ &= 36,924.0 \frac{\text{W}}{\text{m}^2} \text{ for a relative humidity of 50 \%} \end{aligned}$$

The conditional probability of death following exposure is calculated using Eq. (B.29)

$$\begin{aligned} Y &= -14.9 + 2.56 \cdot \ln(q''^{1.3333} \times 10^{-4} \cdot t_{\text{ex}}) \\ &= -14.9 + 2.56 \cdot \ln(39,144.7^{1.3333} \times 10^{-4} \cdot 9.69 \text{ s}) = 3.4306 \end{aligned}$$

and Eq. (2.55). The latter gives the conditional probability of death as

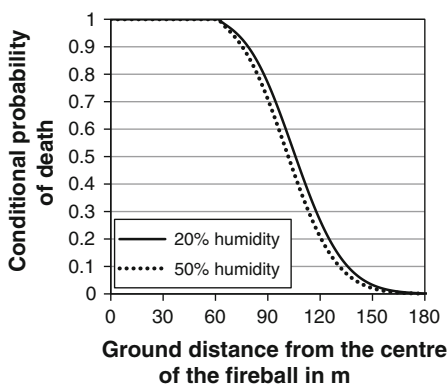
$$\phi(3.4306 - 5) = 5.83 \times 10^{-2}$$

For a relative humidity of the air of 50 % the conditional probability of death is

$$\phi(3.2314 - 5) = 3.85 \times 10^{-2}$$

The stochastic parameter ‘humidity of the air’, which cannot be predicted for the moment of occurrence of the fireball, has a substantial influence on the conditional probability of death, as can also be seen from Fig. 10.30.

Fig. 10.30 Conditional probability of death for a fireball from 10,000 kg of propane as a function of the distance on the ground (distance between the point of reference and the point where the vertical through the centre of the fireball hits the ground)



□

10.6.2.2 Jet Fire

Jet fires can occur with releases from apertures either deliberately (e.g. flare) or unwantedly (e.g. leak or rupture). According to [44] a jet fire is understood to be “a turbulent diffusion (non-premixed) flame resulting from the combustion of a fuel continuously released with some significant momentum in a particular range of directions”. The horizontal direction is often the most hazardous one because the flame can then impinge on neighbouring installations. Depending on the release conditions a jet fire may arise from single or two-phase discharges. Although CFD calculations were applied to jet fires already some time ago [45], semi-empirical models are still in use [2, 40, 46]. In [2] several models for jet fires are presented. Below only the relationships by Considine and Grint are given which are accompanied by correlations for hazard assessment.

For the length of the flame, which is assumed to be conical, one has

$$L = 9.1 \cdot \sqrt{\dot{m}} \quad (10.155)$$

and for its radius at the tip

$$R = 0.25 \cdot L \quad (10.156)$$

In Eqs. (10.155) and (10.156) $\dot{m}$ is the mass flow of gas in kg/s, L the length of the flame in m and R its half-width in m.

Additionally, we have two sets of equations for the death of exposed persons. If the persons are standing in the direction of the flame axis, the following end-on relations are used

$$r_{50} = 16 \cdot t_{\text{ex}}^{0.4} \cdot \dot{m}^{0.47} \quad (1 < \dot{m} < 3,000; 10 < t_{\text{ex}} < 300) \quad (10.157)$$

$$r_1 = 2.8 \cdot t_{\text{ex}}^{0.38} \cdot \dot{m}^{0.47} \quad (1 < \dot{m} < 3,000; 10 < t_{\text{ex}} < 300) \quad (10.158)$$

where r is measured from the edge of the flame.

The corresponding side-on relations (person stands at a right angle with the flame axis) are

$$r_{50} = 1.9 \cdot t_{\text{ex}}^{0.4} \cdot \dot{m}^{0.47} \quad (1 < \dot{m} < 3,000; 10 < t_{\text{ex}} < 300; r > R) \quad (10.159)$$

$$r_1 = 2.8 \cdot t_{\text{ex}}^{0.38} \cdot \dot{m}^{0.47} \quad (1 < \dot{m} < 3,000; 10 < t_{\text{ex}} < 300; r > R) \quad (10.160)$$

where r is measured from the flame axis.

In the above equations r_{50} denotes the distance of 50 % lethality and r_1 that of 1 % lethality; t_{ex} is the duration of exposure in s.

Example 10.23 Jet fire of propylene

A mass flow of $\dot{m} = 2$ kg/s of propylene is discharged from a leak. The propylene ignites immediately and a jet fire occurs. What are the dimensions of the fire and the distances for lethalties of 50 % and 1 %, if the duration of exposure is $t_{\text{ex}} = 300$ s? Exposures at the end of the flame and on its side are to be considered.

Solution

According to Eq. (10.155) we have a flame length of

$$L = 9.1 \cdot \sqrt{\dot{m}} = 9.1 \cdot \sqrt{2} = 12.9 \text{ m}$$

and according to Eq. (10.156) a half-width of

$$R = 0.25 \cdot L = 0.25 \cdot 12.9 \text{ m} = 3.23 \text{ m}$$

The distances are determined using Eqs. (10.157)–(10.160)

- distances from the edge the flame

$$r_{50} = 16 \cdot t_{\text{ex}}^{0.4} \cdot \dot{m}^{0.47} = 16 \cdot 300^{0.4} \cdot 2^{0.47} = 217.0 \text{ m}$$

$$r_1 = 2.8 \cdot t_{\text{ex}}^{0.38} \cdot \dot{m}^{0.47} = 2.8 \cdot 300^{0.38} \cdot 2^{0.47} = 33.9 \text{ m}$$

- distances from the axis of the flame (exposure on the side of the flame)

$$r_{50} = 1.9 \cdot t_{\text{ex}}^{0.4} \cdot \dot{m}^{0.47} = 1.9 \cdot 300^{0.4} \cdot 2^{0.47} = 25.8 \text{ m}$$

$$r_1 = 2.8 \cdot t_{\text{ex}}^{0.38} \cdot \dot{m}^{0.47} = 2.8 \cdot 300^{0.38} \cdot 2^{0.47} = 33.9 \text{ m}$$

□

10.6.3 Explosions

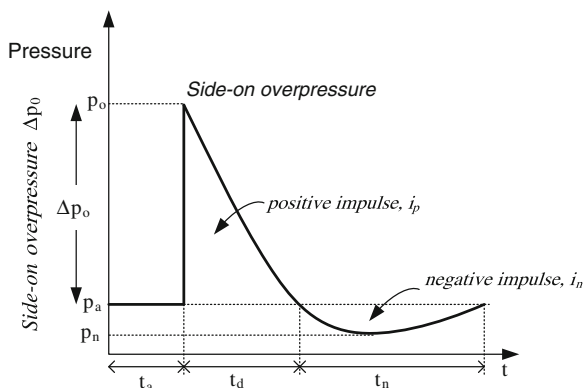
Important mechanisms for harm to humans as well as damage to the environment and property, which may arise from process plants, are explosions. An explosion results from a spontaneous release of energy. This causes a pressure wave. If the pressure is measured at right angles to the pressure wave we speak of side-on overpressure, which is occasionally also called free field overpressure. If the pressure measuring device is placed in the middle of a wall onto which the pressure wave travels we measure the reflected overpressure. The dynamic pressure is defined as $1/2 \cdot \rho u^2$, where ρ is the density of the gas involved and u its travelling velocity.

The variation of overpressure with time for a vapour cloud explosion is shown in Fig. 10.31 [47]. One can see that a phase of overpressure is followed by one of underpressure, whose damaging potential should also be considered.

The following types of explosions can be distinguished:

- release of stored pressure energy (e.g. compressed gas),
- release with change of state of a pressure liquefied gas (e.g. flash release),
- release of chemical energy (e.g. explosive, flammable gas, decomposition),

Fig. 10.31 The variation of overpressure with time for a vapour cloud explosion



- release from fast surface reactions (z.B. dust explosion, steam explosion, aerosols),
- thermal explosion (runaway reaction),
- condensed phase explosion.

It is clear that the origin of an explosion may be chemical or physical or a combination of both. Material properties and conditions which may lead to an explosion were already treated in Chap. 2 and runaway reactions in Chap. 3.

Explosions can be confined and unconfined. Intermediate states are possible as well, for example an explosion in a room with pressure relief flaps.

Confined explosions cause higher pressures than unconfined ones. Explosions may be deflagrations (with lower peak pressures) or detonations (with higher peak pressures), as described in Sect. 2.1.1.9.

The consequences of an explosion can be:

- missile flight (vid. Sect. 10.9)
- pressure waves
- heat radiation
- crater formation
- earth shocks

In what follows mainly unconfined explosions are discussed (for confined explosions see Sect. 2.1.1.9). A number of models exist (vid. [48, 49]):

- *Empirical models*, which are also called quasi-theoretical. They are based on a limited amount of experimental data and represent the simplest models for treating vapour cloud explosions. The TNT-model (vid. [2]), the TNO multi-energy model [15] and the Baker-Strehlow model [50] belong to this group.
- *Phenomenological models* are simplified models, which only include the most important aspects of the physics of explosions. SCOPE ('Shell-Code for Over-pressure Prediction in gas Explosions') [51] and CLICHÉ ('Confined Linked Chamber Explosion') [52, 53] are inscribed in this group.
- *CFD models* solve the partial differential equations which describe the explosion process. Presumably the best-known program of this group is FLACS ('Flame Acceleration Simulator') [54].

According to [48] empirical models are well suited for screening, phenomenological models are a good alternative for CFD, and CFD permits a detailed representation of real processes.

Nevertheless limitations and uncertainties in modelling explosions still exist. This became evident when the Buncefield accident was analyzed [55, 56]. None of the models reproduced the observed high pressure peaks.

In what follows the three empirical models are presented; as to the other model types the reader is referred to the literature.

10.6.3.1 The TNT Equivalent Model

In order to compare the energy release, for example of the depressurisation of a gas stored under pressure, the explosion of an explosive or the combustion of a flammable gas, a common reference must be found.

For this purpose the knowledge on the effects of explosives forms a basis. Many of the available correlations refer to the effect of explosions of TNT (trinitrotoluene). The important difference between the explosion of an explosive and that of a flammable gas is its brisance. It is reflected by a particularly short pressure wave. This is true as well for TNT. Despite this difference the TNT equivalent is the most frequently used model for assessing explosion effects. Values between 4,190 and 4,650 kJ/kg are quoted for the equivalent (cf. [15]). In [2] a value of 4,681 kJ/kg is used. In what follows a value of 4,650 kJ/(kg TNT) is chosen. It serves to convert the energy released in an explosion into an equivalent quantity of TNT.

An important parameter for describing explosion effects is the peak side-on overpressure, p_s . It can be represented by the following relationship for p_s (in kPa), which stems from [57] and was scaled here to produce agreement with the Marshall curve (cf. [15])

$$p_s = 159.5077 \cdot \frac{808 \cdot \left[1 + \left(\frac{r'}{4.5}\right)^2\right]}{\sqrt{\left[1 + \left(\frac{r'}{0.048}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{0.32}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{1.35}\right)^2\right]}} \quad (10.161)$$

In Eq. (10.161) r' is the scaled distance. It is obtained from the expression $r' = r/W_{\text{TNT}}^{1/3}$. W_{TNT} is obtained by dividing the energy released in the explosion by the TNT equivalent of 4,650 kJ/kg. Figure 10.32 represents Eq. (10.161).

The model treatment of an explosion uses the following relationship

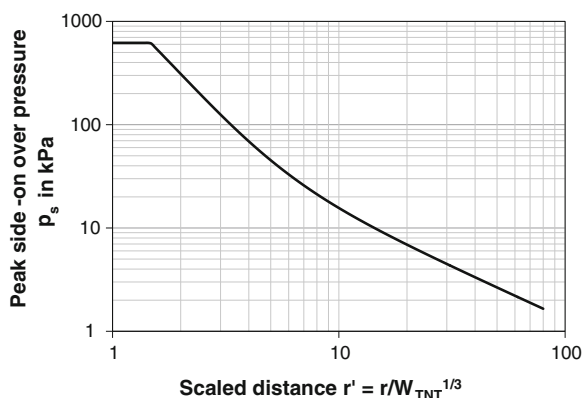


Fig. 10.32 Peak side-on overpressure as a function of the scaled distance (so-called Marshall curve) according to Eq. (10.163) (Note since the curve is not defined in the region of pressures above 6.2 bar the corresponding region is set here equal to 6.2 bar; as to the conditional probability of death this makes no difference, because it is already equal to 1 for 6.2 bar)

$$W_{\text{TNT}} = \alpha \cdot \frac{W \cdot \Delta H_c}{E_{\text{TNT}}} \quad (10.162)$$

In Eq. (10.162) W is the mass of the reacting fuel, ΔH_c its enthalpy of combustion in kJ/kg, E_{TNT} the energy released in an explosion of TNT ($E_{\text{TNT}} = 4,650$ kJ/kg) and α the yield factor of the explosion.

Explosives

Explosives exhibit a particular form of the release of chemical energy with an ensuing blast wave. They do not require the oxygen of the air, but contain the oxygen needed for combustion already in the chemical compound. Thus they can explode as well in the absence of air (for example under water).

Explosions of explosives are characterized by high rates of energy release and high brisance. Contrary to the explosion of flammable gases explosions of explosives are of very short duration. This highlights the weakness of using the TNT equivalent for flammable gases.

Explosions of explosives are treated according to Eq. (10.161) together with Eq. (10.162), where a yield of $\alpha = 1$ is used.

Vapour cloud explosions

A vapour cloud explosion may occur after the release of a flammable gas. The condition is that a cloud with a sufficient quantity of a mixture of fuel and air between the explosion limits is accumulated before ignition. The rich mixture portion of the cloud contributes to the fire following the explosion. Additionally there must be a certain degree of turbulence. This may result from the release process itself or be caused by obstacles to cloud spreading. If these conditions are not fulfilled a flash fire or a fireball are to be expected.

If the consequences of the vapour cloud explosion are to be assessed using the TNT equivalent model this is accounted for, contrary to an explosive, by a yield factor $\alpha < 1$. Different experience-based values are quoted for the yield factor. The range lies between 0.0002 and 0.2; occasionally even higher values are given [15]. The differences show that the yield factor is a quantity which strongly depends on the (not foreseeable) boundary conditions of release and explosion. For practical calculations a value of $\alpha = 0.2$ is recommended. It is the upper bound of the indicated region. The duration of the positive phase of a vapour cloud explosion (t_d in Fig. 10.31), which is the only one to be treated with the TNT equivalent model, amounts to 100–300 ms.

Example 10.24 Effects of an explosion of hexogen according to the TNT model

In the plant of case study 4.2 there are 101.5 kg of the explosive hexogen during stationary production. What is the peak side-on overpressure at a distance of $r = 20$ m in case of an explosion? What are the health effects to be expected for a person standing at this distance from the reactor and what is the probability for structural damage?

Datum: $\Delta H_c = 5,647$ kJ/kg

Solution

In the first place the TNT equivalent according to Eq. (10.162) is calculated. This gives

$$W_{\text{TNT}} = \alpha \cdot \frac{W \cdot \Delta H_c}{E_{\text{TNT}}} = 1 \cdot \frac{101.5 \text{ kg} \cdot 5,647 \frac{\text{kJ}}{\text{kg}}}{4,650 \frac{\text{kJ}}{\text{kg}}} = 123.26 \text{ kg}$$

After that the scaled distance is formed

$$r' = \frac{r}{W_{\text{TNT}}^{1/3}} = \frac{20 \text{ m}}{(123.26 \text{ kg})^{1/3}} = 4.0187 \frac{\text{m}}{\text{kg}^{1/3}}$$

The peak side-on overpressure follows from Eq. (10.161)

$$\begin{aligned} p_s &= 159.5077 \cdot \frac{808 \cdot \left[1 + \left(\frac{r'}{4.5}\right)^2\right]}{\sqrt{\left[1 + \left(\frac{r'}{0.048}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{0.32}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{1.35}\right)^2\right]}} \\ &= 159.5077 \cdot \frac{808 \cdot \left[1 + \left(\frac{4.0187}{4.5}\right)^2\right]}{\sqrt{\left[1 + \left(\frac{4.0187}{0.048}\right)^2\right] \cdot \left[1 + \left(\frac{4.0187}{0.32}\right)^2\right] \cdot \left[1 + \left(\frac{4.0187}{1.35}\right)^2\right]}} = 69.97 \text{ kPa} \end{aligned}$$

This value is inserted into the probit Eq. (B.22) which gives

$$Y = -77.1 + 6.91 \cdot \ln p_s = -77.1 + 6.91 \cdot \ln 69,970 = -1.3271 \times 10^{-2}$$

and according to Eq. (2.56) a conditional probability of death of

$$\phi(Y - 5) = 2.68 \times 10^{-7}$$

where, however, the possibility of being hit by a flying fragment is not included.

Ruptures of the eardrum are calculated according to Eq. (B.23a), which gives a probit value of

$$Y = -15.6 + 1.93 \cdot \ln p_s = -15.6 + 1.93 \cdot \ln 69,970 = 5.9307$$

and according to Eq. (2.56) a conditional probability of

$$\phi(Y - 5) = 0.824$$

Structural damage is assessed according to Eq. (B.27)

$$Y = -23.8 + 2.92 \cdot \ln p_s = -23.8 + 2.92 \cdot \ln 69,970 = 8.7750$$

which gives a conditional probability of

$$\phi(Y - 5) = 0.9999$$

Example 10.25 Effect of an explosion of a cloud of propane

After the release of 1,000 kg of propane a cloud is formed. It is ignited and a vapour cloud explosion occurs. What is the peak side-on overpressure at a distance of $r = 100$ m from the point of ignition?

Data: $\Delta H_c = 46,085.77$ kJ/kg, atmospheric pressure $p_a = 1$ bar, yield factor $\alpha = 0.2$

Solution

In the first place the TNT equivalent according to Eq. (10.162) is calculated

$$W_{\text{TNT}} = \alpha \cdot \frac{W \cdot \Delta H_c}{E_{\text{TNT}}} = 0.2 \cdot \frac{1,000 \text{ kg} \cdot 46,085.77 \frac{\text{kJ}}{\text{kg}}}{4,650 \frac{\text{kJ}}{\text{kg}}} = 1,982.18 \text{ kg}$$

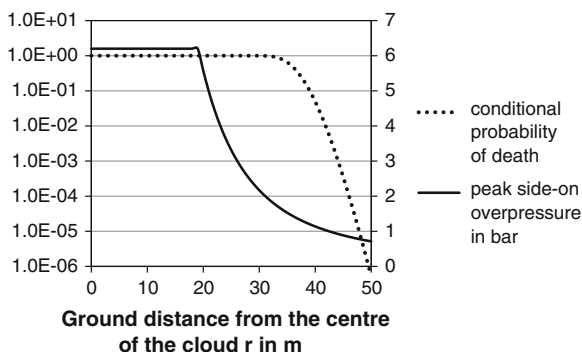
After that the scaled distance is formed

$$r' = \frac{r}{W_{\text{TNT}}^{1/3}} = \frac{100 \text{ m}}{(1,982.18 \text{ kg})^{1/3}} = 7.9607 \frac{\text{m}}{\text{kg}^{1/3}}$$

$$\begin{aligned} p_s &= 159.5077 \cdot \frac{808 \cdot \left[1 + \left(\frac{r'}{4.5}\right)^2\right]}{\sqrt{\left[1 + \left(\frac{r'}{0.048}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{0.32}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{1.35}\right)^2\right]}} \\ &= 159.5077 \cdot \frac{808 \cdot \left[1 + \left(\frac{7.9607}{4.5}\right)^2\right]}{\sqrt{\left[1 + \left(\frac{7.9607}{0.048}\right)^2\right] \cdot \left[1 + \left(\frac{7.9607}{0.32}\right)^2\right] \cdot \left[1 + \left(\frac{7.9607}{1.35}\right)^2\right]}} = 21.55 \text{ kPa} \end{aligned}$$

Figure 10.33 shows the peak side-on overpressure as a function of the distance on the ground (distance between the point of reference and the point where a vertical line through the centre of the fireball hits the ground) and the corresponding conditional probabilities of death according to Eqs. (B.22) and (2.56).

Fig. 10.33 Peak side-on overpressure in bar (*right hand side ordinate*) and conditional probability of death as a function of distance for the explosion of a cloud of propane



Example 10.26 Comparison of two production processes (reduction of inventory)

Two types of plants for producing nitroglycol are compared with each other. In the first case a reactor with an inventory of 100 kg is used and in the second an injector nitration process with an inventory of 3 kg. What is the peak side-on overpressure in case of explosions at a distance of 10 m? What are the TNT equivalents and what are the distance-dependent overpressures and the conditional probabilities of death for both cases?

Datum: $\Delta H_c = 6,743 \text{ kJ/kg}$

Solution

In the first place the TNT equivalents and then the scaled distances are calculated. We have for the case

$$W_{\text{TNT}} = 100 \text{ kg} \cdot \frac{6,743 \frac{\text{kJ}}{\text{kg}}}{4,650 \frac{\text{kJ}}{\text{kg}}} = 145.01 \text{ kg}$$

and for the second case

$$W_{\text{TNT}} = 3 \text{ kg} \cdot \frac{6,743 \frac{\text{kJ}}{\text{kg}}}{4,650 \frac{\text{kJ}}{\text{kg}}} = 4.35 \text{ kg}$$

In the first case the scaled distance is

$$r' = \frac{r}{W_{\text{TNT}}^{1/3}} = \frac{10 \text{ m}}{(145.01 \text{ kg})^{1/3}} = 1.9034 \frac{\text{m}}{\text{kg}^{1/3}}$$

and in the second case

$$r' = \frac{r}{W_{\text{TNT}}^{1/3}} = \frac{10 \text{ m}}{(4.35 \text{ kg})^{1/3}} = 6.1259 \frac{\text{m}}{\text{kg}^{1/3}}$$

This gives the following peak side-on overpressures

$$\begin{aligned} p_s &= 159.5077 \cdot \frac{808 \cdot \left[1 + \left(\frac{r'}{4.5}\right)^2\right]}{\sqrt{\left[1 + \left(\frac{r'}{0.048}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{0.32}\right)^2\right] \cdot \left[1 + \left(\frac{r'}{1.35}\right)^2\right]}} \\ &= 159.5077 \cdot \frac{808 \cdot \left[1 + \left(\frac{0.9517}{4.5}\right)^2\right]}{\sqrt{\left[1 + \left(\frac{0.9517}{0.048}\right)^2\right] \cdot \left[1 + \left(\frac{0.9517}{0.32}\right)^2\right] \cdot \left[1 + \left(\frac{0.9517}{1.35}\right)^2\right]}} = 367.4 \text{ kPa} \end{aligned}$$

for the case with an inventory of 100 kg and analogously for an inventory of 3 kg

$$p_s = 32.35 \text{ kPa}$$

These values are inserted into the probit Eq. (B.22)

$$Y = -77.1 + 6.91 \cdot \ln p_s = -77.1 + 6.91 \cdot \ln 367,400 = 11.45$$

This gives according to Eq. (2.56) a conditional probability of death of virtually 1. For the smaller inventory we have

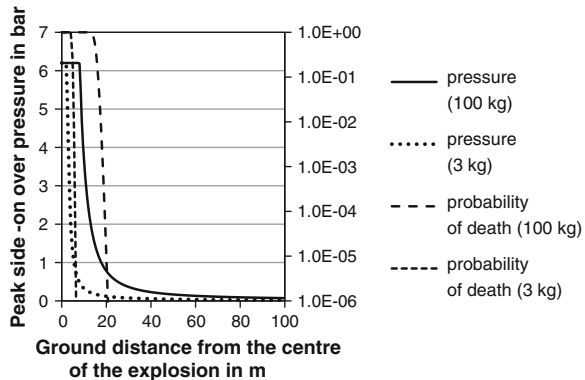
$$Y = -5.344$$

Hence the probability of death is virtually equal to 0.

Figure 10.34 shows pressures and conditional probabilities of death as functions of the distance from the plant.

□

Fig. 10.34 Comparison of the distance-dependent peak side-on overpressures and conditional probabilities of death for two explosions of different quantities of nitroglycol



10.6.3.2 The TNO Multienergy Model

The TNT model postulates a linear relationship between the mass of fuel and that of TNT in order to express the explosion potential of a gas cloud. This implies that the cloud is regarded as a homogeneous unit. This is normally is not true. Rather we have to expect turbulent zones (caused either by the initial momentum or by obstacles such as structural elements of the plant) and quiet zones. Whilst in turbulent zones an explosion may occur, in the quiet zones slow combustion without notable pressure rise is to be expected.

These aspects are accounted for by the TNO multienergy model [15]. The cloud is modelled by several regions. The hazard due to a vapour cloud explosion is determined by the fuel masses in regions with obstacles and partial confinement rather than by the total mass of the fuel/air mixture. In regions of partial confinement the flame is accelerated thus forming a source of explosion. If the distances between these sources are large enough they should be treated individually. If this is not the case they are treated as a single source of explosion.

The calculations are based on a set of ten empirical curves (vid. Fig. 10.35) for the peak side-on overpressure. The strength of the explosion is reflected by a number between 1 (small) and 10 (strong).

The curves can be represented by the following equation [58]

$$p_{s'} = \begin{cases} a \cdot R^b & \text{if } c = d = 0 \\ 10^{-c \cdot \log R - d} & \text{if } a = b = 0 \end{cases} \quad (10.163)$$

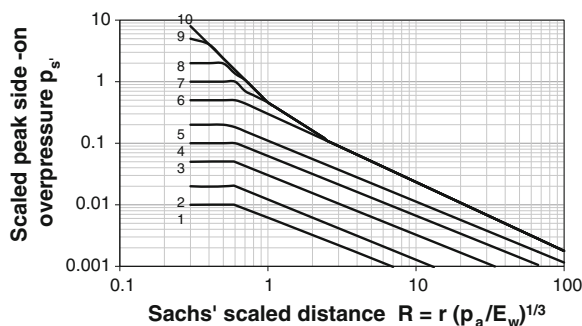
The values of the constants in Eq. (10.163) are listed in Appendix D.

Curve 10 represents a detonation, the others deflagrations, which at larger distances from the source may build up stronger blast waves.

The model enables one to determine further explosion parameters such as the duration of the phase of positive pressure, the dynamic peak pressure and the pressure momentum. With respect to these the reader is referred to [15].

Before applying the multienergy model the volume and the location of the vapour cloud must be determined or assumed. Its determination may be done with a dispersion calculation. Furthermore, details on the building structure in the surroundings of the cloud must be known.

Fig. 10.35 Explosion pressure curves of the multienergy model according to Eq. (10.163)



The volume of the cloud, V_w in m^3 , results from

$$V_w = \frac{W}{\rho \cdot c_{st}} \quad (10.164)$$

In Eq. (10.164) W is the mass of fuel in kg, ρ its density in kg/m^3 and c_{st} the stoichiometric concentration of the fuel in the gas-fuel mixture of the cloud. The radius of the cloud, r_0 in m, is derived from Eq. (10.164) assuming that it is considered to be of hemispherical shape, i.e.

$$r_0 = \sqrt[3]{\frac{3 \cdot V_w}{2 \cdot \pi}} \quad (10.165)$$

The total available energy of the cloud, E_w in J, (with complete combustion) is

$$E_w = W \cdot \Delta H_c \quad (10.166)$$

The following steps are then carried out:

- Determination of the scaled distance (Sachs' dimensionless scaled distance)

$$R = r \cdot \left(\frac{p_a}{E_w} \right)^{1/3} \quad (10.167)$$

where p_a denotes the initial pressure (as a rule atmospheric pressure).

- Calculation of the peak side-on overpressure according to Eq. (10.163)

$$p_s = p_{s'} \cdot p_a \quad (10.168)$$

The initial strength of the blast wave and hence the selection of the curve depends on the following factors:

- dimension of the flame expansion,
- reactivity of the flammable gas,
- obstacle density.

Dimension of the flame expansion, which may be one (1-D), two (2-D) or three (3-D) dimensional

- 3-D expansion implies that the flame expands without hinderance in an unconfined space. It expands from the place of origin spherically or hemispherically, flame speed and overpressure are lower than with the other two expansion modes.

Table 10.10 Reactivity classification of several materials (after [37])

Reactivity	Material
Low	Ammonia, methane, natural gas, carbon monoxide
Medium	Ethane, ethylene, propane, propylene, butane, isobutane
High	Hydrogen, acetylene, ethylene oxide, propylene oxide

- 2-D expansion means that a cylindrical flame expands between two limiting surfaces.
- 1-D expansion means that there is only direction for flame expansion as, for example, in pipes.

The explosions considered mainly belong to the cases 2-D and 3-D.

Reactivity of the flammable gas

Reactivities are classified according to laminar flame speeds. Table 10.10 gives an overview.

Obstacle density

The density of obstacles can only roughly be distinguished. Planes vertical to the direction of the expansion of the blast wave are considered and the degree of confinement is estimated; we use

- low: obstacle area blockage ratio for the plane $<10\%$
- medium: obstacle area blockage ratio for the plane >10 and $<40\%$
- high: obstacle area blockage ratio for the plane $>40\%$

Considering the above aspects Table 10.11 provides guidance on how to select the appropriate curve for the TNO multienergy model.

Table 10.11 Qualitative criteria for selecting the TNO curve of Fig. 10.14 [59]

Dimension	Reactivity	Obstacle density		
		High	Medium	Low
1-D	High	10	10	10
	Medium	9–10	9	7–8
	Low	9–10	7–8	4–5
2-D	High	9	7–8	6
	Medium	7–8	6–7	2–3
	Low	6	5–6	1–2
3-D	High	6	3	1
	Medium	3–4	2	1
	Low	3	2	1

Example 10.27 Effects of a hexogen explosion using the multienergy model

Example 10.24 is to be treated using the multienergy model.

Solution

Since we are dealing with the explosion of an explosive, curve no. 10 of Fig. 10.14 is used.

In the first place the Sachs' scaled distance is calculated according to Eq. (10.167) to give

$$R = r \cdot \left(\frac{p_a}{E_w} \right)^{1/3} = 20 \text{ m} \cdot \left(\frac{100,000 \text{ Pa}}{101.5 \text{ kg} \cdot 5,647,000 \frac{\text{J}}{\text{kg}}} \right)^{1/3} = 1.1176$$

According to Eq. (10.163) we have the scaled peak side-on overpressure

$$p_{s'} = 10^{-c \cdot \log R - d} = 10^{-1.5236 \cdot \log 1.1176 - 0.3372} = 0.3884$$

and thus according to Eq. (10.168)

$$p_s = p_{s'} \cdot p_a = 0.3884 \cdot 100,000 \text{ Pa} = 38,840 \text{ Pa}$$

This value is inserted into the probit equation (B.22) giving

$$Y = -77.1 + 6.91 \cdot \ln p_s = -77.1 + 6.91 \cdot \ln 38,840 = -4.0806$$

and the conditional probability for death

$$\phi(Y - 5) \approx 0$$

However, the possibility of being hit by a flying fragment is not included.

Ruptures of the eardrum are calculated according to Eq. (B.23a), which gives a probit value of

$$Y = -15.6 + 1.93 \cdot \ln p_s = -15.6 + 1.93 \cdot \ln 38,840 = 4.7947$$

and according to Eq. (2.56) a conditional probability of

$$\phi(Y - 5) = 0.42$$

Structural damage is assessed according to Eq. (B.27) and gives

$$Y = -23.8 + 2.92 \cdot \ln p_s = -23.8 + 2.92 \cdot \ln 38,840 = 7.0562$$

$$\phi(Y - 5) = 0.98$$

It is obvious that smaller pressure values are obtained than with the TNT equivalent model, if a yield factor of 0.2 is used there.

□

Example 10.28 Effects of the explosion of a propane cloud according to the multienergy model

Example 10.25 is to be treated with the TNO multienergy model. The following cases are to be addressed:

- 2-D and 3-D flame expansion,
- low and high obstacle density.

Solution

According to Table 10.10 propane is a material with low reactivity. Based on Table 10.11 the following selections are made:

- 2-D flame expansion: curve no. 3 for low obstacle density and curve no. 8 for high obstacle density
- 3-D flame expansion: curve no. 1 for low obstacle density and curve no. 4 for high obstacle density

In the first place Sachs' scaled distance is calculated according to Eq. (10.167)

$$R = r \cdot \left(\frac{P_a}{E_w} \right)^{1/3} = 100 \text{ m} \cdot \left(\frac{100,000 \text{ Pa}}{1,000 \text{ kg} \cdot 46,085,770 \frac{\text{J}}{\text{kg}}} \right)^{1/3} = 1.2946$$

2-D (low)

According to Eq. (10.163) we obtain the scaled peak side-on overpressure (curve no. 3)

$$p_{s'} = a \cdot R^b = 0.0305 \cdot 1.2946^{-0.97} = 0.0237$$

and hence according to Eq. (10.168)

$$p_s = p_{s'} \cdot p_a = 0.0237 \cdot 100,000 \text{ Pa} = 2,374.0 \text{ Pa}$$

2-D (high)

According to Eq. (10.163) we obtain the scaled peak side-on overpressure (curve no. 8)

$$p_{s'} = 10^{-c \cdot \log R - d} = 10^{-1.5236 \cdot \log 1.2946 - 0.3372} = 0.3104$$

and hence according to Eq. (10.168)

$$p_s = p_{s'} \cdot p_a = 0.3104 \cdot 100,000 \text{ Pa} = 31,040.0 \text{ Pa}$$

3-D (low)

According to Eq. (10.163) we obtain the scaled peak side-on overpressure (curve no. 1)

$$p_{s'} = a \cdot R^b = 0.00623 \cdot 1.2946^{-0.95} = 0.0049$$

and hence according to Eq. (10.168)

$$p_s = p_{s'} \cdot p_a = 0.0049 \cdot 100,000 \text{ Pa} = 490.0 \text{ Pa}$$

3-D (high)

According to Eq. (10.163) we obtain the scaled peak side-on overpressure (curve no. 4)

$$p_{s'} = a \cdot R^b = 0.062 \cdot 1.2946^{-0.97} = 0.0483$$

and hence according to Eq. (10.168)

$$p_s = p_{s'} \cdot p_a = 0.0483 \cdot 100,000 \text{ Pa} = 4,830.0 \text{ Pa}$$

□

10.6.3.3 The Baker-Strehlow-Tang Model

The Baker-Strehlow model was developed for assessing pressures from vapour cloud explosions [50]. It was extended on various occasions [60, 61] and is now known as the Baker-Strehlow-Tang (BST) model. The procedure comprises several steps where amongst others the flame speed, the reactivity of the fuel and the degree of confinement are determined [49]:

- plant walk-around for identifying areas potentially objects of explosion hazards,
- decision on the dimension of confined areas in order to determine the flame speed,
- calculation of the flame speed for the fuel/air mixture.

The disadvantages of the TNT equivalent model are reflected amongst others by the wide range for the yield factor. This can be explained only in part by uncertainties as to the exploding mass of fuel. An important contributor to uncertainty are the different combustion regimes within the cloud. Large differences of flame speeds may result from different degrees of confinement and obstacles in the industrial surroundings. These are represented by a set of curves which account for the different combustion regimes instead of only one as with the TNT equivalent model. The set of curves comprises the phases over and underpressure as well as

the momentum as a function of Sachs' scaled distance [62]. The corresponding values are read from them in dependence on the scaled radius and Mach's number. Below only the peak side-on pressure is addressed, which can be represented by the following approximate equations [58]

$$p_{s'} = \begin{cases} a & \text{if } a \neq 0 \\ 10^{b \cdot (\log R)^6 + c \cdot (\log R)^5 + d \cdot (\log R)^4 + e \cdot (\log R)^3 + f \cdot (\log R)^2 + g \cdot \log R + h} & \text{otherwise} \\ 10^{p \cdot \log R + q} & \text{if } p \neq 0 \text{ and } q \neq 0 \end{cases} \quad (10.169)$$

The values for the constants in Eq. (10.169) are listed in Appendix D (Table D.2). Figure 10.36 shows the curves which were calculated using Eq. (10.169).

The energy E_w , also required for this model, is calculated according to Eq. (10.166) and the peak side-on overpressure according to Eq. (10.168). Concerning the remaining parameters the reader is referred to the cited literature.

An important criterion for selecting the appropriate curve from Fig. 10.36 is Mach's number. It represents flame speed, which is all the higher the larger Mach's number. That is why for explosions of explosives the curve with $M_f = 5.2$ is selected, the highest of the BST curves.

Whilst in the original work the curves were given for Mach's numbers in the Lagrange system of coordinates (moving system) more recently they refer to Euler's coordinate system (relative to an observer at a fixed point).

Mach's number in Euler's system coordinates, M_f , can be calculated iteratively from the following equation [63]

Fig. 10.36 Scaled peak side-on overpressure for several values of Mach's number M_f for the BST model, calculated according to Eq. (10.169)

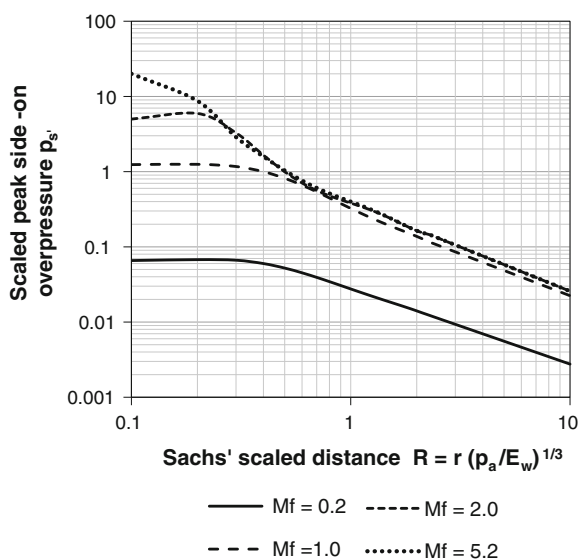


Table 10.12 Constants for applying Eq. (10.170) (after [64])

	a	b	c	d
3-D: no hinderance, unconfined space	0.84	2.75	2.7	0.7
2-D: expansion between two limiting surfaces	3.38	2.25	2.7	0.7

$$\frac{M_f^2}{1 + M_f} = \frac{a}{2.4 \cdot p_a} \cdot \left(\frac{B_r \cdot L_p}{D} \right)^b \cdot v_{\text{flam}}^c \cdot D^d \quad (10.170)$$

In Eq. (10.170) B_r denotes the fraction of blocked volume in the expansion region of the flame, D in m a typical diameter for the surrounding obstacles, v_{flam} the laminar flame speed in m/s and L_p in m the maximum path until the flame hits an obstacle; p_a is the initial pressure in bar.

The constants for Eq. (10.170) are listed in Table 10.12 (1-D is no longer used in connection with the BST model, since the expansion in a structure such as a pipe is a special case).

If there is no curve for a resulting Mach number, the one with the next larger Mach number is selected. This leads to higher peak side-on overpressures than are to be expected according to the model and is therefore conservative.

Example 10.29 Effects of an explosion of hexogen according to the BST model

Example 10.24 is to be calculated using the BST model.

Since we are dealing with an explosive the curve for $M_f = 5.2$ in Fig. 10.15 is used.

Because the curves depend on Sachs' scaled distance, this can be taken over from Example 10.27.

$$R = r \cdot \left(\frac{p_a}{E_w} \right)^{1/3} = 20 \text{ m} \cdot \left(\frac{100,000 \text{ Pa}}{101.5 \text{ kg} \cdot 5,647,000 \frac{\text{J}}{\text{kg}}} \right)^{1/3} = 1.1176$$

The scaled peak side-on overpressure is calculated from Eq. (10.169) to give

$$\begin{aligned} p_{s'} &= 10^{a \cdot (\log R)^6 + b \cdot (\log R)^5 + c \cdot (\log R)^4 + d \cdot (\log R)^3 + e \cdot (\log R)^2 + f \cdot \log R + g} \\ &= 10^{18.600175 - 0.048286^6 + 19.416571 - 0.048286^5 + 0.730754 - 0.048286^4 - 4.407614 - 0.048286^3 - 0.063184 - 0.048286^2 - 1.089879 - 0.048286 - 0.399327} \\ &= 0.3527 \end{aligned}$$

$$p_s = p_{s'} \cdot p_a = 0.3527 \cdot 100,000 \text{ Pa} = 35,270 \text{ Pa}$$

This value is inserted into the probit Eq. (B.22), which gives

$$Y = -77.1 + 6.91 \cdot \ln p_s = -77.1 + 6.91 \cdot \ln 35,720 = -4.7469$$

Therefrom we obtain a probability of death of

$$\phi(Y - 5) \approx 0$$

However, injuries possibly caused by flying fragments are not included.

Ruptures of the eardrum are calculated according to Eq. (B.23a), which gives a probit value of

$$Y = -15.6 + 1.93 \cdot \ln p_s = -15.6 + 1.93 \cdot \ln 35,720 = 4.6331$$

The corresponding conditional probability of occurrence is

$$\phi(Y - 5) = 0.36$$

For structural damage we have according to Eq. (B.27)

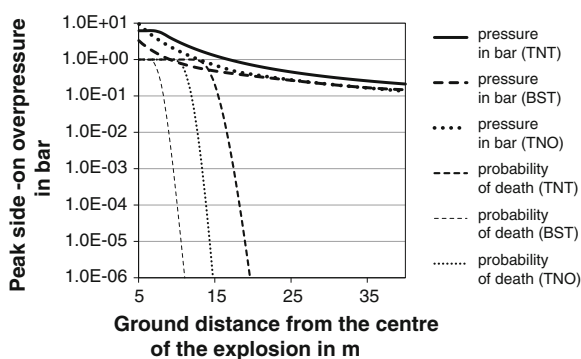
$$Y = -23.8 + 2.92 \cdot \ln p_s = -23.8 + 2.92 \cdot \ln 35,720 = 6.8117$$

This leads to a conditional probability according to Eq. (2.56) of

$$\phi(Y - 5) = 0.96$$

Figure 10.37 shows the results from all three models as functions of the distance from the centre of the explosion to the target point.

Fig. 10.37 Comparison of the distance-dependent pressures and conditional probabilities for death after an explosion of hexogen calculated according to the TNT, TNO and BST models



□

Example 10.30 Effects of an explosion of a propane cloud according to the BST model

Example 10.25 is to be treated using the BST model. The following cases are to be addressed:

- 2-D and 3-D flame expansion,
- low and high obstacle density.

Data: $v_{\text{flam}} = 0.45$ m/s, $B_f = 0.05$ (0.5); $L_p = 10$ m (5 m); $D = 2$ m (values in parentheses for high obstacle density)

Solution

Equation (10.170), whose solution depends on the situation to be considered, is fundamental for the selection of the curve from Fig. 10.15.

Sachs' scaled radius is taken over from Example 10.28. It amounts to $R = 1.2946$.

2-D (low obstacle density)

$$\begin{aligned} \frac{M_f^2}{1 + M_f} &= \frac{a}{2.4 \cdot p_a} \cdot \left(\frac{B_r \cdot L_p}{D} \right)^b \cdot v_{\text{flam}}^c \cdot D^d \\ &= \frac{3.38}{2.4 \cdot 1 \text{ bar}} \cdot \left(\frac{0.05 \cdot 10 \text{ m}}{2 \text{ m}} \right)^{2.25} \cdot \left(0.45 \frac{\text{m}}{\text{s}} \right)^{2.7} \cdot (2 \text{ m})^{0.7} \end{aligned}$$

The above equation is solved iteratively giving $M_f = 0.1142$.

Therefore the values for $M_f = 0.12$ from Table D.2 in Appendix D are used in Eq. (10.169). The scaled peak side-on overpressure then is

$$\begin{aligned} p_{s'} &= 10^{a \cdot (\log R)^6 + b \cdot (\log R)^5 + c \cdot (\log R)^4 + d \cdot (\log R)^3 + e \cdot (\log R)^2 + f \cdot \log R + g} \\ &= 10^{-0.933128 \cdot 0.1121^6 - 2.888832 \cdot 0.1121^5 - 1.737895 \cdot 0.1121^4 + 0.920042 \cdot 0.1121^3 + 0.087748 \cdot 0.1121^2 - 1.005685 \cdot 0.1121 - 1.930488} \\ &= 9.0959 \times 10^{-3} \end{aligned}$$

According to Eq. (10.168) this gives a peak side-on overpressure of

$$p_s = p_{s'} \cdot p_a = 9.0959 \times 10^{-3} \cdot 100,000 \text{ Pa} = 909.59 \text{ Pa}$$

2-D (high obstacle density)

$$\begin{aligned} \frac{M_f^2}{1 + M_f} &= \frac{a}{2.4 \cdot p_a} \cdot \left(\frac{B_r \cdot L_p}{D} \right)^b \cdot v_{\text{flam}}^c \cdot D^d \\ &= \frac{3.38}{2.4 \cdot 1 \text{ bar}} \cdot \left(\frac{0.5 \cdot 5 \text{ m}}{2 \text{ m}} \right)^{2.25} \cdot \left(0.45 \frac{\text{m}}{\text{s}} \right)^{2.7} \cdot (2 \text{ m})^{0.7} \end{aligned}$$

The above equation is solved iteratively giving $M_f = 0.9157$.

Therefore the values for $M_f = 1$ from Table D.2 in Appendix D are used in Eq. (10.169). The scaled peak side-on overpressure then is

$$\begin{aligned}
 p_{s'} &= 10^{a \cdot (\log R)^6 + b \cdot (\log R)^5 + c \cdot (\log R)^4 + d \cdot (\log R)^3 + e \cdot (\log R)^2 + f \cdot \log R + g} \\
 &= 10^{-2.650731 \cdot 0.1121^6 - 5.975678 \cdot 0.1121^5 - 2.655464 \cdot 0.1121^4 + 1.920581 \cdot 0.1121^3 + 0.417161 \cdot 0.1121^2 - 1.408333 \cdot 0.1121 - 0.488746} \\
 &= 0.2295
 \end{aligned}$$

According to Eq. (10.168) this gives a peak side-on overpressure of

$$p_s = p_{s'} \cdot p_a = 0.2295 \cdot 100,000 \text{ Pa} = 22,950.0 \text{ Pa}$$

3-D (low obstacle density)

$$\begin{aligned}
 \frac{M_f^2}{1 + M_f} &= \frac{a}{2.4 \cdot p_a} \cdot \left(\frac{B_r \cdot L_p}{D} \right)^b \cdot v_{\text{flam}}^c \cdot D^d \\
 &= \frac{0.84}{2.4 \cdot 1 \text{ bar}} \cdot \left(\frac{0.05 \cdot 10 \text{ m}}{2 \text{ m}} \right)^{2.75} \cdot \left(0.45 \frac{\text{m}}{\text{s}} \right)^{2.7} \cdot (2 \text{ m})^{0.7}
 \end{aligned}$$

The above equation is solved iteratively giving $M_f = 0.03888$.

Therefore the values for $M_f = 0.07$ from Table D.2 in Appendix D are used in Eq. (10.169). The scaled on-side peak overpressure then is

$$\begin{aligned}
 p_{s'} &= 10^{a \cdot (\log R)^6 + b \cdot (\log R)^5 + c \cdot (\log R)^4 + d \cdot (\log R)^3 + e \cdot (\log R)^2 + f \cdot \log R + g} \\
 &= 10^{-0.933128 \cdot 0.1121^6 - 2.888832 \cdot 0.1121^5 - 1.737895 \cdot 0.1121^4 + 0.920042 \cdot 0.1121^3 + 0.087748 \cdot 0.1121^2 - 1.005685 \cdot 0.1121 - 2.377646} \\
 &= 3.2439 \times 10^{-3}
 \end{aligned}$$

According to Eq. (10.168) this gives a peak side-on overpressure of

$$p_s = p_{s'} \cdot p_a = 3.2439 \times 10^{-3} \cdot 100,000 \text{ Pa} = 324.39 \text{ Pa}$$

3-D (high obstacle density)

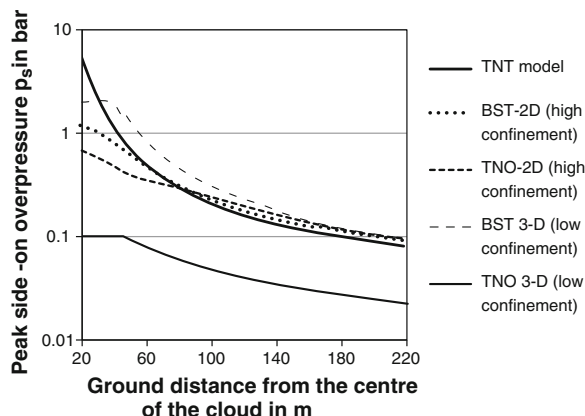
$$\begin{aligned}
 \frac{M_f^2}{1 + M_f} &= \frac{a}{2.4 \cdot p_a} \cdot \left(\frac{B_r \cdot L_p}{D} \right)^b \cdot v_{\text{flam}}^c \cdot D^d \\
 &= \frac{0.84}{2.4 \cdot 1 \text{ bar}} \cdot \left(\frac{0.5 \cdot 5 \text{ m}}{2 \text{ m}} \right)^{2.75} \cdot \left(0.45 \frac{\text{m}}{\text{s}} \right)^{2.7} \cdot (2 \text{ m})^{0.7}
 \end{aligned}$$

The above equation is solved iteratively giving $M_f = 0.4148$.

Therefore the values for $M_f = 0.7$ from Table D.2 in Appendix D are used in Eq. (10.169). The scaled peak side-on overpressure then is

$$\begin{aligned}
 p_{s'} &= 10^{a \cdot (\log R)^6 + b \cdot (\log R)^5 + c \cdot (\log R)^4 + d \cdot (\log R)^3 + e \cdot (\log R)^2 + f \cdot \log R + g} \\
 &= 10^{3.14094 \cdot 0.1121^6 + 4.025197 \cdot 0.1121^5 - 0.520525 \cdot 0.1121^4 - 1.615733 \cdot 0.1121^3 - 0.553277 \cdot 0.1121^2 - 0.724239 \cdot 0.1121 - 0.523105} \\
 &= 0.2435
 \end{aligned}$$

Fig. 10.38 Comparison of the distance-dependent pressures for the explosion of a cloud of propane according to the TNT, TNO and BST models



According to Eq. (10.168) this gives a peak side-on overpressure of

$$p_s = p_{s'} \cdot p_a = 0.2435 \cdot 100,000 \text{ Pa} = 24,350.0 \text{ Pa}$$

Figure 10.38 shows several of the preceding calculations comparing models and different situations of confinement. Whilst the latter cannot be accounted for by the TNT equivalent model, judging the degree of confinement introduces a subjective element into the treatment with the TNO and BST models. The curves show that this judgment can considerably influence the results, particularly in the near field.

10.7 BLEVE

An important hazard in the process industry is the boiling liquid expanding vapour explosion (BLEVE). This is understood to be “the explosively rapid vaporization and corresponding release of energy of a liquid, flammable or otherwise, upon its sudden release from containment under greater-than-atmospheric pressure at a temperature above its atmospheric boiling point” [37]. It is a physical explosion which is a consequence of sudden pressure relief. If a flammable material is involved a chemical explosion or a fireball can follow.

Most BLEVEs occur with storage vessels, rail or road tankers containing a pressure liquefied gas if they are exposed to a fire or mechanical load, for example following crash or derailment. Furthermore a BLEVE may result from a spontaneous vessel failure.

The physical explosion is treated here. If it is followed by a fireball (vid. Sect. 10.6.2.1) the following may be assumed: if 36 % or more of the liquid is vaporized on pressure relief, the total released mass of fuel contributes to the fireball. For hazard assessments it is reasonable to suppose that three times the mass vaporized by depressurization (upper limit 100 %) partakes in the fireball [37].

Since a sudden depressurization is at the start of a BLEVE one may assume that the accompanying turbulences cause an intense mixing of the released material with air. That is why often conservatively and simplifying one assumes that the entire liquid fraction released is vaporized by intake of heat from the air and the condensation of moisture from the air.

Not in every case a BLEVE will follow depressurization. We may rather encounter a strong vaporization. According to [65] the outcome depends on the initial pressure and the degree of superheat.

If a liquid is sufficiently superheated and the pressure to which it is exposed is suddenly relieved microscopic vapour bubbles are formed and a large fraction of the liquid vaporizes within milliseconds.

With a BLEVE a flash vaporization occurs in the first place. It is treated below. After release a cloud is formed, which—depending on material properties—is flammable, toxic or both. In case of a flammable material explosion effects as well as the consequences of heat radiation must be envisaged.

In particular, the following consequences can be expected from a BLEVE:

- pressure wave,
- missile flight (Sect. 10.9)
- fireball (in case of flammable materials, Sect. 10.6.2.1),
- pool fire, if not all the liquid vaporizes (in case of flammable materials, Sect. 10.6.1),
- vapour cloud explosion, if there is no immediate ignition (in case of flammable materials, Sect. 10.6.3),
- flash fire, if there is no immediate ignition (in case of flammable materials, Sect. 10.6.2.1),
- formation and spread of a toxic cloud (Sect. 10.5).

The energy released in a BLEVE depends on the initial pressure p_A . According to [37] this can be determined as follows:

- in case of mechanical failure: storage pressure,
- if the failure is the consequence of a fire: $1.21 \times$ set opening pressure of the safety valve,
- in some cases of fire the failure pressure of the vessel material can be reached, for example $2.5 \times$ the set opening pressure of the safety valve.

The modelling of the expansion is based on calculating the difference of the internal energies of the fluid between the initial stage (under initial pressure) and the final stage (under atmospheric pressure). Furthermore it is considered whether the energy of the flash vaporization makes a contribution to the explosion energy, given the initial temperature and pressure of the fluid. An analogous procedure is proposed if the gas involved does not behave as ideal, for example because of very high pressures [2, 15].

The energy contents of an enclosed pressure liquefied gas is determined by its internal energy, $u(T,v)$. The corresponding values can be read from tables. These mostly only list enthalpies, $h(T,v)$, so that the following relationship has to be used

$$u(T, v) = h(T, v) - p \cdot v \quad (10.171)$$

In Eq. (10.171) T is the absolute temperature in K, v the specific volume in m^3/kg and p the pressure in Pa. If we are dealing with mixtures of substances their thermodynamic properties are not generally known. The sum of the internal energies may then serve as a coarse approximation [15].

In case of a pressure liquefied gas a liquid and a gas phase are always present inside the containment. The energy released by expansion is normally calculated assuming an isentropic (adiabatically reversible) process. In reality we are dealing with an irreversible process. However, the assumption of being adiabatic mostly applies, since often extremely fast processes have to treated, which leave no time for a tangible exchange of energy with the surroundings. For example, the catastrophic failure of a pressure vessel takes only a few hundred milliseconds.

The assumption of isentropy connects the gas fraction of the gas phase (subscript g) before depressurization (1) with that after depressurization (2) as follows:

$$s_{1,g} = x_g \cdot s_{2,g} + (1 - x_g) \cdot s_{2,f}, \quad \text{so that } x_g = \frac{s_{1,g} - s_{2,f}}{s_{2,g} - s_{2,f}} \quad (10.172)$$

Analogously we have for the liquid phase (subscript f), which is vaporized in part after depressurization:

$$s_{1,f} = x_f \cdot s_{2,g} + (1 - x_f) \cdot s_{2,f}, \quad \text{so that } x_f = \frac{s_{1,f} - s_{2,f}}{s_{2,g} - s_{2,f}} \quad (10.173)$$

The energy released in the depressurization process is then obtained as follows:

$$E = u_{1,g} \cdot \phi + u_{1,f} \cdot \varphi - (u_{2,g} \cdot x_g + (1 - x_g) \cdot u_{2,f}) \cdot \phi - (u_{2,g} \cdot x_f + (1 - x_f) \cdot u_{2,f}) \cdot \varphi \quad (10.174)$$

In Eq. (10.174) ϕ is the mass of gas in the containment and φ the mass of liquid before depressurization, i.e.

$$\phi = \frac{V}{v_{1,g}} \cdot \theta \quad \text{and} \quad \varphi = \frac{V}{v_{1,f}} \cdot (1 - \theta) \quad (10.175)$$

In the above equations u denotes the internal energy, s the entropy and x the mass fraction of vapour.

The maximum volume fraction of vapour, θ , in filled vessels does normally not lie below 0.1 in order to compensate variations of the storage temperature. Table 10.13 lists thermodynamic properties of several materials.

Table 10.13 Thermodynamic properties of selected materials (from [13])

Material	Temperature in K	Pressure in bar	h_f in kJ/kg	h_g in kJ/kg	v_f in m^3/kg	v_g in m^3/kg	s_f in kJ/kg	s_g in kJ/kg
Propane	290	7.7063	566.06	916.54	1.982×10^{-3}	0.0600	4.4257	5.6343
	230.08	1	419.34	848.18	1.719×10^{-3}	0.4309	3.8639	5.7278
Propylene	290	9.3954	135.3	485.3	1.929×10^{-3}	0.0507	0.512	1.719
	225.18	1	-17.59	421.86	1.641×10^{-3}	0.4307	-0.076	1.8753
Ammonia	290	7.741	-638.8	514.7	1.626×10^{-3}	0.165	5.975	10.108
	239.46	1	-915.3	455.4	1.467×10^{-3}	1.153	5.103	10.827
Butane	290.0	1.8765	328.62	697.99	1.781×10^{-3}	0.207	3.9046	5.1783
	272.0	1	287.48	672.17	1.662×10^{-3}	0.382	3.7551	5.1734
Chlorine	293.16	6.702	289.2	543.3	7.1×10^{-4}	0.0471	2.0291	2.8924
	237.88	1	236.07	524.26	6.398×10^{-4}	0.287	1.8288	3.0383
Ethane	290	35.14	709.8	934.7	2.847×10^{-3}	0.0129	5.502	6.278
	183.80	1	394.17	883.73	1.835×10^{-3}	0.5244	4.204	6.870

Note the factor 10^{-3} is missing with indication of the specific volume of the liquid phase of ethane in [13]

Experimental and theoretical work described in [66] suggests that the blast wave caused by a BLEVE is due to the vapour energy whilst the process of flash depressurization after containment failure is too slow for causing a blast wave.

According to [66] the distance-dependent side-on peak overpressure in the far field (Sachs' scaled distance according to Eq. (10.167) $R > 2$) can be calculated using the TNT equivalent model (vid. Sect. 10.6.3.1). For the near field the following relationship should be used (vid. [2])

$$\frac{p_1}{p_2} = \frac{p_{so}}{p_2} \cdot \left[1 - \frac{(\kappa_1 - 1) \cdot \frac{a_0}{a_1} \cdot \left(\frac{p_{so}}{p_2} - 1 \right)}{\sqrt{2 \cdot \kappa_0 \cdot \left[2 \cdot \kappa_0 + (\kappa_0 + 1) \cdot \left(\frac{p_{so}}{p_2} - 1 \right) \right]}} \right]^{\frac{2\kappa_1}{\kappa_1 - 1}} \quad (10.176)$$

In Eq. (10.176) p_1 is the initial pressure (e.g. inside the pressure vessel) in kPa, p_a the ambient pressure (about 100 kPa); p_{so} is the absolute peak side-on overpressure, a_1 the speed of sound in the vapour inside the containment in m/s, a_0 the speed of sound in ambient air (340 m/s), κ_1 is the heat capacity ratio of the vapour (cf. Table 10.14), and κ_0 that of the ambient air ($\kappa_0 = 1.4$). Equation (10.176) is implicit and has to be solved iteratively for p_{so} .

In [66] it is proposed to calculate the blast waves from the depressurizations of vapour and liquid separately in the first place and to add them together thereafter. The latter approach is considered to be conservative. Even if the experiments suggest that the vapour energy alone is responsible for the blast wave it cannot be discarded that the flash vaporization contributes to the blast wave in the far field. Resulting differences are illustrated by Example 10.31.

Example 10.31 BLEVE from the release of pressure liquefied propane

In a pressure vessel $m = 1,500$ kg of propane are stored under pressure at a temperature of $T = 290$ K. The volume fraction of the vapour space (freeboard) is $\theta = 0.1$. Another vessel contains the same mass of propane but it is only filled to 50 % ($\theta = 0.5$). Both suffer a BLEVE. The storage pressure amounts to $p_1 = 7.7063$ bar according to Table 10.13, the atmospheric pressure is $p_2 = p_a = 100,000$ Pa.

What are:

- the released energies,
- the pressure in the near field,
- the heat flux of an ensuing fireball at a distance of $r = 150$ m and the corresponding conditional probability of death?

What is the distance-dependent pressure if a vapour cloud explosion occurs?

Boundary conditions: the energy required for vessel fragmentation and the flight of the fragments is not subtracted, the humidity of air is $\varphi = 20$ %.

Data: speed of sound $a_1 = 270$ m/s, $\kappa = 1.1$

Table 10.14 Heat capacity ratios for selected materials (from [13])

Material	Acrolein	Acrylonitrile	Ammonia	n-Butane	CO
$\kappa = c_p/c_v$	1.151	1.152	1.301	1.095	1.4

Chlorine	Ethene	Benzene	Hydrogen	Dry air	
1.331	1.238	1.075	1.405	1.4	

Solution

Determination of the volume of the vessel

$$V = \frac{m}{\frac{1-\theta}{v_{1,f}} + \frac{\theta}{v_{1,g}}} = \frac{1,500 \text{ kg}}{\frac{0.9}{1.982 \times 10^{-3} \frac{\text{m}^3}{\text{kg}}} + \frac{0.1}{0.06 \frac{\text{m}^3}{\text{kg}}}} = 3.2913 \text{ m}^3$$

Determination of the internal energies according to Eq. (10.171) using the values from Table 10.13.

Initial state (1)

Liquid

$$\begin{aligned} u_{1,f} &= h_{1,f} - p_1 \cdot v_{1,f} = 566,060 \frac{\text{J}}{\text{kg}} - 770,630 \text{ Pa} \cdot 1.982 \times 10^{-3} \frac{\text{m}^3}{\text{kg}} \\ &= 564,532.61 \frac{\text{J}}{\text{kg}} \end{aligned}$$

Gas

$$u_{1,g} = h_{1,g} - p_1 \cdot v_{1,g} = 916,540 \frac{\text{J}}{\text{kg}} - 770,630 \text{ Pa} \cdot 0.06 \frac{\text{m}^3}{\text{kg}} = 870,302.2 \frac{\text{J}}{\text{kg}}$$

Final state (2)

Liquid

$$\begin{aligned} u_{2,f} &= h_{2,f} - p_2 \cdot v_{2,f} = 419,340 \frac{\text{J}}{\text{kg}} - 100,000 \text{ Pa} \cdot 1.719 \times 10^{-3} \frac{\text{m}^3}{\text{kg}} \\ &= 419,168.1 \frac{\text{J}}{\text{kg}} \end{aligned}$$

Gas

$$u_{2,g} = h_{2,g} - p_2 \cdot v_{2,g} = 848,180 \frac{\text{J}}{\text{kg}} - 100,000 \text{ Pa} \cdot 0.4309 \frac{\text{m}^3}{\text{kg}} = 805,090.0 \frac{\text{J}}{\text{kg}}$$

The vapour fraction after depressurization is calculated according to Eq. (10.172) using the data of Table 10.13. This gives

$$x_g = \frac{s_{1,g} - s_{2,f}}{s_{2,g} - s_{2,f}} = \frac{5.6343 \frac{\text{kJ}}{\text{kg}} - 3.8639 \frac{\text{kJ}}{\text{kg}}}{5.7278 \frac{\text{kJ}}{\text{kg}} - 3.8639 \frac{\text{kJ}}{\text{kg}}} = 0.9498$$

The liquid fraction after depressurization is calculated according to Eq. (10.173) using the data of Table 10.13 resulting in

$$x_f = \frac{s_{1,f} - s_{2,f}}{s_{2,g} - s_{2,f}} = \frac{4.4257 \frac{\text{kJ}}{\text{kg}} - 3.8639 \frac{\text{kJ}}{\text{kg}}}{5.7278 \frac{\text{kJ}}{\text{kg}} - 3.8639 \frac{\text{kJ}}{\text{kg}}} = 0.3014$$

Finally the energy is determined according to Eq. (10.174). However, this requires the masses of gas and liquid to be calculated according to Eq. (10.175) first

$$\begin{aligned} \phi &= \frac{V}{v_{1,g}} \cdot \theta = \frac{3.2913 \text{ m}^3}{0.06 \frac{\text{m}^3}{\text{kg}}} \cdot 0.1 = 5.486 \text{ kg} \quad \text{and} \\ \varphi &= \frac{3.2913 \text{ m}^3}{1.982 \times 10^{-3} \frac{\text{m}^3}{\text{kg}}} \cdot 0.9 = 1,494.54 \text{ kg} \end{aligned}$$

$$\begin{aligned} E &= u_{1,g} \cdot \phi + u_{1,f} \cdot \varphi - (u_{2,g} \cdot x_g + (1 - x_g) \cdot u_{2,f}) \cdot \phi - (u_{2,g} \cdot x_f + (1 - x_f) \cdot u_{2,f}) \cdot \varphi \\ &= 870,302.2 \frac{\text{J}}{\text{kg}} \cdot 5.486 \text{ kg} + 564,532.61 \frac{\text{J}}{\text{kg}} \cdot 1,494.54 \text{ kg} \\ &\quad - \left(805,090.0 \frac{\text{J}}{\text{kg}} \cdot 0.9498 + 0.0502 \cdot 419,168.1 \frac{\text{J}}{\text{kg}} \right) \cdot 5.486 \text{ kg} \\ &\quad - \left(805,090.0 \frac{\text{J}}{\text{kg}} \cdot 0.3014 + 0.6986 \cdot 419,168.1 \frac{\text{J}}{\text{kg}} \right) \cdot 1,494.54 \text{ kg} = 43,876,909.8 \text{ J} \end{aligned}$$

The depressurization of the vapour phase contributes the following amount to the above value

$$\begin{aligned} E_D &= u_{1,g} \cdot \phi - u_{2,g} \cdot x_g \cdot \phi \\ &= 870,302.2 \frac{\text{J}}{\text{kg}} \cdot 5.486 \text{ kg} - 805,090.0 \frac{\text{J}}{\text{kg}} \cdot 0.9498 \cdot 5.486 = 579,473.7 \text{ J} \end{aligned}$$

The pressure in the near field is obtained from Eq. (10.176)

$$\frac{p_1}{p_2} = \frac{p_{so}}{p_2} \cdot \left[1 - \frac{(\kappa_1 - 1) \cdot \frac{a_0}{a_1} \cdot \left(\frac{p_{so}}{p_2} - 1 \right)}{\sqrt{2 \cdot \kappa_0 \cdot \left[2 \cdot \kappa_0 + (\kappa_0 + 1) \cdot \left(\frac{p_{so}}{p_2} - 1 \right) \right]}} \right]^{-\frac{2\kappa_1}{\kappa_1 - 1}}$$

whence we have

$$\frac{770,630 \text{ Pa}}{100,000 \text{ Pa}} = \frac{p_{so}}{100,000 \text{ Pa}} \cdot \left[1 - \frac{0.1 \cdot \frac{340 \frac{\text{m}}{\text{s}}}{270 \frac{\text{m}}{\text{s}}} \cdot \left(\frac{p_{so}}{p_2} - 1 \right)}{\sqrt{2 \cdot 1.4 \cdot \left[2 \cdot 1.4 + 2.4 \cdot \left(\frac{p_{so}}{100,000 \text{ Pa}} - 1 \right) \right]}} \right]^{-22}$$

$$\frac{770,630 \text{ Pa}}{100,000 \text{ Pa}} = \frac{p_{so}}{100,000 \text{ Pa}} \cdot [1 - 0.047538]^{-22}$$

The iterative solution of the above equation gives $p_{so} = 263,928.5 \text{ Pa}$. Therefore the peak side-on overpressure in the near field is

$$p_s = p_{so} - 100,000 \text{ Pa} = 263,928.5 \text{ Pa} - 100,000 \text{ Pa} = 163,928.5 \text{ Pa}$$

The separation point between the near field and the far field is derived from the condition that $R > 2$. According to Eq. (10.167) we obtain

$$r > \frac{R}{\left(\frac{p_s}{E_w} \right)^{1/3}} = \frac{2 \text{ m}}{\left(\frac{100,000 \text{ Pa}}{43,876,909.8 \text{ J}} \right)^{1/3}} = 15.2 \text{ m}$$

Based on the vapour phase only the far field condition gives

$$r > \frac{R}{\left(\frac{p_a}{E_w} \right)^{1/3}} = \frac{2 \text{ m}}{\left(\frac{100,000 \text{ Pa}}{579,473.7 \text{ J}} \right)^{1/3}} = 3.59 \text{ m}$$

Since the physical explosion only corresponds to $E/4,650 \text{ kJ/kg} = 9.4 \text{ kg}$ respectively $E_D/4,650 \text{ kJ/kg} = 0.12 \text{ kg}$ of TNT, the explosion effect beyond the near field can be neglected.

Fireball

The diameter of the fireball is obtained from Eq. (10.150), which gives

$$D = k_1 \cdot m^{n_1} = 5.8 \cdot 1,500^{1/3} = 66.39 \text{ m}$$

and its duration from Eq. (10.151)

$$t_d = k_2 \cdot m^{n_2} = 0.45 \cdot 1,500^{1/3} = 5.15 \text{ s}$$

The heat flux follows from Eq. (10.133) together with Eqs. (10.152)–(10.154) and (10.136)

$$F_h = \frac{(D/2)^3}{[x^2 + (D/2)^2]^{3/2}} = \frac{(66.39 \text{ m}/2)^3}{[(150 \text{ m})^2 + (66.39 \text{ m}/2)^2]^{3/2}} = 0.01009$$

$$F_v = \frac{x \cdot (D/2)^2}{[x^2 + (D/2)^2]^{3/2}} = \frac{150 \text{ m} \cdot (66.39 \text{ m}/2)^2}{[(150 \text{ m})^2 + (66.39 \text{ m}/2)^2]^{3/2}} = 0.04558$$

$$\begin{aligned} \tau_a(x) &= 0.4343 \cdot \ln \left(14.1 \cdot \varphi^{-0.108} \cdot (x - r)^{-0.13} \right) \\ &= 0.4343 \cdot \ln \left(14.1 \cdot 20^{-0.108} \cdot (150 - 33.195)^{-0.13} \right) = 0.7399 \end{aligned}$$

$$q''(x) = q''_{\text{act}} \cdot f_{\text{ab}}(x) \cdot \tau_a(x) = 350,000 \frac{\text{W}}{\text{m}^2} \cdot 0.04668 \cdot 0.7399 = 12,088.5 \frac{\text{W}}{\text{m}^2}$$

The conditional probability of death following exposure is obtained from Eq. (B.29) together with Eq. (2.56)

$$\begin{aligned} Y &= -14.9 + 2.56 \cdot \ln \left(q''^{1.3333} \times 10^{-4} \cdot t_{\text{ex}} \right) \\ &= -14.9 + 2.56 \cdot \ln \left(12,088.5^{4/3} \times 10^{-4} \cdot 5.15 \text{ s} \right) = -2.1973 \end{aligned}$$

Hence the probability of death is

$$\phi(Y - 5) = 3.1 \times 10^{-13}$$

Applying Eq. (10.176) to the near field, different expansion energies of the BLEVEs only affect the radius of the near field. In order to illustrate the different impacts, the results of the application of the TNT equivalent model (cf. Example 10.25) to the present problem are shown in Figs. 10.39 and 10.40.

Fig. 10.39 Pressure as a function of the distance from the centre of the vessel for the physical explosion

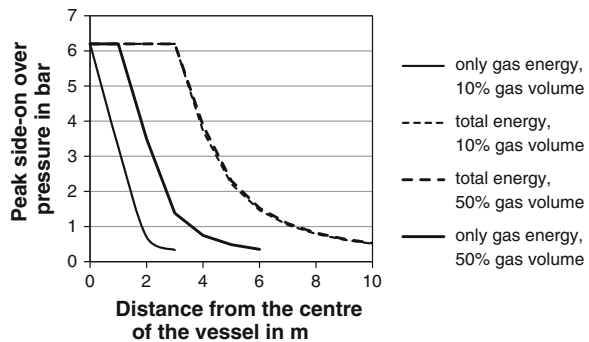
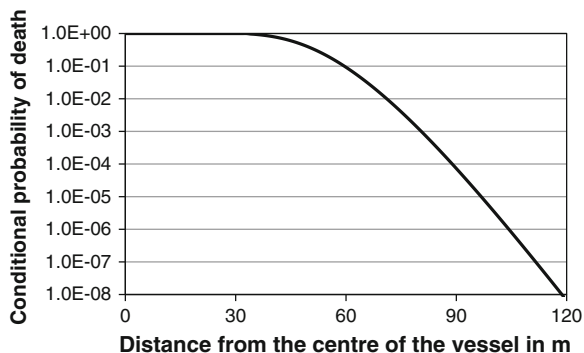


Fig. 10.40 Conditional probability of death following the fireball accompanying the BLEVE as a function of the distance from the centre of the vessel



10.8 Dust Explosion

“The hazard of a dust explosion or fire exists wherever flammable dusts are handled. Generally, a dust explosion occurs only if the dust is dispersed in air, but transition from a fire to an explosion can occur, and vice versa” [2]. The conditions for a dust explosion and the characteristic properties of dusts are treated in Sect. 2.4.

According to [2] the following scenario is often encountered in industry: a primary explosion occurs in a plant area. As a consequence of insufficient explosion protection the dust is finely dispersed in the room leading to a secondary explosion. The latter often involves a larger mass of dust and hence a larger energy release than the primary one. The probability of occurrence of a dust detonation, however, is considered to be small.

In what follows the blast wave caused by a dust explosion is treated. For this purpose the following simplified relationship for the pressure of relieved weak blast waves of dusts and gases at distance r from the cloud centre, p_{so} , is derived in [67]. It is

$$p_{so} = p_a \cdot \left[1 + \frac{\kappa_0 \cdot \left(\frac{(\kappa_0 + 1) \cdot p_{red}}{\rho_a \cdot a_0^2} \right)^{1/2}}{(\kappa_0 + 1) \cdot (\log \hat{r})^{1/2} \cdot \hat{r}} \right] \quad (10.177)$$

where

$$\hat{r} = \frac{r}{\sqrt{A_v^{1/2} \cdot V^{1/3}}} \quad (10.178)$$

In Eqs. (10.177) and (10.178) κ_0 is the heat capacity ratio of air (1.4), A_v is the pressure relief area in m^2 and V the volume in m^3 , where the dust explosion occurs, r is the distance from the centre of the explosion in m, ρ_a the density of air

in kg/m^3 and a_0 the speed of sound in air in m/s. The reduced pressure, p_{red} (in Pa), lies below the maximum explosion pressure, since a pressure relief through relief area A_v takes place during the explosion. The blast wave is assumed to be spherically symmetric.

A detailed discussion of dust explosions is found in [68], whilst [69] provides an overview of the numerous unresolved problems still existent in the investigation of such explosions.

Example 10.32 Dust explosion

A dust explosion occurs in a room with a volume of $V = 300 \text{ m}^3$ and a relief opening of an area of $A_v = 1 \text{ m}^2$. The reduced pressure is supposed to amount to $p_{\text{red}} = 600,000 \text{ Pa}$, the atmospheric pressure to 1 bar. What is the pressure at a distance of 6 m from the centre of the explosion? What would the pressure be if the explosion occurred in a room with a volume of 600 m^3 and a relief opening of 2 m^2 ?

Solution

In the first place the scaled distance according to Eq. (10.178) is determined. We obtain

$$\hat{r} = \frac{r}{\sqrt{A_v^{1/2} \cdot V^{1/3}}} = \frac{6 \text{ m}}{\sqrt{(1 \text{ m}^2)^{1/2} \cdot (300 \text{ m}^3)^{1/3}}} = 2.319$$

If this value is inserted into Eq. (10.177) one has

$$\begin{aligned} p_{\text{so}} &= p_a \cdot \left[1 + \frac{\kappa_0 \cdot \left(\frac{(\kappa_0+1) \cdot p_{\text{red}}}{\rho_a \cdot a_0^2} \right)^{1/2}}{(\kappa_0 + 1) \cdot (\log \hat{r})^{1/2} \cdot \hat{r}} \right] \\ &= 1 \text{ bar} \cdot \left[1 + \frac{1.4 \cdot \left(\frac{2.4 \cdot 600,000 \text{ Pa}}{1.2 \frac{\text{kg}}{\text{m}^3} \cdot (340 \frac{\text{m}}{\text{s}})^2} \right)^{1/2}}{2.4 \cdot (\log 2.319)^{1/2} \cdot 2.319} \right] = 2.3409 \text{ bar} \end{aligned}$$

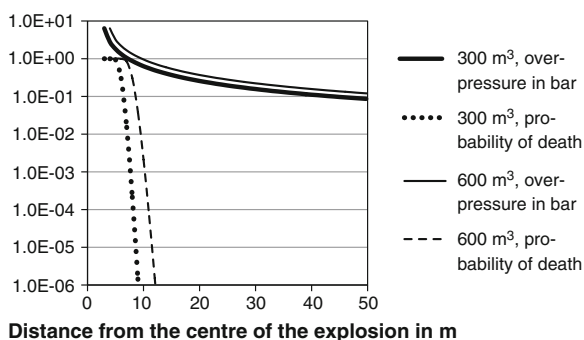
and thus a peak side-on overpressure of

$$p_s = p_{\text{so}} - p_a = 2.3409 \text{ bar} - 1 \text{ bar} = 1.3409 \text{ bar}$$

The corresponding conditional probability of death is obtained from Eq. (B.22) together with Eq. (2.56). The resulting probit value is

$$Y = -77.1 + 6.91 \cdot \ln p_s = -77.1 + 6.91 \cdot \ln 134,090 = 4.4813$$

Fig. 10.41 Distance-dependent peak side-on overpressures and conditional probabilities of death as functions of the distance from the centre of explosion



and the conditional probability of death is

$$\phi(Y - 5) = 0.3$$

In case of $V = 600 \text{ m}^3$ and $A_v = 2 \text{ m}^2$ we obtain analogously $p_{so} = 3.209 \text{ bar}$ and a conditional probability of death of 0.9983.

Figure 10.41 shows the peak side-on overpressures and conditional probabilities of death as functions of the distance from the centre of the explosion.

10.9 Flight of Missiles

The fragmentation of vessels which are under pressure leads to the flight of missiles. These can do harm to humans or damage neighbouring structures. The latter may lead to the so-called Domino effect, i.e. an escalation of accident consequences resulting from the destruction of nearby plants or parts of plants. In what follows the ejection and flight of fragments from vessels is treated on the basis of [70, 71].

The energy of explosion on vessel rupture depends on its internal pressure. That is determined by the boundary conditions of the accident, as described above. The higher the internal pressure the stronger is the explosion.

10.9.1 Calculation of the Trajectory

The trajectory of the missile is calculated in two dimensions accounting for a resistance of air proportional to the square of flight velocity. This applies to the so-called ballistic range which lies between very low velocities, where resistance is proportional to velocity, and supersonic velocities where resistance is a complex function. Fragments from vessel bursts are usually encountered in this range [2]. We then have the following equations of motion

$$\frac{d^2x}{dt^2} + \frac{\rho \cdot c_w \cdot A_{st}}{2 \cdot m} \cdot \left(\frac{dx}{dt}\right)^2 = 0 \quad (10.179)$$

$$\frac{d^2y}{dt^2} \pm \frac{\rho \cdot c_w \cdot A_{st}}{2 \cdot m} \cdot \left(\frac{dy}{dt}\right)^2 + g = 0 \quad (10.180)$$

In Eqs. (10.179) and (10.180) x denotes the horizontal direction and y the vertical direction, m the mass of the fragment, c_w the drag coefficient, A_{st} the drag area of the fragment (projected area), ρ the density of air and g the acceleration due to gravity

Since the drag force is opposed to the direction of motion it should be noted that in the y direction (Eq. (10.180)) the drag force is aligned with the force of gravity during ascent (+) and opposed to it during descent (−).

The non-linear differential Eq. (10.179) is converted by

$$\frac{dx}{dt} = \gamma \cdot \frac{\dot{u}}{u} \quad (10.181)$$

into the linear differential equation

$$u = 0 \quad (10.182)$$

In Eq. (10.181) $\gamma = m/K$ with $K = \rho \cdot c_w \cdot A_{st}/2$. We solve Eq. (10.182) using the initial conditions

$$x(0) = 0 \quad \text{and} \quad \dot{x}(0) = v_0 \cdot \cos \beta, \quad (10.183)$$

where v_0 is the departure velocity of the fragment and β its polar departure angle, and obtain for the flight path in x -direction

$$x(t) = \frac{m}{K} \cdot \ln \left(\frac{K}{m} \cdot t \cdot v_0 \cdot \cos \beta + 1 \right) \quad (10.184)$$

The corresponding flight velocity is

$$\dot{x}(t) = \frac{m \cdot v_0 \cdot \cos \beta}{K \cdot v_0 \cdot t \cdot \cos \beta + m} \quad (10.185)$$

The non-linear differential Eq. (10.180) is transformed by

$$\frac{dy}{dt} = \gamma \cdot \frac{\dot{w}}{w} \quad (10.186)$$

into

$$w \pm \frac{g}{\gamma} \cdot w = 0 \quad (10.187)$$

The general solution of Eq. (10.187) with the positive sign is

$$w(t) = A \cdot \cos(\alpha t) + B \cdot \sin(\alpha t) \quad (10.188)$$

In Eq. (10.188) $\alpha = \sqrt{g \cdot K/m}$. Thus we obtain the general solution of Eq. (10.188) with the positive sign

$$y(t) = \frac{m}{K} \cdot \ln[A \cdot \cos(\alpha t) + B \cdot \sin(\alpha t)] \quad (10.189)$$

Applying the initial conditions

$$y(0) = 0 \quad \text{and} \quad \dot{y}(0) = v_0 \cdot \sin \beta \quad (10.190)$$

we have

$$y(t) = \frac{m}{K} \cdot \ln\left(\cos(\alpha t) + \frac{v_0 \cdot K \cdot \sin \beta}{m \cdot \alpha} \cdot \sin(\alpha t)\right) \quad (10.191)$$

for the flight path in the y-direction.

The corresponding flight velocity is

$$\dot{y}(t) = \frac{v_0 \cdot \sin \beta \cdot \cos(\alpha t) - \frac{m \cdot \alpha}{K} \cdot \sin(\alpha t)}{\cos(\alpha t) + \frac{v_0 \cdot K \cdot \sin \beta}{m \cdot \alpha} \cdot \sin(\alpha t)} \quad (10.192)$$

For the descent Eq. (10.187) is solved with the minus sign. One obtains the general solution

$$y(t) = -\frac{m}{K} \cdot \ln[A \cdot \exp(-\alpha t) + B \cdot \exp(\alpha t)] \quad t \geq t^* \quad (10.193)$$

In Eq. (10.193) t^* is the instant in time when the highest point of the trajectory is reached; t^* is obtained from the condition that Eq. (10.192) has to adopt the value 0. This is the case for

$$t^* = \frac{1}{\alpha} \cdot \arctan\left(\frac{v_0 \cdot K \cdot \sin \beta}{m \cdot \alpha}\right) \quad (10.194)$$

The constants of solution A and B result from the condition that

$$y(t^*) = y_{\max} \quad \text{and} \quad \dot{y}(t^*) = 0 \quad (10.195)$$

In Eq. (10.195) the results of Eqs. (10.191) and (10.192) are set equal to those of Eq. (10.193), where $y_{\max} = y(t^*)$ from Eq. (10.191). One then obtains for the height of the trajectory

$$y(t) = y_{\max} - \frac{m}{K} \cdot \ln \left[\frac{\exp[-\alpha \cdot (t - t^*)] + \exp[\alpha \cdot (t - t^*)]}{2} \right] \quad t \geq t^* \quad (10.196)$$

and for the corresponding velocity

$$\dot{y}(t) = \frac{m \cdot \alpha}{K} \cdot \frac{\exp[-\alpha \cdot (t - t^*)] - \exp[\alpha \cdot (t - t^*)]}{\exp[-\alpha \cdot (t - t^*)] + \exp[\alpha \cdot (t - t^*)]} \quad t \geq t^* \quad (10.197)$$

10.9.2 Determination of the Coefficients for the Equations of the Flight Trajectory

If the above equations are to be applied to vessel rupture, several input quantities are needed, namely

- operating pressure,
- failure pressure,
- energy content of the vessel on rupture,
- degree of filling of the vessel at the initiation of the accident in case of superheated storage,
- percentage of initial energy imparted to the fragments on the whole,
- number of fragments,
- shape and mass of fragments,
- percentage of initial energy imparted to the individual fragments,
- orientation of trajectory (azimuthal and polar angles of departure),
- drag coefficient,
- wind direction and speed during the accident.

All parameters mentioned are either stochastic or uncertain because of lack of knowledge. Hence, they either lead to aleatory or epistemic uncertainties in the calculations to be performed. That is why they are treated with probability distributions whose selection is indicated and justified below.

10.9.2.1 Velocity of Departure of a Fragment

The velocity of departure of a fragment is obtained from the well-known relationship between velocity and energy

$$v_0 = \left(\frac{2 \cdot E_k}{m} \right)^{\frac{1}{2}} \quad (10.198)$$

In Eq. (10.198) E_k denotes the kinetic energy imparted to the fragment concerned, m its mass, and v_0 its velocity of departure.

The determination of E_k requires the energy content of the vessel to be calculated in the first place. In doing this we have to distinguish between the storage of a gas and that of a superheated liquid. For treating the expansion of an ideal gas under pressure several relations are in use (cf. [37]), namely

Brode's equation

$$E = \frac{p_1 - p_2}{\kappa - 1} \cdot V \quad (10.199)$$

Baker's equation

$$E = \left[1 - \left(\frac{p_2}{p_1} \right)^{(\kappa-1)/\kappa} \right] \cdot \frac{p_1}{\kappa - 1} \cdot V \quad (10.200)$$

Baum's equation

$$E = \left[1 - \left(\frac{p_2}{p_1} \right)^{(\kappa-1)/\kappa} + (\kappa - 1) \cdot \frac{p_2}{p_1} \cdot \left(1 - \left(\frac{p_2}{p_1} \right)^{-1/\kappa} \right) \right] \frac{p_1}{\kappa - 1} \cdot V \quad (10.201)$$

The symbols in Eqs. (10.199)–(10.201) have the following meaning:

- E energy of expansion of the vessel content in J,
- V volume of the vessel in m^3 ,
- p_1 failure pressure of the vessel in Pa,
- p_2 pressure after depressurization (ambiental pressure) in Pa,
- κ ratio of specific heats of the stored gas

A detailed discussion of the merits and drawbacks of Eqs. (10.199)–(10.201) is given in [15]. In conclusion it is stated there that no consensus exists on the measure for defining the energy of an explosion of a pressure vessel. We are dealing with a typical case of modelling uncertainties.

As already mentioned, the pressure of failure of a vessel depends on the accident scenario. In case of overpressure failure, the failure pressure of the vessel, i.e. its maximum working pressure times a safety factor should be used. Mechanical failures should be dealt with by applying the normal operating pressure. In case of fire engulfment a value of 1.21 times the starting relief pressure of the safety valve is recommended in [37].

In any case the pressure at the time of accident initiation can never be known exactly. Therefore it is treated as an uncertain parameter and assumed to lie between 90 and a 110 % of the above values. It is represented by the rectangular distribution of Eq. (C.33).

The energy content of the vessel at the moment of bursting is the source for

- widening of the vessel,
- rupture,
- blast wave,
- fragmentation.

Hence, only a fraction of this energy content appears as kinetic energy of the fragments. In order to arrive at this energy, E_k , E must be multiplied by a factor, η , which ranges between 0.2 and 0.5, with 0.2 being the recommended value (cf. [15]). The tendency to prefer 0.2 is interpreted by a right-sided triangular distribution on [0.2, 0.5] with an expected value of 0.3. Equation (C.34) is the corresponding probability density function.

In case of a superheated liquid (BLEVE) the procedure outlined in Sect. 10.7 is adopted. It is based on thermodynamically assessing the difference of internal energies between the initial and expanded states. Additionally, consideration is granted to the question of whether, given initial pressure, temperature and type of substance, flashing of the liquid phase makes a contribution to explosion energy or not. An analogous procedure is adopted if a gas does not behave as ideal, for example, due to very high pressures.

10.9.2.2 Number, Mass, and Energy Distribution of the Fragments

There is little information on the number of fragments originated by the rupture of spheres. According to [72] values of 3, 4, 5, 5, 6, 16 and 19 were observed in accidents. These values were fitted by a log-normal distribution according to Eqs. (9.50) to (9.55). The above numbers lead to parameter values of $\mu_x = 1.8875$ and $s_x = 0.6997$.

Since no appropriate information is available on the mass distribution of fragments, all fragments are assumed to be of equal mass. Their shape is treated as a section from a spherical shell, since it is impossible to foresee the deformation on vessel burst. Because of a lack of pertinent information it is assumed that the fraction of the total kinetic energy imparted to each of the fragments is the same. This is closely related to the question of how much leakage between fragments is there at the launch stage, when separation due to expansion begins.

10.9.2.3 Angles of Departure

The orientation of the fragment trajectory is characterized by its polar and azimuthal angles. No indication for preferential directions of the polar angle of the flight trajectory has been found. Hence it is described by a rectangular distribution according to Eq. (C.33) on the range -90° to 90° . The negative part of the range of the polar angle becomes important, if the elevation of the vessel above ground is taken into account. In [72] the azimuthal angle is divided into 12 sectors. Symmetry about the 0° – 180° axis is assumed, the latter being taken as the mean fragment direction. The analysis of accidents provides the following probabilities for the sectors: 0° – 30° and 330° – 360° , 0.138; 30° – 60° and 300° – 330° , 0.104; 60° – 90° and 270° – 300° , 0.129; 90° – 120° and 240° – 270° , 0.104; 120° – 150° and 210° – 240° , 0.008; 150° – 180° and 180° – 210° , 0.017. These are represented by piecewise constant pdfs [rectangular distributions according to Eq. (C.33)].

10.9.2.4 Drag Coefficient

The drag coefficient, c_w , depends on factors such as geometry, surface roughness, orientation with respect to direction of the flow. A blunt, sharp edged shape with negligible Reynolds number dependence is assumed. A reasonable range is $c_w = 0.8\text{--}1.4$ which applies to shells for differing angles of attack. It is described by a constant pdf according to Eq. (C.33). The fragments are considered as chunky, so that lift forces are not taken into account.

10.9.2.5 Degree of Filling at the Time of the Burst

The fill condition at the time of the accident, which is important for the calculation of the total energy imparted to the fragments in case of the storage of pressure liquefied gases, cannot be predicted for the random moment in time of failure. It is therefore assumed to lie between the reasonable limits of 0.1 and 0.8, and is described by the constant pdf of Eq. (C.33).

10.9.2.6 Monte Carlo Evaluation

The preceding equations and considerations form the basis for a Monte Carlo evaluation. For this purpose the solutions of Eqs. (10.184) and (10.185) as well as Eqs. (10.191)–(10.197) are evaluated N times. Each time we obtain values for $x(t)$, $y(t)$, $\dot{x}(t)$, and $\dot{y}(t)$, from which parameters of interest, e.g. the distance of fragment impact and the corresponding energy are easily derived. The procedure corresponds to that shown in Fig. 4.22.

The results converge stochastically with increasing N (number of trials) proportional to $1/\sqrt{N}$ towards their real values. Each evaluation is a trial in which the input quantities mentioned above are determined in conformity with the statistical distributions indicated. This is done as follows for the three types of distributions used.

If $Z_{n,1}$ and $Z_{n,2}$ are two independent random numbers uniformly distributed on $[0,1]$ we have for (cf. [73])

- log-normally distributed quantities

$$X_n = \exp\left(\sqrt{-2 \cdot \ln Z_{n,1}} \cdot \cos(2 \cdot \pi \cdot Z_{n,2}) \cdot s_x + \mu_x\right) \quad (10.202)$$

- rectangularly distributed quantities

$$X_n = a + (b - a) \cdot Z_{n,1} \quad (10.203)$$

- right-sided triangularly distributed quantities

$$X_n = b + (a - b) \cdot \sqrt{1 - Z_{n,1}} \quad (10.204)$$

where n denotes the n th trial.

Example 10.33 Missile flight after vessel burst

A vessel with a volume of $V = 800 \text{ m}^3$ contains a gas under a pressure of $p_1 = 10 \text{ bar}$. A catastrophic failure at operating pressure occurs. Three fragments of equal size are produced.

Calculate the characteristic parameters of the flight trajectory of one of the fragments using Baker's equation for calculating the energy.

Data: mass of the vessel 79,140 kg, $\eta = 0.3$, $c_w = 1$; $\beta = 45^\circ$, $p_2 = 1 \text{ bar}$, $\kappa = 1.4$, $A_{st} = 78.14 \text{ m}^2$, $\rho = 1.2 \text{ kg/m}^3$

Solution

The energy content of the vessel is calculated according to Eq. (10.200), which gives

$$\begin{aligned} E &= \left[1 - \left(\frac{p_2}{p_1} \right)^{(\kappa-1)/\kappa} \right] \cdot \frac{p_1}{\kappa - 1} \cdot V \\ &= \left[1 - \left(\frac{1 \text{ bar}}{10 \text{ bar}} \right)^{0.4/1.4} \right] \cdot \frac{1,000,000 \text{ Pa}}{0.4} \cdot 800 \text{ m}^3 = 964,105,064.1 \text{ J} \end{aligned}$$

The amount of energy impacted to each of the fragments is

$$E_k = \frac{1}{3} \cdot \eta \cdot E = \frac{1}{3} \cdot 0.3 \cdot 964,105,064.1 \text{ J} = 96,410,506.41 \text{ J}$$

This results in a velocity of departure according to Eq. (10.198) of

$$v_0 = \left(\frac{2 \cdot E_k}{m} \right)^{\frac{1}{2}} = \left(\frac{2 \cdot 96,410,506.41 \text{ J}}{26,380 \text{ kg}} \right)^{\frac{1}{2}} = 85.49 \frac{\text{m}}{\text{s}}$$

where m is one third of total mass of vessel.

First the moment in time of the fragment reaching the highest point of its trajectory is calculated according to Eq. (10.194), which gives

$$\begin{aligned} t^* &= \frac{1}{\alpha} \cdot \arctan \left(\frac{v_0 \cdot K \cdot \sin \beta}{m \cdot \alpha} \right) \\ &= \frac{1}{0.13204 \text{ s}^{-1}} \cdot \arctan \left(\frac{85.49 \frac{\text{m}}{\text{s}} \cdot 46.88 \frac{\text{kg}}{\text{m}} \cdot 0.7071}{26,380 \text{ kg} \cdot 0.13204 \text{ s}^{-1}} \right) = 5.17 \text{ s} \end{aligned}$$

where

$$K = \rho \cdot c_w \cdot A_{st}/2 = 1.2 \frac{\text{kg}}{\text{m}^3} \cdot 1 \cdot \frac{78.14 \text{ m}^2}{2} = 46.88 \frac{\text{kg}}{\text{m}} \text{ and}$$

$$\alpha = \sqrt{g \cdot \frac{K}{m}} = \sqrt{9.81 \frac{\text{m}}{\text{s}^2} \cdot \frac{46.88 \frac{\text{kg}}{\text{m}}}{26,380 \text{ kg}}} = 0.13204 \text{ s}^{-1}.$$

The maximum height of the trajectory follows from Eq. (10.191), which gives

$$y(t^*) = y_{\max} = \frac{m}{K} \cdot \ln \left(\cos(\alpha t^*) + \frac{v_0 \cdot K \cdot \sin \beta}{m \cdot \alpha} \cdot \sin(\alpha t^*) \right) = \frac{26,380 \text{ kg}}{46.88 \frac{\text{kg}}{\text{m}}} \cdot \ln \left(\cos(0.13204 \text{ s}^{-1} \cdot 5.17 \text{ s}) + \frac{85.49 \frac{\text{m}}{\text{s}} \cdot 46.88 \frac{\text{kg}}{\text{m}} \cdot \sin 45^\circ}{26,380 \text{ kg} \cdot 0.13204 \text{ s}^{-1}} \cdot \sin(0.13204 \text{ s}^{-1} \cdot 5.17 \text{ s}) \right)$$

$$= 562.71 \text{ m} \cdot 0.2540 = 142.92 \text{ m}$$

Equation (10.196) enables one now to calculate the time until the end of the flight, t_e , i.e.

$$y(t_e) = 0 = y_{\max} - \frac{m}{K} \cdot \ln \left[\frac{\exp[-\alpha \cdot (t_e - t^*)] + \exp[\alpha \cdot (t_e - t^*)]}{2} \right] \quad t_e \geq t^*$$

whence we obtain

$$\exp \left(\frac{y_{\max} \cdot K}{m} \right) - \ln \left[\frac{\exp[-\alpha \cdot (t_e - t^*)] + \exp[\alpha \cdot (t_e - t^*)]}{2} \right] = \exp \left(\frac{142.93 \text{ m} \cdot 46.88 \frac{\text{kg}}{\text{m}}}{26,380 \text{ kg}} \right)$$

$$- \ln \left[\frac{\exp[-0.13204 \frac{1}{\text{s}} \cdot (t_e - 5.17 \text{ s})] + \exp[0.13204 \frac{1}{\text{s}} \cdot (t_e - 5.17 \text{ s})]}{2} \right] = 0$$

The above equation is solved iteratively to give $t_e = 20.03 \text{ s}$.

The flight distance is calculated according to Eq. (10.184), which gives

$$x(t_e) = \frac{m}{K} \cdot \ln \left(\frac{K}{m} \cdot t_e \cdot v_0 \cdot \cos \beta + 1 \right)$$

$$= \frac{26,380 \text{ kg}}{46.88 \frac{\text{kg}}{\text{m}}} \cdot \ln \left(\frac{46.88 \frac{\text{kg}}{\text{m}}}{26,380 \text{ kg}} \cdot 20.03 \text{ s} \cdot 85.49 \frac{\text{m}}{\text{s}} \cdot 0.7071 + 1 \right) = 646.0 \text{ m}$$

The energy of impact E_A is given by

$$E_A = \frac{m}{2} \cdot (\dot{x}(t_e)^2 + \dot{y}(t_e)^2)$$

where $\dot{x}(t_e)$ is calculated according to Eq. (10.185) and $\dot{y}(t_e)$ according to Eq. (10.197). This gives

$$E_A = \frac{26,380 \text{ kg}}{2} \cdot \left(\left(19.18 \frac{\text{m}}{\text{s}} \right)^2 + \left(-71.42 \frac{\text{m}}{\text{s}} \right)^2 \right) = 72,132,005.3 \text{ J}$$

which corresponds to 74.8 % of the energy of departure.

If the usual model, which does not account for the resistance of air, is used we obtain the following results:

Velocity in the x-direction

$$\dot{x} = v_0 \cdot \cos \beta = 85.49 \frac{\text{m}}{\text{s}} \cdot 0.7071 = 60.45 \frac{\text{m}}{\text{s}}$$

Flight path in the x-direction

$$x(t) = v_0 \cdot t \cdot \cos \beta$$

Velocity in the y-direction

$$\dot{y}(t) = v_0 \cdot \cos \beta - g \cdot t$$

Flight path in the y-direction

$$y(t) = v_0 \cdot t \cdot \cos \beta - \frac{g}{2} \cdot t^2$$

The moment in time for the fragment to reach the highest point of its trajectory is calculated from the condition that $\dot{y}(t^*) = 0$, i.e.

$$t^* = \frac{v_0 \cdot \cos \beta}{g} = \frac{85.49 \frac{\text{m}}{\text{s}} \cdot 0.7071}{9.81 \frac{\text{m}}{\text{s}^2}} = 6.16 \text{ s}$$

The corresponding maximum height of the trajectory is

$$\begin{aligned} y(t^*) &= y_{\max} = v_0 \cdot t^* \cdot \cos \beta - \frac{g}{2} \cdot t^{*2} \\ &= 85.49 \frac{\text{m}}{\text{s}} \cdot 6.16 \text{ s} \cdot 0.7071 - 4.905 \frac{\text{m}}{\text{s}^2} \cdot (6.16 \text{ s})^2 = 186.25 \text{ m} \end{aligned}$$

The total time of flight results from the condition

$$y(t_e) = v_0 \cdot t_e \cdot \cos \beta - \frac{g}{2} \cdot t_e^2 = 0$$

and hence

$$t_e = \frac{2 \cdot v_0 \cdot \cos \beta}{g} = \frac{2 \cdot 85.49 \frac{\text{m}}{\text{s}} \cdot 0.7071}{9.81 \frac{\text{m}}{\text{s}^2}} = 12.32 \text{ s}$$

The distance flown by the fragment then is

$$x(t_e) = v_0 \cdot t_e \cdot \cos \beta = 85.49 \frac{\text{m}}{\text{s}} \cdot 12.32 \text{ s} \cdot 0.7071 = 744.74 \text{ m}$$

Comparison of the results suggests that the resistance of air should not be neglected when treating missile flight.

Case study 10.1: BLEVE in Mexico City

Amongst others a BLEVE occurred during the catastrophe in Mexico City in 1984. Probably two spherical vessels containing pressure liquefied propane, butane or a mixture of both substances burst [74]. Each vessel had a volume of 1,600 m³, a wall thickness of 0.028 m and a mass of 146,529 kg. The failure pressure is assumed to have been 1.34 MPa. For propane, which was supposed to be contained in the vessel, because it was the substance mainly handled in the installation, this corresponds to a saturation temperature of 310.9 K.

An expansion energy of 2 MJ/m³ is read from the corresponding graph in [37]. This refers to the vapour fraction in the vessel, since flash vaporization of the liquid fraction is improbable at this temperature. The uncertainty in assessing the expansion energy is accounted for by using a constant pdf according to Eq. (C.33). The interval [1.8, 2.2] MJ/m³ is used.

The empirical findings on fragment ranges given in [74] can be represented by a truncated normal distribution [vid. Eq. (C.25) in Appendix C]. It is shown in Fig. 10.42 together with the calculation results obtained with the procedure described above. That procedure uses the Monte Carlo method [73] to process the probability distributions for stochastic and not exactly known input quantities indicated above. The calculated ranges are in good agreement with the observed ones.

Figure 10.43 shows the conditional probabilities for death by being hit by a fragment in the surroundings of the vessel assuming that being hit implies a

Fig. 10.42 Probability for the flight distance of a fragment r being smaller or equal to R (measured in [73] and calculated with 5,000,000 Monte Carlo trials)

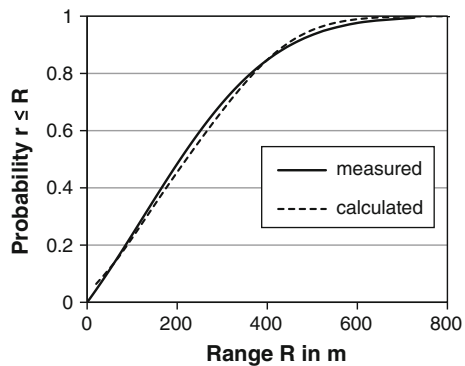
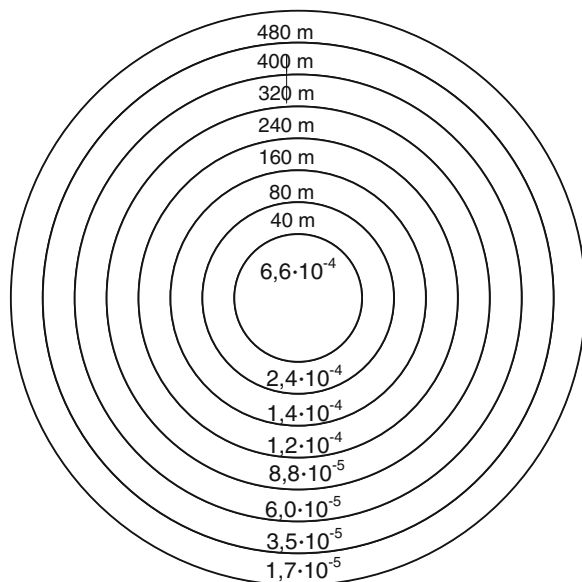


Fig. 10.43 Conditional probabilities for a person in the surroundings of the vessel being hit by a fragment



probability of death of 1. In order to obtain the expected frequency of death of a person these probabilities must still be multiplied with the expected frequency of vessel burst. This frequency naturally depends on the boundary conditions of the accident. For example, for spontaneous failure one finds a value of 10^{-6} per year in Table 10.1. Additionally, fires and fragment hits from the neighbouring vessels would have to be accounted for. The corresponding expected frequencies would in turn depend on the prevailing boundary conditions.

The foregoing considerations show how the decisions on distances between objects inside a plant and between plant and residential areas can be supported by calculations.

10.10 Scenarios and Probability Assignments

The literature indicates numerous, often widely different values for assigning probabilities to scenarios such as those of Figs. 10.2, 10.3 and 10.4. This reflects uncertainties due to lack of knowledge (epistemic) and stochastic (aleatory) effects. If properly treated these uncertainties should be represented by probability distributions. Table 10.15 gives an overview of conditional probabilities for the consequences of a puff release of a pressurized flammable gas from various sources. Not only are the differences in probabilities evident but also the differences as to the endpoints.

In what follows mainly results from [10] are used. These relationships and numerical values were obtained in a project carried out by the “Explosion Research Cooperative”, a consortium of chemical companies. The relationships

Table 10.15 Conditional probabilities for the event tree “instantaneous (puff) release” of a flammable gas under pressure (from [75])

Source	Immediate (instantaneous) ignition			Delayed ignition	Flash fire	Fireball	No ignition	Endpoints considered
Ref. [33] for medium to high reactivity	<1,000 kg 1,000–10,000 kg >10,000 kg	0.2	0.8	0.6	0.7	0	0	Fireball
		0.5	0.5					Flash fire
		0.7	0.3					Explosion Dispersion without ignition
Ref. [76]	0.1		0.2	0.67	–		0.72	Flash fire Explosion Jet fire Dispersion without ignition
Ref. [77]	0.4		0.12	0.8	0.4		0.88	Fireball Flash fire Explosion Dispersion without ignition
Ref. [78]	0.3		Model calculation; assumption 0.7	0.6	–			BLEVE/fireball Flash fire Explosion Dispersion without ignition
Ref. [79]	0.17		0.4	0.9	–		0.6	Catastrophic local fire Major local fire Vapour cloud explosion Catastrophic flash fire then local fire Major flash fire then local fire Catastrophic unignited release Major unignited release

are based on empirical findings and expert judgment. They were converted here into metric units. Additionally, default values are indicated. These are used if no calculation is carried out for the phenomenon in question.

10.10.1 Probability of Immediate Ignition

The default value for immediate ignition is 0.15. As probability for the ignition of a flammable material immediately after release one obtains

$$P_{\text{immediate ignition}} = \underbrace{\left[1 - 5,000 \cdot \exp\left(-9.5 \cdot \frac{T \cdot 1.8 - 459.67}{T_s \cdot 1.8 - 459.67}\right) \right]}_A + \left[0.005852894 \cdot \frac{p^{1/3}}{E_{\min}^{2/3}} \right] \quad (10.205)$$

where

$$A = \begin{cases} 0 & \text{if } \frac{T \cdot 1.8 - 459.67}{T_s \cdot 1.8 - 459.67} < 0.9 \\ 1 & \text{if } \frac{T \cdot 1.8 - 459.67}{T_s \cdot 1.8 - 459.67} > 1.2 \end{cases}$$

In Eq. (10.205) T_s is the autoignition temperature in K, p the pressure before release in bar (atmospheric pressure is taken to be 1 bar) and $E_{\min}$ the minimum ignition energy (MIE) in mJ for standard conditions. If formally $p_{\text{immediate ignition}} > 1$, $p_{\text{immediate ignition}}$ is set equal to 1.

For mixtures Le Chatelier's rule is used to calculate the MIE

$$E_{\min, \text{mixture}} = \frac{1}{\sum_i \frac{y_i}{E_{\min, i}}}$$

where y_i is the mole fraction of material i in the mixture.

10.10.2 Probability of Delayed Ignition

Delayed ignition is understood to occur in situations when there is sufficient time between release and ignition for a gas cloud to be formed. The default value is 0.30.

In order to calculate the probability the following factors are needed:

Material factor for describing the type of material

$$M_1 = 0.6 - 0.85 \cdot \log E_{\min} \quad (10.206)$$

This value has an upper bound of 3 and a lower bound of 0.1, which replace the calculated value if it lies outside the range.

Mass factor for describing the quantity of released material

$$M_2 = 7 \cdot \exp(0.642 \cdot \ln \dot{m} - 4.1625) \quad (10.207)$$

where $\dot{m}$ is the mass flow rate in kg/s. M_2 is limited by a maximum value of 2.

Factor accounting for the duration of the release t

$$M_3 = \frac{[1 - (1 - S^2) \cdot \exp(-0.015 \cdot S \cdot t)]}{0.3} \quad (10.208)$$

In Eq. (10.208) S is adapted to specific situations according to Table 10.16.

Table 10.16 Values for “ S ” characterizing different sources of ignition for use in Eq. (10.208)

Source type	Source	Probability of ignition in one minute (“strength” S)
Specific (point) sources	<i>If the flammable cloud size is known, use the following relationships for process plants</i>	
	Fired heater	0.9
	Boiler	0.3
	Flare	1
	Motor vehicle	0.3
	Train engine	0.5
Line sources	High power electrical line	0.00328 L
	Roadway	$1-0.7^V$
Area sources	Process unit	F
	Residential population	$1-0.99^N$
	<i>If the flammable cloud size is not known, use the following relationships for process plants</i>	
	High equipment density	0.5
	Medium equipment density	0.25
	Low equipment density	0.1
	Confined space with virtually no equipment	0.02

L length of line covered by the cloud, in m

V average number of vehicles covered by the cloud in the flammable range

F fraction of process unit covered by the cloud in the flammable range

N number of people covered by the cloud in the flammable range. This includes people who are in buildings without flammable range inside, but having a flammable atmosphere outside

Indoor or outdoor ignition

The *volume* of an enclosed space is characterized by B_{es} with a maximum value of 3 and a minimum of 0.5; 3 is applied to small volumes and 0.5 for big volumes as compared with standard volume of 4,248 m³. The probability of ignition is proportional to $1/V^{1/3}$, so that a space eight times the standard volume has half the probability of ignition.

The *ventilation rate* of the enclosed space is represented by B_{vr} with a maximum value of 3 and a minimum of 0.3. Higher ventilation rates lead to lower probabilities of ignition; the probability of ignition varies proportional to $1/L^{1/2}$, where L is the ventilation rate.

The *ventilation draught direction* is accounted for by B_{vdd} with

$$B_{vdd} = \begin{cases} 0.5 & \text{draught is designed such that flammable gases are drawn away from likely ignition sources,} \\ 1 & \text{draught is designed with no particular strategy in mind,} \\ 2 & \text{draught is designed such that flammable gases are drawn through likely ignition sources.} \end{cases}$$

The preceding factors are combined to give

$$M_4 = 2 \cdot B_{es} \cdot B_{vr} \cdot B_{vdd} \quad (10.209)$$

where $M_4 = 1$ is used for releases outdoors.

The probability of delayed ignition is then calculated as follows:

$$P_{\text{delayed ignition}} = \begin{cases} 1 - \frac{0.7}{\prod_{i=1}^4 M_i} & \text{if } \prod_{i=1}^4 M_i > 1 \\ 0.3 \cdot \prod_{i=1}^4 M_i & \text{if } \prod_{i=1}^4 M_i < 1 \end{cases} \quad (10.210)$$

10.10.3 Explosion

The default value of the conditional probability for explosion is 0.2. In order to determine the probability that a delayed ignition leads to an explosion the following relationship is used

$$P_{\text{explosion}} = 0.03385 \cdot \dot{m}^{0.435} \quad (10.211)$$

This value is multiplied by

- 0.3 for low reactivity
- 1.0 for medium reactivity
- 3 for high reactivity of the material involved (vid. Table 10.10) and has to be set equal to 1, if formally we arrive at $p_{\text{explosion}} > 1$.

Example 10.34 Determination of probabilities of ignition and explosion for a release of methane

A leak in a pipe emits for 10 s $\dot{m} = 3151,2$ kg/s of methane at a pressure of 70 bar and a temperature of 15 °C.

Calculate the ignition and explosion probabilities.

Data: minimum ignition energy MIE = 0.29 mJ, $T_s = 810.4$ K

Solution

- Immediate ignition

In the first place the criterion for determining A in Eq. (10.205) is calculated to be

$$\frac{T \cdot 1.8 - 459.67}{T_s \cdot 1.8 - 459.67} = \frac{288.15 \text{ K} \cdot 1.8 \frac{\text{F}}{\text{K}} - 459.67\text{F}}{810.4 \text{ K} \cdot 1.8 \frac{\text{F}}{\text{K}} - 459.67\text{F}} = 0.0591$$

Hence $A = 0$ and one obtains

$$\begin{aligned} P_{\text{immediate ignition}} &= \left[1 - 5,000 \cdot \exp\left(-9.5 \cdot \frac{T \cdot 1.8 - 459.67}{T_s \cdot 1.8 - 459.67}\right) \right] + \left[0.005852894 \cdot \frac{P^{1/3}}{E_{\min}^{2/3}} \right] \\ &= 0 + 0.005852894 \cdot \frac{70^{1/3}}{0.29^{2/3}} = 5.51 \times 10^{-2} \end{aligned}$$

- Delayed ignition

The factors according to Eqs. (10.206)–(10.208) are determined; this gives *Material factor* for describing the type of material

$$M_1 = 0.6 - 0.85 \cdot \log E_{\min} = 0.6 - 0.85 \cdot (-0.5376) = 1.05696$$

Mass factor for describing the quantity of released material

$$\begin{aligned} M_2 &= 7 \cdot \exp(0.642 \cdot \ln \dot{m} - 4.1625) \\ &= 7 \cdot \exp(0.642 \cdot \ln 3151.2 - 4.1625) = 19.2 > 2 \text{ hence } M_2 = 2 \end{aligned}$$

Factor accounting for the duration of the release t

Since the size of the cloud is not known, the value for low equipment density $S = 0.1$ from Table 10.13 is selected. We then have

$$\begin{aligned}
 M_3 &= \frac{[1 - (1 - S^2) \cdot \exp(-0.015 \cdot S \cdot t)]}{0.3} \\
 &= \frac{[1 - (1 - 0.1^2) \cdot \exp(-0.015 \cdot 0.1 \cdot 10)]}{0.3} = 0.0825
 \end{aligned}$$

Since we are dealing with an outdoor release the factor to account for enclosed spaces M_4 is set equal to 1 and we obtain

$$\prod_{i=1}^4 M_i = 1.05696 \cdot 2 \cdot 0.0825 \cdot 1 = 0.1744$$

and thus according to Eq. (10.210)

$$P_{\text{delayed ignition}} = 0.3 \cdot \prod_{i=1}^4 M_i = 0.3 \cdot 0.1744 = 0.05232$$

- Explosion

The conditional probability for an explosion follows from Eq. (10.121). Taking into account that methane according to Table 10.10 has low reactivity we obtain

$$P_{\text{explosion}} = 0.3 \cdot 0.03385 \cdot \dot{m}^{0.435} = 0.3 \cdot 0.03385 \cdot 3151.2^{0.435} = 0.3377 \quad \square$$

10.11 Case Study: Risk Assessment for the Failure of a Natural Gas High Pressure Pipeline

The present case study combines several of the models treated above in order to assess a risk. The treatment uses the boundary conditions given in [80].

A natural gas high pressure pipeline with a diameter of 20'' (508 mm), a wall thickness of 8 mm subject to a pressure of $p_1 = 70$ bar is planned in the vicinity of a residential area. For the section passing close by this residential area a risk assessment is to be performed. This is a so-called risk-based analysis, since the expected frequency of the undesired event (rupture of the pipeline and gas release) is directly taken from statistical material (actuarial approach) and not determined by a detailed analysis of the engineered systems involved.

The natural gas consists to more than 90 % of methane. Therefore the properties of this material are used.

Data: density at standard conditions $\rho = 0.714$ kg/m³, $R = 518.26$ J/(kg · K), $\kappa = 1.2$, $\rho'_{\text{ga}} = 0.552$, $d_0 = \sqrt{2F \cdot 4/\pi}$, enthalpy of combustion $H = 35,800$ kJ/Nm³, compressibility factor $Z = 0.85$, gas temperature $T_1 = 288.15$ K, discharge coefficient $\mu = 0.61$, atmospheric pressure $p_1 = 1$ bar, humidity of the air $\varphi = 20$ %

Probit equations for determining conditional probabilities of death from

- blast wave: Eq. (B.22)
- heat radiation: Eq. (B.29)

10.11.1 Expected Frequencies of Occurrence, Release Processes and Relevant Accident Consequences

10.11.1.1 Expected Frequency of Pipeline Rupture and Conditional Probability for Ignition

Only the total failure of the pipeline is considered. It is regarded as dominating all leak sizes.

This frequency can be derived from [81] where the rate for gas release is given as 5.8×10^{-4} per km and year. About 9 % of this value represent spontaneous total rupture.

It is assumed for the accident consequence calculation that the relevant pipeline section has a length of 10 m. The expected frequency for a total failure in this section then is

$$H = 0.01 \text{ km} \cdot 0.09 \cdot 5.8 \times 10^{-4} (\text{km a})^{-1} = 5.22 \times 10^{-7} \text{ a}^{-1}$$

Because of the vicinity of residential areas the conditional probability of ignition after release is assumed to be

$$P_{\text{ignition}} = 0.9$$

10.11.1.2 Mass Flow Rate and Released Mass

The mass flow rate is calculated according to Sect. 7.4.3 (cf. Example 10.4). It has to be observed that total rupture implies an open cross sectional area on both ends of the pipe, so that the entire aperture is two times the cross sectional area of the pipe.

Since $w = p_2/p_1 < w_{\text{crit}}$, i.e. $1.43 \times 10^{-2} < 0.545$ discharge is critical. In order to assess the mass flow rate the density of the gas at operating conditions is calculated using Eq. (7.10)

$$\begin{aligned} \rho_1 &= \frac{p_1}{Z \cdot R \cdot T_1} = \frac{7,000,000 \text{ Pa}}{0.85 \cdot 518.26 \frac{\text{J}}{\text{kg} \cdot \text{K}} \cdot 288.15 \text{ K}} = 55.15 \frac{\text{kg}}{\text{m}^3} \\ \dot{m}_{\text{max}} &= \mu \cdot F \cdot \left\{ \rho_1 p_1 \kappa \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa+1}{\kappa-1}} \right\}^{1/2} \\ &= 0.61 \cdot 2 \cdot 0.2027 \text{ m}^2 \cdot \left[55.15 \frac{\text{kg}}{\text{m}^3} \cdot 7,000,000 \cdot 1.2 \cdot 0.3505 \right]^{1/2} = 3,151.2 \frac{\text{kg}}{\text{s}} \end{aligned}$$

10.11.2 Accident Consequences

10.11.2.1 Fireball

The calculation follows the procedure of Sect. 10.2.6.1. It is assumed that the released gas ignites after 10 s. Hence a total mass of $W = 3,151.2 \text{ kg/s} \cdot 10 \text{ s} = 31,512 \text{ kg}$ is available for the fireball (thereafter a jet fire might occur at the aperture).

The diameter of the fireball is determined according to Eq. (10.150). We obtain

$$D = k_1 \cdot m^{n_1} = 5.8 \cdot 31,512^{1/3} = 183.2 \text{ m}$$

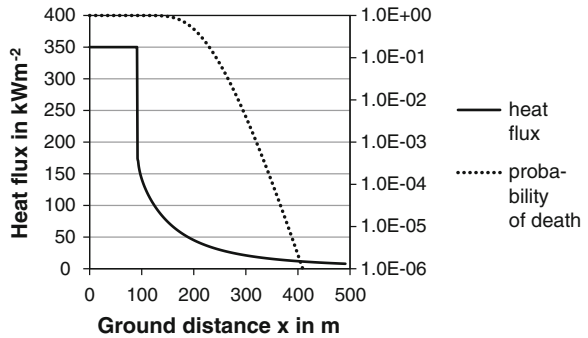
and for its duration according to Eq. (10.151) with the constants of no. 2 from Table 10.6

$$t_d = k_2 \cdot m^{n_2} = 2.57 \cdot 31,512^{1/6} = 14.4 \text{ s}$$

The radius of the fireball then is $R = 91.6 \text{ m}$

Assuming an SEP of $q''_{\text{act}} = 350 \text{ kW/m}^2$ the procedure of Example 10.23 gives the distance-dependent heat flux density and the conditional probability of death shown in Fig. 10.44.

Fig. 10.44 Heat flux (*left-hand ordinate*) as a function of the distance on the ground for a fireball (inside the fireball the heat flux density is set fictitiously equal to 350 kW/m^2) and conditional probability of death (*right hand ordinate*)



10.11.2.2 Torch Fire

In case of a leakage from a high pressure pipeline the usual relationships for flame dimensions of Sect. 10.6.1.1 cannot be applied, since they are only valid for pool fires (low initial momentum).

According to [82] the flame length for a flame assumed as cylindrical is

$$h = \frac{\frac{b_1 + b_2}{J_m \cdot b_1} + (\rho'_{\text{ga}} - 1)}{\frac{0.32 \cdot \rho'_{\text{ga}}}{d_0 \sqrt{\mu \cdot \rho'_{\text{g0}}}}}$$

Its diameter is

$$d = \frac{2d_0\sqrt{\mu}}{3K_1\sqrt{b_2}}$$

In the above equations we have:

$$\begin{aligned}\rho'_{g0} &= \rho'_{ga} \frac{p_i}{p_a} \left(\frac{2}{\kappa + 1} \right)^{\frac{1}{\kappa-1}} \\ b_1 &= 50.5 + 48.2 \cdot \rho'_{ga} - 9.95 \cdot (\rho'_{ga})^2 \\ b_2 &= 23 + 41 \cdot \rho'_{ga} \\ K_1 &= \frac{0.32 \cdot \rho'_{ga}}{\sqrt{\rho'_{g0}}} \cdot \frac{b_1}{b_1 + b_2} \cdot J_m\end{aligned}$$

- d_0 diameter of the leak aperture in m
- p_a atmospheric pressure in Pa
- p_i inside air pressure in Pa
- ρ'_{ga} density of gas at atmospheric conditions relative to that of air
- ρ'_{g0} density of gas at the outlet conditions relative to that of air
- μ discharge coefficient
- J_m volumetric fraction at ignition limit

The best agreement with experimental values is reached, if the cylinder length is calculated with $J_m = 13$ vol% and its diameter with $J_m = 5$ vol%.

For solving the problem we need the view factor for vertical cylinders, which is [82]

$$\begin{aligned}F &= \frac{1}{\pi \cdot B} \cdot \arctan \frac{A}{\sqrt{B^2 - 1}} + \frac{A}{\pi} \\ &\cdot \left(\frac{X - 2 \cdot B}{B \cdot \sqrt{XY}} \cdot \arctan \sqrt{\frac{X \cdot (B - 1)}{Y \cdot (B + 1)}} - \frac{1}{B} \cdot \arctan \sqrt{\frac{B - 1}{B + 1}} \right)\end{aligned}$$

with

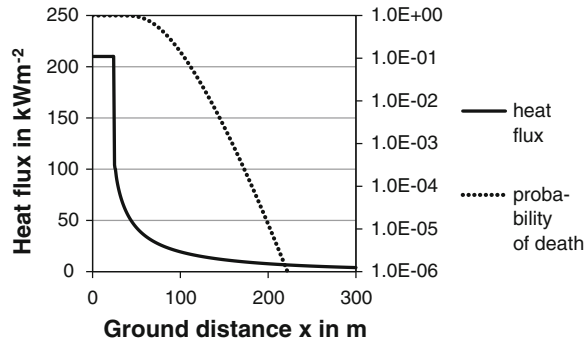
$$A = \frac{2h}{d} \quad \text{and} \quad B = \frac{2x}{d}$$

and

$$X = (B + 1)^2 + A^2 \quad \text{and} \quad Y = (B - 1)^2 + A^2$$

In these equations x is the distance from the centre of the bottom of the cylinder, so that the calculation starts for a distance of $x = d/2$ (side of the cylinder).

Fig. 10.45 Heat flux (*left hand ordinate*) and conditional probability of death for an exposure of 30 s duration (*right hand ordinate*) as functions of the distance on the ground for the torch fire (inside the flame fictitiously $q''_{act} = 210 \text{ kW/m}^2$ is assumed)



With the numerical values we obtain

$$d = 49.6 \text{ m and } h = 186.3 \text{ m}$$

An SEP of 210 kW/m^2 , i.e. $q''_{act} = 210 \text{ kW/m}^2$, is used for the torch fire. The heat flux and the conditional probability of death as functions of the distance on the ground are shown in Fig. 10.45.

10.11.2.3 Flash Fire

The range of dangerous impacts from a flash fire is smaller or equal to that of a torch fire. Therefore its impact is set equal to that of a torch fire.

10.11.2.4 Explosion in the Pressure Reducing and Metering Station

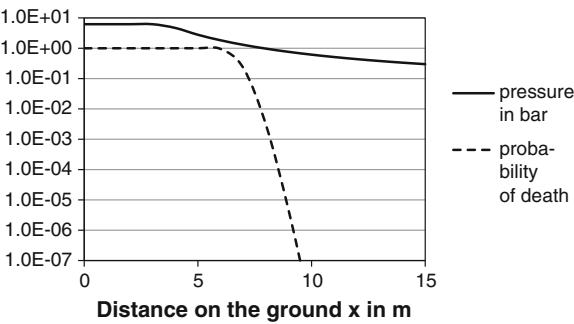
In the investigated section of the pipeline there is a pressure reducing and metering station. Inside this station a pipe leak is expected with a frequency of $7.0 \times 10^{-2} \text{ a}^{-1}$. As a consequence of this leak the station is filled with gas which explodes after ignition.

Dimensions of the gas filled space in the station	$2.95 \cdot 5.75 \cdot 4.85 = 82.3 \text{ m}^3$
Diameter of the ingoing pipe	4'' (114.3 mm)
Wall thickness	5 mm
Inlet pressure	25–64 bar
Outlet pressure	2–5 bar
Volumetric gas flow rate:	2,000 Nm ³ /h

For calculating the energy of combustion, E , a gas concentration of 10 vol% is assumed, so that 8.23 Nm^3 are available for combustion. Hence we have $E = 8.23 \text{ Nm}^3 \cdot 35,800 \text{ kJ/Nm}^3 = 294,634 \text{ kJ}$.

The distance-dependent pressure was calculated using the TNT equivalent model of Sect. 10.6.3.1. A yield factor of 20 % was assumed. The use of curve no. 7 of the multienergy mode, whose application is recommended in [80], does not lead to substantially different results. Pressure and conditional probability of death as functions of the distance on the ground are shown in Fig. 10.46.

Fig. 10.46 Pressure and conditional probability of death caused by an explosion in the pressure reducing and metering station as functions of the distance on the ground from the centre of the explosion



10.11.3 Determination of the Expected Frequencies for the Occurrence of the Scenarios and Representation of the Risk

The scenarios and the conditional probabilities for their occurrence used in [80] are shown in Table 10.17. A comparison with Table 10.15 illustrates how different the valuations in this field are.

Table 10.17 Events and conditional probabilities of occurrence for developing scenarios

Event	Conditional probability	Event	Conditional probability
Immediate ignition	0.25	Fireball	0.34
		Torch fire	0.66
No immediate ignition, formation of a gas cloud	0.75	Flash fire	0.9
		No ignition	0.1

With this information the event tree of Fig. 10.47 is developed, which shows the different expected scenarios and their corresponding expected frequencies of occurrence.

For determining the risk the phenomena “torch fire” and “flash fire” are combined. No differentiation is made between immediate and delayed ignition. Thus the following expected frequencies of occurrence result:

Fireball	$4.44 \times 10^{-8} \text{ a}^{-1}$
Torch fire	$4.38 \times 10^{-7} \text{ a}^{-1}$
Explosion in the pressure reducing and metering station	$7.00 \times 10^{-2} \text{ a}^{-1}$

The latter is an additional scenario, but it is not included in the event tree.

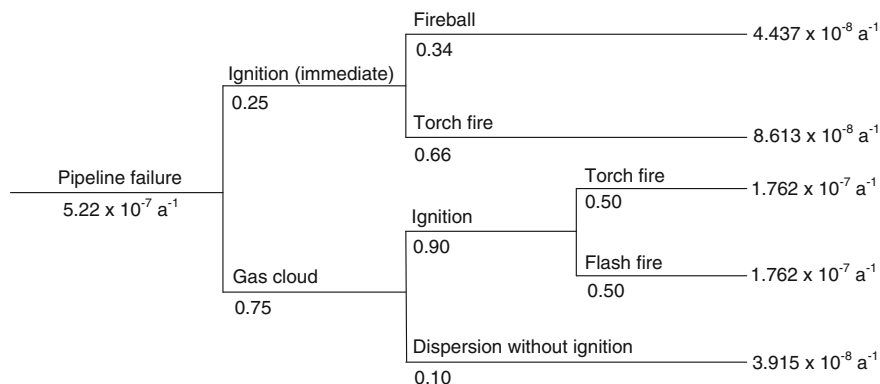


Fig. 10.47 Potential event sequences after pipeline failure with indication of their expected frequencies of occurrence and conditional probabilities for the occurrence of the different conceivable phenomena

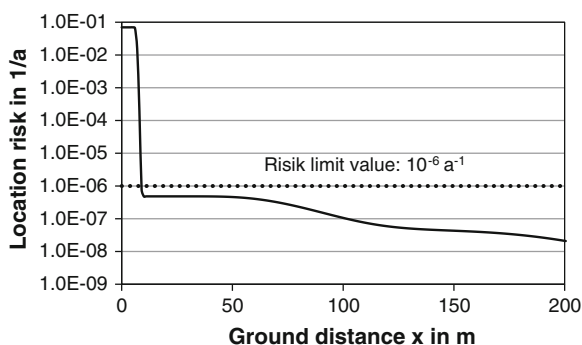
10.11.3.1 Location Risk

Accounting for all damaging phenomena we obtain the location risk in the vicinity of the pipeline and the pressure reducing and measuring station. This risk is equal to the individual risk if a person stays for 24 h at that location. The risk is shown in Fig. 10.48.

When comparing the calculated risk with the risk limit value it is assumed that the pipeline constitutes the only engineering risk for the neighbouring population. The limit value may then be “fully used up”. If there were to exist further technological risks their sum would have to be compared with the limit value and the permissible risk for the pipeline would have to be reduced accordingly.

The calculated risk falls below the risk value applicable for death in the Netherlands for the individual risk at a distance of 8–9 m. This value is $1.0 \times 10^{-6} \text{ a}^{-1}$ and applies for a duration of stay of 24 h (in reality it is therefore a location risk limit). The short range of 8–9 m justifies the choice of a pipe section of 10 m length initially made.

Fig. 10.48 Location risk for death as a function of distance from the source of the risk



10.11.3.2 Collective Risk

In order to calculate the collective, population or societal risk we assume an average population density of $\rho_B = 1,200 \text{ km}^{-2}$ (Ruhr area). It is further assumed that the residential area gets as close as $a = 30 \text{ m}$ to the hazard source (pipeline and station). For simplicity's sake we conservatively suppose that the population is permanently present.

In the relevant segment of a circle with an outer radius of $R = 300 \text{ m}$ (truncation at 300 m is justified because the location risk amounts to $1.8 \times 10^{-10} \text{ a}^{-1}$ there) we find $R^2 \cdot \alpha \cdot \rho_B = (300 \text{ m})^2 \cdot 1.4706 \cdot 1,200 \times 10^{-6} = 158.8$ people. In this $\alpha = \arccos \frac{0.03}{0.3} = 1.4706$ is half the central angle. To every radius r_i ($i = 1, \dots, I$) (the discretization is chosen such that in the segment between r_i and r_{i-1} there is just one person) we assign a probability of death, which is calculated as $p_i = 0.25 \cdot 0.34 \cdot p_{b,i} + (0.75 \cdot 0.9 + 0.25 \cdot 0.66) \cdot p_{f,i}$. The numerical values are taken from Table 10.17, $p_{b,i}$ is the probability of death from fireball radiation and $p_{f,i}$ that from the torch fire at distance r_i .

The number of persons in the ring segment between r_{i+1} and r_i is

$$N_i = \rho_B \cdot \left(r_{i+1}^2 \arccos \frac{a}{r_{i+1}} - r_i^2 \arccos \frac{a}{r_i} \right)$$

The expected frequency for $>N$ fatalities to occur is calculated as follows. One forms the expression

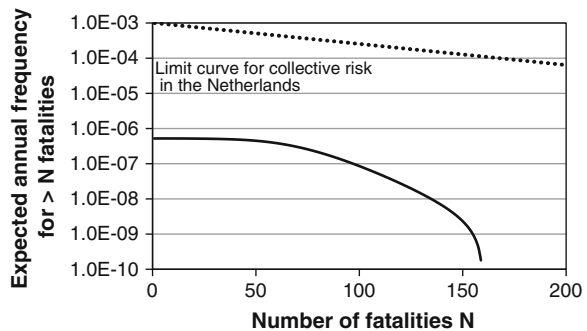
$$C_{i-1} = p_{m,i-1} + C_i \cdot (1 - p_{m,i-1}) \quad i = I, I-1, I-2, \dots, i_{\min}$$

where

$$p_{m,i-1} = \frac{p_i + p_{i-1}}{2}$$

is the mean value for the probability in the ring segment between r_i and r_{i-1} ; $r_{i_{\min}-1}$ is the distance of 30 m . It must be made sure that in any ring segment we have just one person. We then form

Fig. 10.49 Complementary frequency distribution for the collective risk caused by the pipeline



$$F\{N_i > N\} = H \cdot C_i$$

The result is shown in Fig. 10.49.

It is obvious that the criterion for the collective risk is fulfilled, too.

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If safety is too expensive, try an accident
Attributed to Trevor Kletz

During the 1990s the concept of Safety Integrity Levels (SIL) was developed [1]. It serves to assess safety-related systems and concerns all components and sub-systems required to realize safety functions from the sensor to the final element. Apart from that it applies to application software, which was developed for systems with limited variability language (no branching) or programmable logic controllers (PLC).

Within the framework of [1] the standards [2]–[4] refer to the process industry. In these standards the continuous spectrum of failure frequencies and unavailabilities is divided into four discrete bands, the safety integrity levels, as shown in Tables 11.1 and 11.2. The bands apply to safety-related systems. These are systems which play a role for safety and can therefore in addition to safety systems also comprise elements from the operating level. The bands in Tables 11.1 and 11.2 are targets whose selection and fulfilment are presented below.

The standards [1]–[3] concern the entire life cycle of a plant (“safety life cycle”), i.e. “all activities required for realizing safety functions during a period which begins with the concept phase of a project and ends when all safety functions are no longer available for use.” In addition to quantitative requirements the standards contain numerous qualitative requirements, which are not discussed here. However, it must be borne in mind that fulfilling the qualitative requirements does not automatically lead to the quantitative requirements being fulfilled.

The fundamental idea of the concept is that a plant or an establishment may only cause a risk below a limit value (tolerable risk). This value enables one to determine the tolerable frequency of the undesired event or events (e.g. fires, explosions, toxic releases). If that frequency and the expected number of demands of the safety barriers (expected frequency of initiating events) are known, the maximum probability of failure on demand of the safety-related systems can be

Table 11.1 Safety integrity levels: probabilities of failure on demand (pfd) (after [1])

Type of demand (stand-by, low demand rate)	
Safety integrity level (SIL)	Target bands for the average probability of failure on demand (pfd) (unavailability)
4	$\geq 10^{-5}$ to $<10^{-4}$
3	$\geq 10^{-4}$ to $<10^{-3}$
2	$\geq 10^{-3}$ to $<10^{-2}$
1	$\geq 10^{-2}$ to $<10^{-1}$

Table 11.2 Safety integrity levels: frequencies of dangerous failures of the safety-related function in h^{-1} (after [1])

Type of demand (continuous demand, high demand rate) ^a	
Safety integrity level (SIL)	Target bands for the frequency of dangerous failures of the safety-related function in h^{-1}
4	$\geq 10^{-9}$ to $<10^{-8}$
3	$\geq 10^{-8}$ to $<10^{-7}$
2	$\geq 10^{-7}$ to $<10^{-6}$
1	$\geq 10^{-6}$ to $<10^{-5}$

^aTo be applied as well to standby systems if these are demanded more frequently than once per year

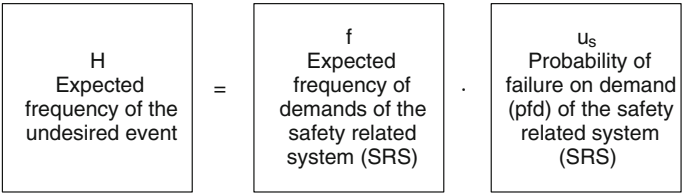


Fig. 11.1 Schematic for determining the frequency of undesired events in engineered systems

derived (vid. Fig. 11.1). Basically we are dealing with a reversal of the risk assessment shown in Figs. 8.1 and 8.2. We proceed in theses diagrams from right to left instead of going from left to right.

It should be remembered that the procedure applies to different kinds of risk, for example health damage, death of staff members or people from the public in general, damage to the environment or to property. Quantitative targets, which are required for the application of the procedure and may differ depending on the kind of risk considered, are not given in [2–4]. However, the standard makes proposals by way of information on how such values may be fixed [4]. Amongst others, we can read there “for fixing the tolerable risk for a particular application amongst others the following topics are considered”:

- Guidelines of administrations which formulate safety rules,
- Discussions and agreements with different parties involved in the application,
- Industrial standards and guidelines,
- Recommendations from industry and from science experts,
- Legal requirements of a general nature as well as those directly referring to the application. (vid. Sect. 8.2).

As well by way of information the following methods for determining the required SIL class are listed in [4]:

- calibrated risk graph,
- LOPA (vid. Sect. 9.1.2.6).

In [3] the following methods for determining the probability of failure on demand of the safety-related function are mentioned:

- reliability block diagram,
- fault tree analysis (Sect. 9.1.2.7 et seqq.),
- Markov analysis (Sect. 9.5.2.2).

Out of these, fault tree analysis is applied in what follows.

As usual for safety analyses a team should be formed for determining the SIL classifications. It should comprise the following experts [4]:

- process specialist,
- PCE engineer,
- plant manager,
- safety specialist,
- collaborator experienced in operating the process in question.

A relationship exists between the requirements from Tables 11.1 and 11.2, which can be described as follows. As already shown in Example 9.17, the expected frequency for system failure is the product of the expected number of demands of the safety system and its unavailability (probability of failure on demand, pfd), i.e.

$$H = f \cdot u_s \quad (11.1)$$

This is illustrated by Fig. 11.1.

Equation (9.89) describes the maximum unavailability of a component subject to periodic functional tests. This equation can be applied to the safety system as a whole. One then obtains (in the standard the approximation to the exponential function for small arguments is always used)

$$u_s = \lambda_s \cdot \theta \quad (11.2)$$

The “functional tests” in this case are the operational demands of the safety system which occur with frequency f and hence in time intervals $\theta = 1/f$.

Inserting this into Eq. (11.1) we obtain

$$H = \lambda_s \quad (11.3)$$

i.e. the maximum permissible failure rate of the safety-related system is equal to the frequency of the undesired event.

The procedure of applying the standard is illustrated by the following examples. It must be borne in mind that the SIL requirements are only fulfilled, if

- the failure rates remain the same over the entire life cycle,
- the test intervals are not modified during the entire life cycle,
- the functional tests are complete (sensor to final element),
- failures are discovered with certainty during functional tests and the failed components are repaired in such a way that they can be regarded as “as good as new” after repair (vid. Sect. 9.5.2.1).

Example 11.1 Retrofit of the nitrator for producing hexogen

From Table 9.48 we infer that the total expected frequency of initiating events leading to the explosion of the nitrator amounts to $f = 1.36 \text{ a}^{-1}$. Furthermore, one finds there that the unavailability of the existing safety-related system is $u_s = 4.0 \times 10^{-2} \text{ a}^{-1} / 1.36 \text{ a}^{-1} = 0.0295$.

Employees are present at the reactor during 10 % of the time of the year ($p_B = 0.1$). They then move at a distance of less than 5 m around the reactor. The calculations along the lines of Example 10.23 show that in such case the probability of death is $p_{\text{death}} = 1$, if an explosion occurs, even when neglecting missile flight.

The company internal safety target for the individual risk of death is $R_i \leq 10^{-4} \text{ a}^{-1}$.

In order to reach this target and additional safety barrier is required whose SIL is to be determined. Its unavailability (pfd) is denoted by u_z . The expected frequency of demands of this additional safety barrier amounts to $f \times u_s = 1.36 \text{ a}^{-1} \times 0.0295 = 0.0401 \text{ a}^{-1}$, i.e. less than once a year. That is why the assessment is based on the targets of Table 11.1.

Data: failure rates: temperature switch $\lambda_1 = 61.7 \times 10^{-6}$, pneumatic valve $\lambda_2 = 20 \times 10^{-6} \text{ a}^{-1}$, intervals between functional tests for both components $\theta = 4,380 \text{ h}$

Solution

$$u_z = \frac{R_i}{f \cdot u_s \cdot p_B \cdot p_{\text{death}}} = \frac{10^{-4} \text{ a}^{-1}}{1.36 \text{ a}^{-1} \times 0.0295 \times 0.1 \times 1} \leq 0.0249$$

A look at Table 11.1 shows that the additional safety barrier must satisfy the requirements of SIL1. For this purpose the manual valve in the bypass of the

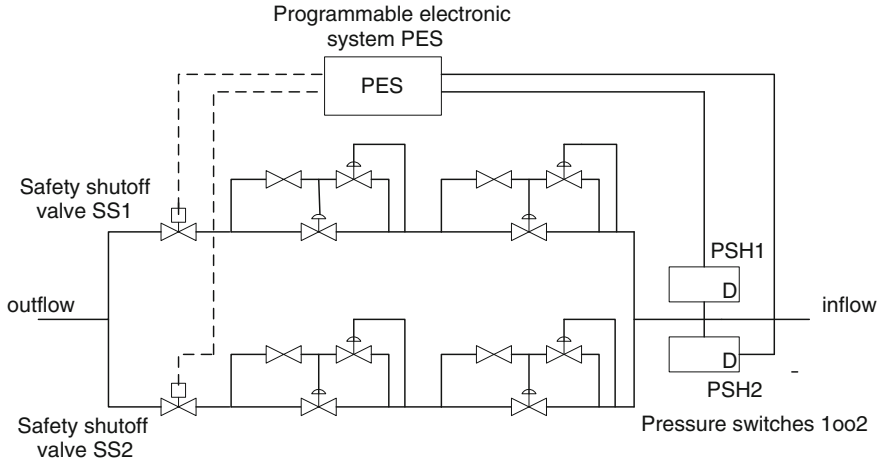


Fig. 11.2 Pressure control system (the planned safety shutoff system is already shown) (after [5])

coolant flow control valve in Figs. 4.10 and 4.11 is replaced by a pneumatic valve, which is opened if the set point of an additional dedicated temperature switch is reached.

The new system is a series system in the sense of reliability (vid. Sect. 9.4.1). That is why we obtain its unavailability by using Eqs. (9.61) and (9.90), which give

$$\begin{aligned}
 u_z &= u_1 + u_2 - u_1 \cdot u_2 = 1 + \frac{1}{61.7 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} \cdot \left(e^{-61.7 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} - 1 \right) \\
 &\quad + 1 + \frac{1}{20 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} \cdot \left(e^{-20 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} - 1 \right) \\
 &\quad - \left[1 + \frac{1}{61.7 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} \cdot \left(e^{-61.7 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} - 1 \right) \right] \cdot \\
 &\quad \left[1 + \frac{1}{20 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} \cdot \left(e^{-20 \times 10^{-6} \text{h}^{-1} \times 4,380 \text{h}} - 1 \right) \right] \\
 &= 0.1237 + 0.04255 - 0.005263 = 0.1610
 \end{aligned}$$

i.e., the new safety barrier does not satisfy the SIL 1 target. Therefore the interval between functional tests is reduced to 2 weeks ($\theta = 336 \text{ h}$). This leads to

$$u_z = u_1 + u_2 - u_1 \cdot u_2 = 0.01029 + 0.00335 - 3.45 \times 10^{-5} = 0.0136$$

Now the SIL 1 target is fulfilled.

This shows, amongst others, that the intervals for functional tests are constitutive for SIL classification. Only if they are observed, is the SIL class satisfied. $\square$

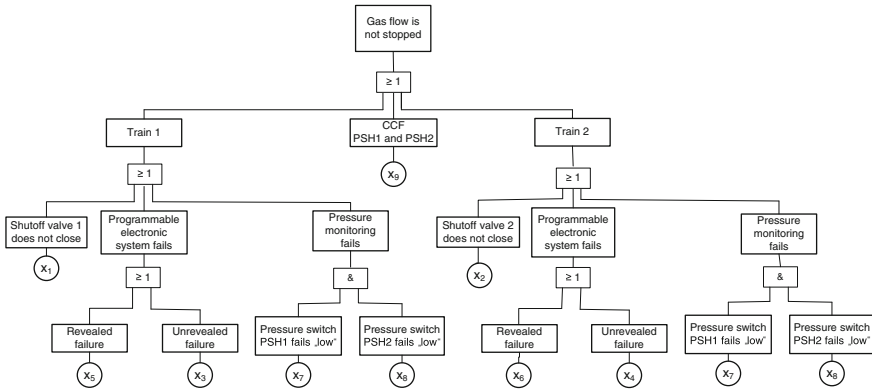


Fig. 11.3 Fault tree for the additional safety system

Example 11.2 Pressure control system (after [5])

A plant supplying gas to offsite is considered. The gas pressure is regulated by a two-train regulating station, as shown in Fig. 11.2. A HAZOP study has produced the following insights. A failure of the regulating station would result in high pressure downstream. This in turn leads to pipe rupture, gas release and an explosion causing one fatality. Operating experience shows that the expected frequency of overpressure following the failure of the regulating valves or their pilot valves is $f = 2.5 \times 10^{-3} \text{ a}^{-1}$.

Since we are dealing with a risk outside the plant, a target value for the maximum tolerable risk of 10^{-5} a^{-1} (this is applicable to existing plants in the U.K., vid. Sect. 8.2) is stipulated.

It is assumed that a quantitative risk analysis showed, that the probability for overpressure, pipe rupture and ignition of the released gas is $p_z = 0.2$. Furthermore it was found that the conditional probability for death amounts to $p_{\text{death}} = 0.5$.

It is assumed that the plant causes a total of 10 equally large risks for the same group of population (e.g. tanker deliveries, other pipelines, site explosion), so that the system under consideration may only use up 1/10 of the maximum tolerable risk target.

Thus we obtain a tolerable frequency for failures of the system of Fig. 11.2, H_z , of

$$H_z = \frac{10^{-5} \text{ a}^{-1}}{10 (\text{risks}) \cdot 0.2 \cdot 0.5} = 10^{-5} \text{ a}^{-1}$$

Since $2.5 \times 10^{-3} \text{ a}^{-1} > 10^{-5} \text{ a}^{-1}$, the installation of an additional protection system consisting of a redundant pressure measurement, a programmable electronic system (PES) and two safety shutoff valves is envisaged. The system closes the shutoff valves in each stream (SS1 and SS2) following the signal for high pressure from the independent redundant measurement (1oo2) of the pressure upstream by PSH1 and PSH2. Each valve (SS1 and SS2) has its dedicated non-redundant channel inside the PES.

The objective of the modification is to make the protection system fulfil the target value of 10^{-5} a^{-1} . This implies a maximum tolerable unavailability (pfd) of

$$u_z = \frac{10^{-5} \text{ a}^{-1}}{2.5 \cdot 10^{-3} \text{ a}^{-1}} = 4 \times 10^{-3}, \text{ i.e. SIL 2 (according to Table 11.1)}$$

The quantification is done on the basis of a qualitative analysis, which is reflected by the fault tree of Fig. 11.3, and its evaluation in terms of probabilities.

The fault tree of Fig. 11.3 has the following minimal cut sets

$$\begin{aligned} \kappa_1 &= x_1; & \kappa_2 &= x_2; & \kappa_3 &= x_3; & \kappa_4 &= x_4; & \kappa_5 &= x_5 \\ \kappa_6 &= x_6; & \kappa_7 &= x_7 x_8; & \kappa_9 &= x_9 \end{aligned}$$

and the approximate expected value of its structure function (cf. Eq. 9.75)

$$E[\Psi(\vec{x})] \approx \sum_{i=1}^9 E[\kappa_i]$$

The numerical evaluation requires the unavailabilities of the components involved. These are given below. The following failure rates and assumptions are used:

1. Shutoff valve: $\lambda = 0.8 \times 10^{-6} \text{ h}^{-1}$; PES: $\lambda = 0.25 \times 10^{-6} \text{ h}^{-1}$; pressure switch: $\lambda = 0.5 \times 10^{-6} \text{ h}^{-1}$.
 2. The average time of repair after failure detection (MTTR) amounts $T_r = 4 \text{ h}$.
 3. The auto-test cycle of the PES is less than 5 min. This covers 90 % of the failures. Hence, the mean duration of unavailability (MDT) in Eq. (9.111) amounts to $T_r = 4.083 \text{ h}$.
 4. The functional test intervals of those components which are not tested automatically are $\theta = 8,000 \text{ h}$. It is assumed that all failures are detected and repaired. Equation (9.90) is used.
 5. There are no waiting times before a repair begins due to other commitments of the personnel.
 6. The fraction of failures due to a common cause (CCF) is assumed to be 10 % [$\beta = 0.1$ in Eq. (9.113)] of the total failure rate.
- (a) x_1 : shutoff valve SS1 does not close according to Eq. (9.90)¹

$$\begin{aligned} u_1 &= 1 + \frac{1}{0.8 \times 10^{-6} \text{ h}^{-1} \times 8,000 \text{ h}} \cdot \left(e^{-0.8 \times 10^{-6} \text{ h}^{-1} \times 8,000 \text{ h}} - 1 \right) \\ &= 3.19 \times 10^{-3} \quad \mathbf{(0.0032)} \end{aligned}$$

(b) x_2 : shutoff valve SS2 does not close according to Eq. (9.90)

¹ The values in bold print in the brackets result from the application of the approximation $u = \lambda \cdot \theta/2$ used in the standards.

$$u_2 = 1 + \frac{1}{0.8 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} \cdot \left(e^{-0.8 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} - 1 \right)$$

$$= 3.19 \times 10^{-3} \text{ (0.0032)}$$

(c) x_3 : PES output signal 1 fails, unrevealed (undetected) failure according to Eq. (9.90)

$$u_3 = 0.1 \cdot \left[1 + \frac{1}{0.25 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} \cdot \left(e^{-0.25 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} - 1 \right) \right]$$

$$= 9.99 \times 10^{-5} \text{ (0.0001)}$$

(d) x_4 : PES output signal 2 fails, unrevealed (undetected) failure according to Eq. (9.90)

$$u_4 = 0.1 \cdot \left[1 + \frac{1}{0.25 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} \cdot \left(e^{-0.25 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} - 1 \right) \right]$$

$$= 9.99 \times 10^{-5} \text{ (0.0001)}$$

(e) x_5 : PES output signal 1 fails, revealed (detected) failure according to Eq. (9.111)

$$u_5 = 0.9 \cdot \left[1 - \frac{\frac{1}{0.25 \times 10^{-6} \text{h}^{-1}}}{\frac{1}{0.25 \times 10^{-6} \text{h}^{-1}} + 4.083 \text{h}} \right] = 9.19 \times 10^{-7}$$

(f) x_6 : PES output signal 2 fails, detected failure according to Eq. (9.111)

$$u_6 = 0.9 \cdot \left[1 - \frac{\frac{1}{0.25 \times 10^{-6} \text{h}^{-1}}}{\frac{1}{0.25 \times 10^{-6} \text{h}^{-1}} + 4.083 \text{h}} \right] = 9.19 \times 10^{-7}$$

(g) x_7 : pressure switch PSH1 fails “low” according to Eq. (9.90)

$$u_7 = 1 + \frac{1}{0.9 \times 0.5 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} \cdot \left(e^{-0.9 \times 0.5 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} - 1 \right)$$

$$= 1.798 \times 10^{-3} \text{ (0.0018)}$$

(h) x_8 : pressure switch PSH2 fails “low” according to Eq. (9.90)

$$u_8 = 1 + \frac{1}{0.9 \times 0.5 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} \cdot \left(e^{-0.9 \times 0.5 \times 10^{-6} \text{h}^{-1} \times 8,000 \text{h}} - 1 \right)$$

$$= 1.798 \times 10^{-3} \quad \mathbf{0.0018}$$

- (i) x_9 : common cause failure (CCF) of the pressure switches according to Eq. (9.90)

$$u_9 = 1 + \frac{1}{0.1 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 8,000 \text{ h}} \cdot \left(e^{-0.1 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 8,000 \text{ h}} - 1 \right)$$

$$= 1.997 \times 10^{-4} \quad \mathbf{0.0002}$$

Evaluation of the structure function leads to an approximate value of

$$E[\Psi(\vec{x})] \approx \sum_{i=1}^9 E[k_i] = 6.78 \times 10^{-3}$$

This value fulfils SIL 2 (vid. Table 11.1) but not the calculated target value. Therefore the test intervals are halved. This leads to the following changes:

- (a) x_1 : shutoff valve SS1 does not close according to Eq. (9.90)

$$u_1 = 1 + \frac{1}{0.8 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} \cdot \left(e^{-0.8 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} - 1 \right)$$

$$= 1.598 \times 10^{-3} \quad (\mathbf{0.0016})$$

- (b) x_2 : shutoff valve SS2 does not close according to Eq. (9.90)

$$u_2 = 1 + \frac{1}{0.8 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} \cdot \left(e^{-0.8 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} - 1 \right)$$

$$= 1.598 \times 10^{-3} \quad (\mathbf{0.0016})$$

- (c) x_3 : PES output signal 1 fails, unrevealed (undetected) failure according to Eq. (9.90)

$$u_3 = 0.1 \cdot \left[1 + \frac{1}{0.25 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} \cdot \left(e^{-0.25 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} - 1 \right) \right]$$

$$= 4.998 \times 10^{-5} \quad (\mathbf{5 \times 10^{-5}})$$

- (d) x_4 : PES output signal 2 fails, unrevealed (undetected) failure according to Eq. (9.90)

$$u_4 = 0.1 \cdot \left[1 + \frac{1}{0.25 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} \cdot \left(e^{-0.25 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} - 1 \right) \right]$$

$$= 4.998 \times 10^{-5} \quad (\mathbf{5 \times 10^{-5}})$$

- (e) x_5 : PES output signal 1 fails, revealed (detected) failure according to Eq. (9.111)

$$u_5 = 0.9 \cdot \left[1 - \frac{\frac{1}{0.25 \times 10^{-6} \text{ h}^{-1}}}{\frac{1}{0.25 \times 10^{-6} \text{ h}^{-1}} + 4.083 \text{ h}} \right] = 9.19 \times 10^{-7}$$

(f) x_6 : PES output signal 2 fails, revealed (detected) failure according to Eq. (9.111)

$$u_6 = 0.9 \cdot \left[1 - \frac{\frac{1}{0.25 \times 10^{-6} \text{ h}^{-1}}}{\frac{1}{0.25 \times 10^{-6} \text{ h}^{-1}} + 4.083 \text{ h}} \right] = 9.19 \times 10^{-7}$$

(g) x_7 : pressure switch PSH1 fails “low” according to Eq. (9.90)

$$\begin{aligned} u_7 &= 1 + \frac{1}{0.9 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} \cdot \left(e^{-0.9 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} - 1 \right) \\ &= 8.994 \times 10^{-4} \quad (9 \times 10^{-4}) \end{aligned}$$

(h) x_8 : pressure switch PSH2 fails “low” according to Eq. (9.90)

$$\begin{aligned} u_8 &= 1 + \frac{1}{0.9 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} \cdot \left(e^{-0.9 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} - 1 \right) \\ &= 8.994 \times 10^{-4} \quad (9 \times 10^{-4}) \end{aligned}$$

(i) x_9 : common cause failure (CCF) of the pressure switches according to Eq. (9.90)

$$\begin{aligned} u_9 &= 1 + \frac{1}{0.1 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} \cdot \left(e^{-0.1 \times 0.5 \times 10^{-6} \text{ h}^{-1} \times 4,000 \text{ h}} - 1 \right) \\ &= 9,993 \times 10^{-5} \quad (1 \times 10^{-5}) \end{aligned}$$

Now we obtain the numerical result

$$E[\Psi(\vec{x})] \approx \sum_{i=1}^9 E[k_i] = 3.39 \times 10^{-3}$$

which lies below the target value of 4×10^{-3} and thus fulfils the target. □

Example 11.3 Gas with excessive temperature flows into a vessel (after [5])

A gas from a process is cooled before it flows into a vessel. The undesired event is the cooling failure which would result in an excessive temperature in the vessel. This causes the vessel to burst and the released gas is ignited. Three fatalities are expected. The following probabilities are assumed to apply:

Conditional probability of vessel burst: 0.05

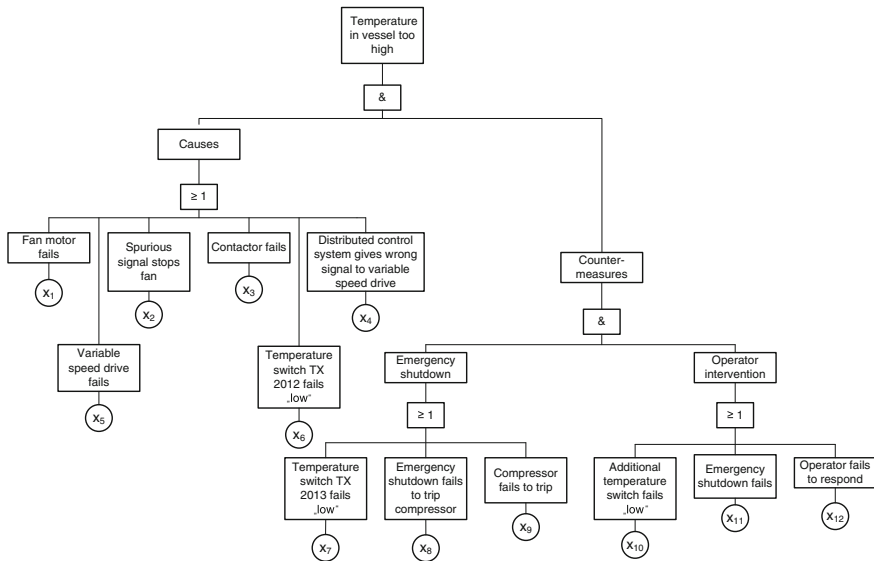


Fig. 11.4 Fault tree for the undesired event “temperature in the vessel too high”

Conditional probability for people being in the vicinity of the vessel (pessimistic): 0.5

Conditional probability for ignition: 0.9

Conditional probability of death: 1.0

If a maximum tolerable risk of 10^{-5} a^{-1} for up to three fatalities is assumed, the maximum tolerable frequency of system failure (the system is demanded more than once per year, vid. Table 11.2) is

$$H_{\max} = \frac{10^{-5} \text{ a}^{-1}}{0.05 \times 0.5 \times 0.9} = 4.44 \times 10^{-4} \text{ a}^{-1}$$

The fault tree for the system is shown in Fig. 11.4. Table 11.3 contains the data for its quantification.

The system has 54 minimal cut sets. They result from combining the 6 initiating events (causes) with the 9 minimal cut sets for the unavailability of the system function (counter-measures).

The total expected frequency of the initiating events amounts to $f = 1.26 \text{ a}^{-1}$ and the unavailability of the system function to $u_s = 0.0206$.

With these values the expected frequency for excessive temperature in the vessel is

$$H_s = f \cdot u_s = \lambda_s = 1.26 \text{ a}^{-1} \times 0.0206 = 0.0327 \text{ a}^{-1} > ; H_{\max}$$

In order to fulfil the target weekly functional tests are adopted. These lead to the values in bold print in Table 11.3. Using them we obtain an unavailability of the system function of

Table 11.3 Data for quantifying the fault tree of Fig. 11.4 (modification in bold print)

Primary event	Designation	Failure rate in 10^{-6} h^{-1}	Interval between functional tests θ in h	Unavailability according to Eq. (9.90)
x_1	Fan motor fails ^a	77.9		
x_2	Spurious signal stops fan ^a	0.37		
x_3	Contactors fails ^a	2.0		
x_4	Distributed control system gives wrong signal to variable speed drive ^a	0.37		
x_5	Variable speed drive fails ^a	2.0		
x_6	Temperature switch TX 2012 fails “low” ^a	61.7		
x_7	Temperature switch TX 2013 fails “low”	61.7	4,380	0.14
			168	0.00518
x_8	Emergency shutdown fails to trip compressor	0.37	4,380	0.00081
			168	0.000031
x_9	Compressor fails to trip	2.0	4,380	0.00438
			168	0.000168
x_{10}	Additional temperature switch fails “low”	61.7	4,380	0.14
			168	0.00518
x_{11}	Emergency shutdown fails	0.5	4,380	0.0011
			168	0.000042
x_{12}	Operator fails to respond	0.001 ^b		

^a initiating event; ^bprobability

$$u'_s = 3.35 \times 10^{-5}$$

and an expected frequency for excessive temperature in the vessel of

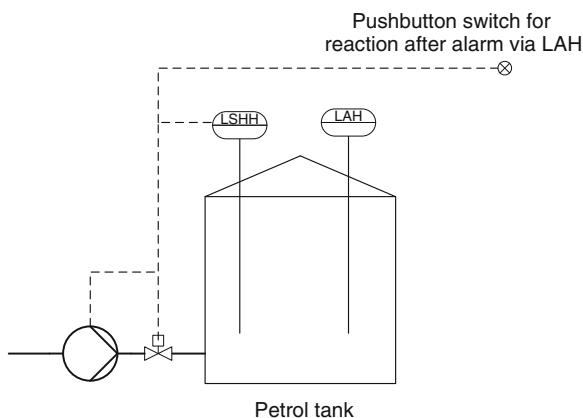
$$H_s = f \cdot u'_s = \lambda'_s = 1.26 \text{ a}^{-1} \times 3.35 \times 10^{-5} = 4.22 \times 10^{-5} \text{ a}^{-1} < H_{\max}$$

This fulfils the target, which is inscribed in SIL 3 according to Table 11.2. □

Case study 11.1 Overfilling of a petrol tank with subsequent fire and explosion

A tank for petrol is filled with a mass flow rate of about 120 kg/s. Filling takes place 13 times per year [6]. In order to avoid possible overfilling and a release of petrol to the environment a level alarm “high” (LAH) is installed. On hearing the alarm the operator should activate a pushbutton switch which stops the pump and closes the shutoff valve by interrupting the electric supply. The motor stops and the

Fig. 11.5 Flow sheet of the petrol tank with shut-off system



valve closes because the excitation ends (“fail safe” design). For this reason the stopping of the motor and the closing of the valve are assumed to be perfect and a possible failure is neglected. The flow sheet of the tank is shown in Fig. 11.5.

For safety reasons an automatic function for stopping the pump and closing the shut-off valve is implemented (LSHH). The safety function is tested completely every half year. For this purpose the level switch LSHH is placed in the position “maintenance”, which disconnects it. After testing the pump stop and the closing of the valve it has to be returned to the position “operation” and thus to be re-connected. The level switch itself is subject to annual functional tests.

The closest point to the tank outside the premises of the plant lies at a distance of 200 m. Taking into consideration further industrial risks at that point the tolerable location risk from “overfilling” should have a maximum value of $H_{\max} = 10^{-6} \text{ a}^{-1}$.

Accounting for the experience with a real accident ignition occurs relatively late, namely after a delay of 2,500 s. At that point in time 300,000 kg of petrol had been spilled of which about 10 % vaporized. Therefore the following calculations are based on $m = 30,000 \text{ kg}$ of petrol vapour.

Which SIL has to be demanded for the safety-related system?

Solution

In the first place the location risk is determined. If the operation level and safety shutoff fail a continuous release of a flammable material (petrol) is to be expected. Scenarios according to Fig. 11.6 are then conceivable.

The probabilities of ignition are calculated according to Sect. 10.10 assuming that the delivery pressure of the fluid is 2 bar, its temperature 15 °C and the strength factor is 3. The results are shown in Table 11.4.

Thus we obtain the conditional probabilities for the endpoints of the event tree of Fig. 11.5, which are listed in Table 11.5.

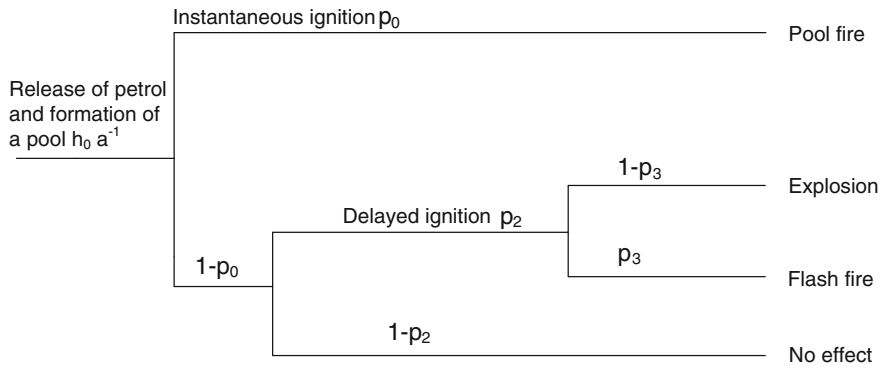


Fig. 11.6 Event tree for the continuous release of petrol

Table 11.4 Ignition probabilities for quantifying the event tree of Fig. 11.5

Immediate ignition p_0	0.02
Delayed ignition p_2	0.91
Flash fire p_3	0.73

Table 11.5 Conditional probabilities for quantifying the endpoints of the event tree of Fig. 11.5

Designation	Calculation	Conditional probability
Pool fire	p_0	0.020
Explosion	$(1 - p_0) \times p_2 \times (1 - p_3)$	0.241
Flash fire	$(1 - p_0) \times p_2 \times p_3$	0.651
No effect	$(1 - p_0) \times (1 - p_2)$	0.088
Sum		1.0

The following phenomena have to be modelled:

- Pool fire according to Sect. 10.6.1
- Flash fire according to Sect. 10.6.2.1
- Explosion according to Sect. 10.6.3.1

The results of the calculations are shown in Table 11.6. The conditional probabilities of death at a distance of 200 m are found there, just as they result from the loads by pool fire etc. Furthermore the conditional probability of death at a distance of 200 m is given. The latter is the product of the conditional probability of the respective type of damage from Table 11.5 and the last column of Table 11.5.

Table 11.6 Conditional probability of death and conditional probabilities for the occurrence of the endpoints of the event tree of Fig. 11.5

Designation	Conditional probability of death at a distance of 200 m	Conditional probability for the occurrence of the endpoints of Fig. 11.5
Pool fire	0.9786	0.0196
Explosion	0	0
Flash fire	0.0145	0.0094
No effect	0	0
Sum: p_{death}		0.029

Fig. 11.7 Distance-dependent conditional probabilities of death, as caused by the different damage mechanisms

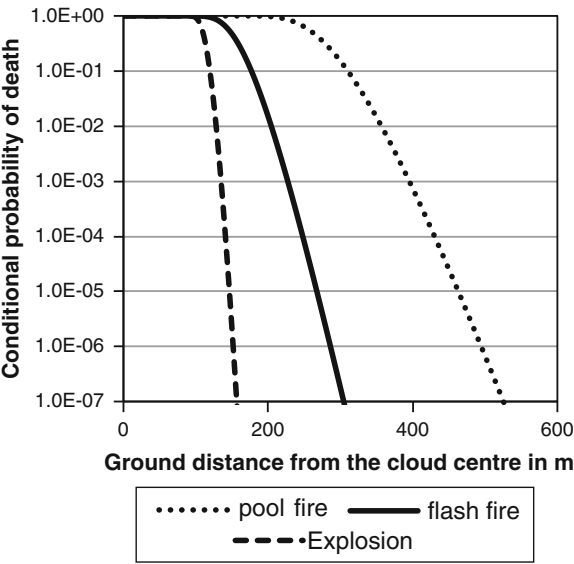


Figure 11.7 shows the conditional probabilities of death for the different damage mechanisms as functions of the ground distance from the centre of the petrol cloud.

Determination of the SIL

In order to determine the required safety integrity level, the expected number of demands on the overfilling protection is calculated in the first place. These demands stem from the operational level, which is modelled by the fault tree of Fig. 11.8. This fault tree is quantified with the data from Table 11.7.

Fig. 11.8 Fault tree for modelling the expected frequency of demands of the protection against overfilling

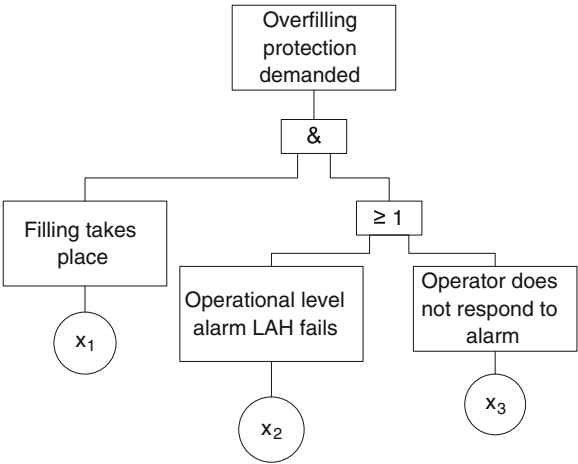


Table 11.7 Data for quantifying the fault tree of Fig. 11.8

Primary event	Designation	Failure rate/failure probability	Time intervals between functional tests
x ₁	Frequency of filling	13 a ⁻¹	
x ₂	Failure of the level alarm LAH	1.6 × 10 ⁻⁶ h ⁻¹	8,760 h a ⁻¹ /13 a ⁻¹ = 673.8 h
x ₃	No operator response to level alarm	0.016	

By applying Eqs. (9.69) and (9.90) an expected frequency of demands of $f = 0.22 \text{ a}^{-1}$ results.

The equation for determining the maximum tolerable unavailability of the safety-related system, u_s , is

$$u_s = \frac{H_{\max}}{f \cdot p_{\text{death}}} = \frac{10^{-6} \text{ a}^{-1}}{0.22 \text{ a}^{-1} \times 0.029} = 1.6 \times 10^{-4}$$

where p_{death} is from Table 11.6. The result means that according to Table 11.1 a design for SIL 3 is required.

Analysis of the existing design

Figure 11.9 shows the fault tree for the overfilling protection in the configuration before the accident happened.

The fault tree of Fig. 11.9 is evaluated using the data of Table 11.8.

Fig. 11.9 Fault tree for the failure of the protection against overfilling

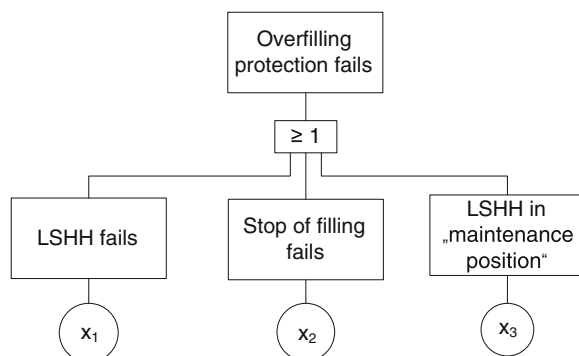


Table 11.8 Data for quantifying the fault tree of Fig. 11.9

Primary event	Designation	Failure rate/failure probability	Time intervals between functional tests
x_1	Level switch LSHH fails	$1.6 \times 10^{-6} \text{ h}^{-1}$	4,380 h
x_2	Stop of filling fails	$2.0 \times 10^{-6} \text{ h}^{-1}$	4,380 h
x_3	LSHH in “maintenance position” because re-connection was forgotten by the operator	0.032	

We are dealing with a series system in the sense of reliability. Hence we obtain a probability of failure on demand (pfd) of

$$\begin{aligned}
 u_s &= u_1 + u_2 + u_3 - u_1 \cdot u_2 - u_1 \cdot u_3 - u_2 \cdot u_3 + u_1 \cdot u_2 \cdot u_3 \\
 &= 0.0035 + 0.0044 + 0.032 - 1.5 \times 10^{-5} - 1.1 \times 10^{-4} \\
 &\quad - 1.4 \times 10^{-4} + 4.9 \times 10^{-7} = 0.04
 \end{aligned}$$

This satisfies SIL 1 and therefore does not fulfil the design target. A look at the numerical values suggests that the system would not even fulfil SIL 3 if it only consisted of LSHH. For this reason the level switch is replaced by a 1-out-of-2 (1oo2) configuration (LSHH in Fig. 11.5 is replaced by LSHH1 and LSHH2) and an interlock is implemented. This interlock impedes the pump from running and keeps the shutoff valve closed, if level switches LSHH1 and LSHH2 are in the position “maintenance”. This is modelled in the fault tree of Fig. 10.10. Furthermore monthly functional testing of the protection against overfilling is implemented.

The fault tree of Fig. 11.10 is quantified with the data from Table 11.9.

The unavailabilities are calculated according to Eq. (9.90) and the fault tree is evaluated according to Eq. (9.75). The common cause failures (CCF) are treated according to Eq. (9.113) with $\beta = 0.1$.

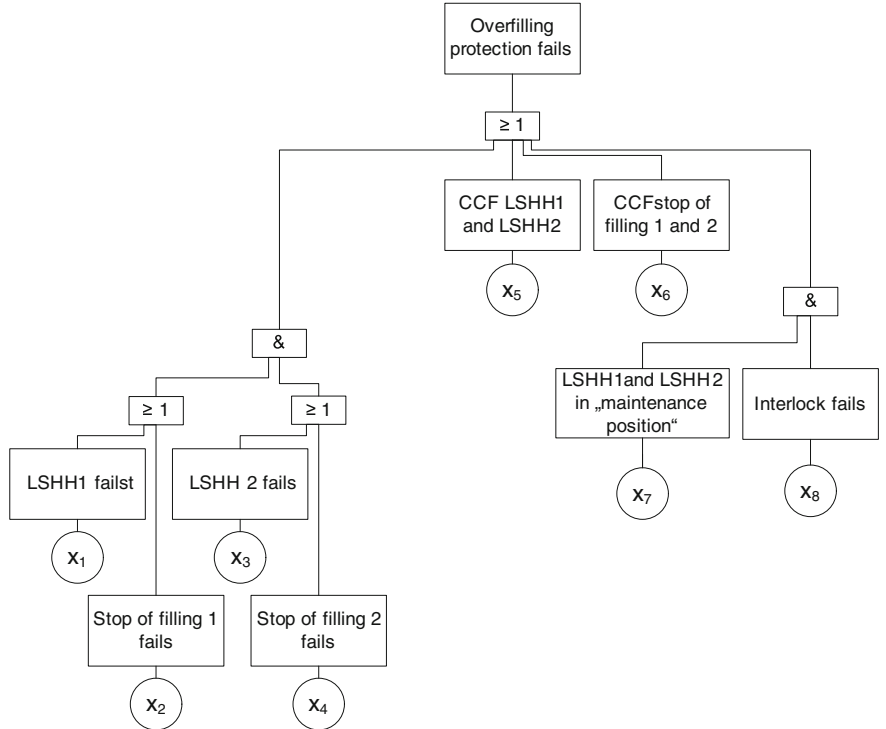


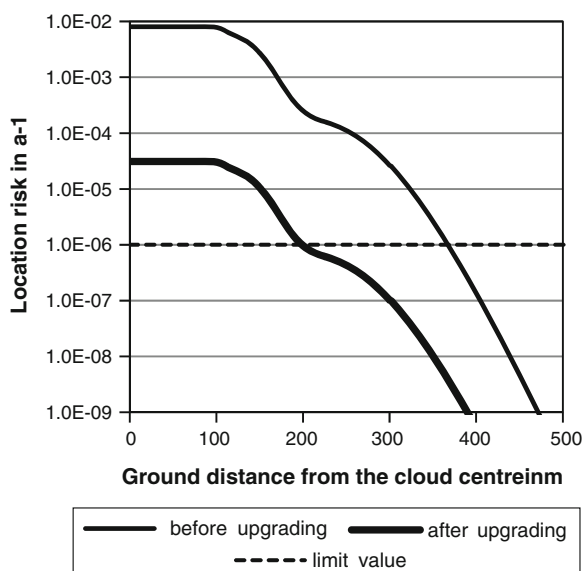
Fig. 11.10 Fault tree for the protection against overfilling with interlock and level protection in 1oo2-configuration

Table 11.9 Data for quantifying the fault tree of Fig. 11.10

Primary event	Designation	Failure rate/failure probability	Time intervals between functional tests
x ₁	Level switch LSHH1 fails	$1.44 \times 10^{-6} \text{ h}^{-1}$	720 h
x ₂	Stop of filling 1 fails	$1.8 \times 10^{-6} \text{ h}^{-1}$	720 h
x ₃	Level switch LSHH2 fails	$1.44 \times 10^{-6} \text{ h}^{-1}$	720 h
x ₄	Stop of filling 2 fails	$2.0 \times 10^{-6} \text{ h}^{-1}$	720 h
x ₅	CCF LSHH1 and LSHH2	$1.6 \times 10^{-7} \text{ h}^{-1}$	720 h
x ₆	CCF stop of filling 1 and 2	$2.0 \times 10^{-7} \text{ h}^{-1}$	720 h
x ₇	LSHH1 and LSHH2 forgotten in “maintennce position” ^a	0.096	
x ₈	Interlock fails	$0.7 \times 10^{-6} \text{ h}^{-1}$	720 h

^aprobability of failure

Fig. 11.11 Distance-dependent location risk for death and limit value



$$\begin{aligned}
 u_s &\approx u_1 \cdot u_3 + u_1 \cdot u_4 + u_2 \cdot u_3 + u_2 \cdot u_4 + u_5 + u_6 + u_7 \cdot u_8 = 2.69 \times 10^{-7} + 3.36 \times 10^{-7} \\
 &\quad + 3.36 \times 10^{-7} + 4.20 \times 10^{-7} + 5.76 \times 10^{-5} + 7.20 \times 10^{-5} \\
 &\quad + 2.42 \times 10^{-5} = 1.55 \times 10^{-4}
 \end{aligned}$$

This satisfies the target. Should the test interval be considered too short, self-announcing components could be used, the degree of redundancy could be increased or the contribution of CCFs be reduced by using diverse equipment. Alternatively, the surroundings of the tank could be monitored for hydrocarbons activating the stop of the pump and the closing of the shutoff valve. This would reduce the released quantity thus mitigating the consequences of the accident (level 4 in Table 4.1).

Figure 11.11 shows the location risk for death as a function of the distance on the ground from the centre of the cloud.

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12.1 Introduction

According to the Seveso Directive [1] “Member States shall ensure that their land-use and/or other relevant policies and the procedures for implementing those policies take account of the need, in the long term, to maintain appropriate distances between establishments covered by this Directive and residential areas, areas of public use and areas of particular natural sensitivity or interest...”. This is implemented in the German legislation in [2].

The demand for distances is justified by the argument that in addition to plant engineered safety measures a further barrier for protecting the population from potential harm due to the operation of industrial installations shall be implemented (level 4 of Table 4.1). Should an appropriate distance not be possible in case of existing establishments, additional technical measures are to be implemented so as not to increase the risk to people.

Whilst in Germany a deterministic approach for fixing appropriate distances is pursued [3], this is done probabilistically or at least using probabilistic elements in a number of European countries [4].

The possibility of “compensating” insufficient distance by technical measures suggests a probabilistic approach. Risk then is the “common denominator” which makes technical measures and distance comparable with each other.

Furthermore, if one bases the fixing of appropriate distances on rarely occurring maximum distances, as shown in Table 12.1, this would lead to distances which would be prohibitive in most countries and particularly in Germany. However, in view of the small risk they constitute they would not be an adequate basis for decision. This favours a risk-based approach for fixing appropriate distances.

It must be emphasized that a risk-based approach requires a number of conventions, just as the deterministic procedure does. Hence, we are dealing with conventions which enable one to treat generally occurring cases such as

Table 12.1 Observed ranges of damaging effects from accidents in process plants (after [5])

Explosions: up to 30 km (albeit with small effects)
Releases of toxic materials: up to 16 km (albeit with small effects)
Gas clouds: Fire effects up to 5,000 m
Missile flights: 400–1,200 m (Mexico City)
Pool fires: 50–80 m
Jet fires: 90–100 m

- the siting of new establishments,
- modifications to existing establishments,
- new developments, such as transport links, locations frequented by the public and residential areas in the vicinity of existing establishments on the same footing.

It is not an intent to determine the “true” risk which might, if at all, only be approximated by a detailed risk analysis (vid. Chaps. 8–10).

12.2 Risk-Based Approach

As explained above we must generally expect the following damaging phenomena in process plants:

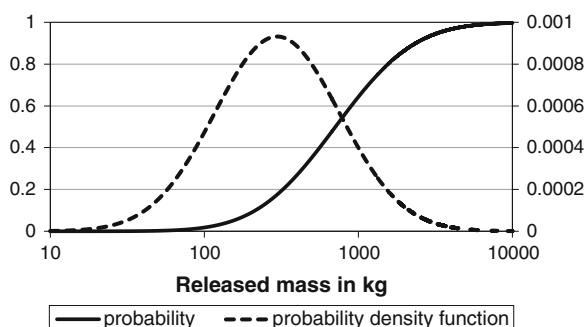
- explosion,
- fire,
- release of toxic materials.

A large number of event sequences and consequences are possible (vid. Fig. 10.1). For example, fires and explosions may occur within the containment of materials inside the equipment or result from a release of materials. Hazardous substances may be present in the process or be generated because of deviations of process parameters from their values (e.g. larger quantities of dioxin in Seveso) or be formed in the course of an accident (e.g. combustion gases). It is evident that even in a comprehensive and detailed risk analysis it is difficult to treat all conceivable event sequences. This is even less the case in a risk-based analysis.

For this reason the following phenomena are treated in [6], which is the basis of the following presentation. They are considered to be dominant for determining appropriate distances:

- release of toxic materials,
- explosion of a released gas,
- BLEVE,
- vessel burst and fireball,
- fragmentation and missile flight.

Fig. 12.1 Probability density function (*right hand ordinate*) and probability distribution (*left hand ordinate*) for the release of gaseous ammonia from storages; 5th percentile: 39.7 kg, expected value: 1,096.1 kg, 95th percentile: 4,126.5 kg (calculated from released quantities in several accidents from [7])



Each phenomenon contributes to risk according to its expected frequency of occurrence. That frequency is determined as far as possible from observations of past events, i.e. empirically.

An important aspect for the treatment of empirical data in the present context is that we are dealing with random variables, i.e. quantities which adopt a certain value with a certain probability. These variables are described by probability distributions whose parameters are estimated on the basis of observed data. Figure 12.1 gives an example.

The procedure follows the steps of Fig. 8.1. The way the different steps are executed is explained below, where the differences with respect to a detailed analysis are underlined.

12.2.1 Initiating Events and Scenarios

12.2.1.1 Frequencies of Release

Instead of analyzing the engineered systems of the plant and the potential event sequences in detail (vid. Chap. 9) generic values for the occurrence of accidents are used. These depend on numerous factors, amongst them

- type of process,
- available safety systems,
- size of the plant,
- number and type of process units,
- safety culture.

All of these and further important factors of influence are not yet known at the moment of land-use planning. That is why the recourse is to base considerations on a fictitious “generic” plant. This is difficult because amongst others reliability data at the level of process units are available, if at all, only for some classes of units, e.g.

- units with large hazards

and

- units with average hazards.

That is why the following approach is chosen. The information of the data bank of the Federal Institute for the Environment ZEMA enables one to derive an expected value of 6.4×10^{-6} per plant and year for an accident with harm to persons outside the premises of plant. This value is arrived at using Bayesian zero failure statistics (vid. Example 9.6). It is about one order of magnitude smaller than that for a fatal occupational accident in the chemical industry, for which about $2.2 \times 10^{-5} \text{ a}^{-1}$ is obtained (vid. Fig. 1.1).

In order to put these frequencies into perspective they can be compared with the frequency of death by lightning. This is stated to be 10^{-7} a^{-1} [8] and is considered as negligible.

Assuming that about 10 % of the accidents cause harm to people we would expect a frequency of a major release of about 6×10^{-5} ($6.4 \times 10^{-6}/0.1 \approx 6 \times 10^{-5}$) per plant and year.

Release frequencies per process unit are needed for the calculations. They are estimated as follows. One assumes that a plant comprises on the average 50 process units, which implies an expected frequency of failure of 1×10^{-6} per process unit and year. This value is used below. Since this quantity is very uncertain a large error factor of $K_{95} = 10$ for a corresponding log-normal distribution (vid. Sect. 9.3.4) is assumed. The parameters of that distribution then are $\mu = -14.795$ and $s = 1.3998$.

This annual frequency of release may be lowered by an order of magnitude if technical upgrading is necessary and possible. This is the lower limit of credits given for active protective measures in [9].

In order to build a generic plant on the basis of the preceding considerations we still need a reasonable assumption on the number of relevant process units. This number depends on the area of the site to be assigned to the plant. Indications from the insurance sector suggest that a distribution with an expected value of 0.00014 process units per m^2 (Eq. (C.26) with parameters $a = 0.000177925$ and $s = 0.00014215$) is reasonable.

The expected annual frequency of major releases from an establishment or a plant with an area of a certain number of square meters is then obtained as the product of this area with the convolution (“product” formation for random variables) of the expected frequency of release and the number of process units per m^2 .

Concerning the failure frequencies of storage vessels there is some information, as compiled in Table 12.2. In [9] a band of 10^{-5} – 10^{-7} a^{-1} is indicated for the failure of pressure vessels. A band of 10^{-3} – 10^{-5} a^{-1} is given there for the failure of atmospheric vessels.

In order to represent the range of values of Table 12.2, a rectangular distribution with bounds 10^{-7} – 10^{-5} a^{-1} in Eq. (C.33) is used for pressure vessels and a

Table 12.2 Expected frequencies of vessel failures

Object	Expected annual failure rate	Source
Pressure vessel (total rupture)	3×10^{-6}	Ref. [8]
Refrigerated storage (total rupture)	5×10^{-6}	Ref. [8]
Ammonia storage	6×10^{-4}	Ref. [8]
Atmospheric storage	3×10^{-5}	Ref. [8]
Refrigerated storage		
• Single walled	1×10^{-5}	Ref. [8]
• Double walled	1×10^{-6}	Ref. [8]
Liquefied methane (refrigerated storage)	–	Ref. [10]
• With liner	6.1×10^{-5}	–
• Double walled (self-supporting)	6.3×10^{-5}	–
Pressure vessel	3.1×10^{-6}	Ref. [11]
Atmospheric storage	1.5×10^{-5}	Ref. [11]

gamma distribution according to Eq. (C.28) with an expected value of $1.9 \times 10^{-5} \text{ a}^{-1}$ for atmospheric and refrigerated storage vessels. Existing data suggest that technical upgrading justifies these values to be lowered by a factor of 10. The type of vessel is selected according to the material and the type of storage involved.

The number of vessels per m^2 is determined as follows. The bottom area of vessels ranges from 20 m^2 to $2,000 \text{ m}^2$. Between 10 and 20 % of the available terrain are covered by vessels. Both quantities are described by rectangular distributions according to Eq. (C.33). They enable one to determine the number of vessels per m^2 . This gives $3.5 \times 10^{-4} \text{ m}^{-2}$.

12.2.1.2 Released Quantities of Materials

The masses of materials potentially involved in accidents are derived from accident reports. The main bases were the ARIP data bank of the U.S. Environmental Protection Agency [7] and the ZEMA data bank of the German Environmental Protection Agency [12]. The released quantities are regarded as random variables and represented by probability distributions. Thus discussions on assumptions of leak sizes, of pressure differences between the interior of vessels and their exterior as well as of durations of releases become superfluous. Table 12.3 gives examples for mean values of releases from process plants and storages.

If a liquid is released vaporization is assessed with simple models. In any case the dispersion calculations are performed conservatively assuming a puff release, even if the vaporization process extends over considerable time spans.

The different production processes and storages are assessed on the basis of several materials which are considered to be representative for the hazard potential.

Table 12.3 Selected mean released quantities from processes and storages in kg

Data bank	Production plants			Storages		
	ARIP		ZEMA	ARIP		ZEMA
	Liquid	Vapour	Liquid	Liquid	Vapour	Not indicated
Acrylonitrile	2,207.9	3,020.1	–	731.4	–	–
Ammonia	44,932.8	1,053.3	1,715.6	585.4	1,977.2	756.0
Chlorine	471.4	664.2	635.8	–	259.8	828.4
Hydrogen chloride	8,840.0	529.8	137.5	14,081.1	–	–
Hydrogen cyanide	19.7	79.1	–	–	–	–
Ethylene oxide	4,375.6	554.1	–	–	–	–
Ethylene	–	19,439.5	–	–	–	–
Methanol	15,410.5	5,118.8	–	74,425.0	–	–
Phosgene	6.7	69.3	–	–	–	–
Sulphur dioxide	156.8	19,888.3	–	–	581.2	–
Hydrogen sulphide	–	1,030.3	–	–	155.0	–

12.2.2 Characteristics and Exposure

The thorough treatment of initial and boundary conditions as well as of exposure sequences in a detailed risk analysis is replaced by a representation of the phenomena based on observations. If these do not exist recourse is had to simple calculation models or a combination of model and observations.

From the plethora of potential accident sequences a few are selected which determine to a large extent the accident sequences. In particular the following models are used:

- Explosion blast wave: largely on the basis of observed explosions, TNT equivalent model (vid. Sect. 10.6.3.1)
- Dispersion of gases: VDI models for airborne and dense gas dispersion (vid. Sect. 10.5)
- Fragment flight: observation supported models for cylindrical and spherical vessels (vid. Sect. 10.9)
- Fireball: empirical correlations (vid. Sect. 10.6.2.1).

12.2.3 Consequences of Material Releases

The impacts of material releases stem from toxicity, fire or explosion if the materials have the corresponding properties. The possibility exists that a material exhibits several of the properties mentioned. This is accounted for accordingly.

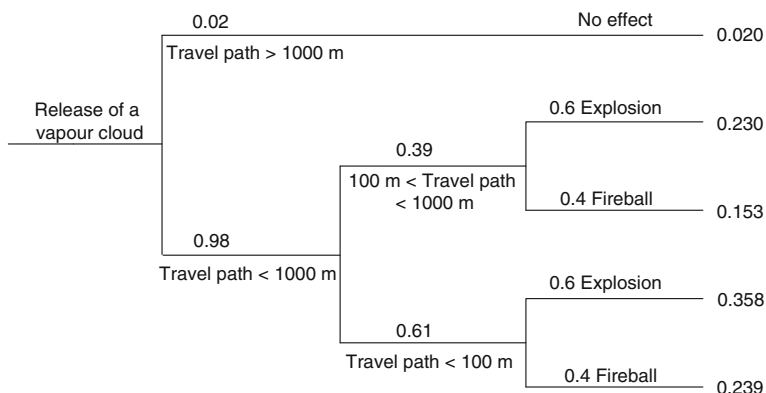


Fig. 12.2 Event tree for the release of a vapour cloud along with the conditional probabilities for the different scenarios and endpoints

12.2.3.1 Flammable Materials

Empirical findings on the release of flammable materials lead amongst others to the following conclusions (vid. [8]):

In case of released quantities of >10,000 kg the probability of ignition lies between 0.1 and 0.5.

- With releases of smaller quantities an ignition probability of 10^{-4} is to be expected.
- In more than 60 % of all cases ignition took place within 100 m from the point of release (fireball).
- In 2 % of the cases the cloud drifted more than 1 km before ignition.
- In approximately 60 % of the cases the cloud exploded and otherwise a fire occurred.

From the above information the following conclusions are drawn for the modelling:

- The fireball is considered to be the gravest outcome. Therefore flash fires are not treated. The conditional probability of an explosion is 0.6 and that of a fireball 0.4.
- Because of the low probability of a cloud drifting far away from its point of release and igniting then this process is not treated.
- It is assumed conservatively that the cloud always ignites.

The event tree of Fig. 12.2 was derived from the above information. It contains the event sequences after the release of flammable materials and the corresponding conditional probabilities.

If a material is toxic and flammable it is assumed that with a probability of 0.9 there is no ignition. The main damaging mechanism then is its toxic impact. The consequences according to Fig. 12.2 occur with a probability of 0.1.

If the released quantity is <10,000 kg, the probability for igniting is determined by

$$p_{\text{ignition}} = 10^{-4} + 9.999 \times 10^{-6} m \quad (12.1)$$

In Eq. (12.1) m is the released mass in kg and p_{ignition} the probability of ignition. If a material is only flammable and not toxic it follows the sequences of the event tree of Fig. 12.2 where ignition is assumed with probability $p_{\text{ignition}} = 1$. All of the above assumptions are conservative.

12.2.3.2 Toxic Materials

As a consequence of a release atmospheric dispersion occurs. The dispersion is airborne if the material is lighter than air. However, if it is heavier than air it is dispersed as a dense gas. Additionally issues such as minimum released mass or minimum mass flow rates and the release temperature are considered in deciding on one of the two kinds of dispersion. A combination of both kinds of dispersion is possible. For example, refrigerated ammonia is initially dispersed as a dense gas and after being warmed by heat transfer from the surrounding air and diluted as an airborne gas. It should be noted that the release of any dense gas becomes airborne after a certain distance due to dilution of the gas with air (vid. Sect. 10.5).

The weather conditions

- unstable (0.107),
- neutral (0.062),
- stable (0.27) and
- average (0.561)

are considered with the corresponding probabilities of occurrence, which are given in brackets [13]. The average conditions refer to neutral temperature layering without an inversion lid. The category “neutral” on the other hand includes an inversion lid. The probability for neutral conditions was assigned to 90 % to “average” and 10 % to “neutral” conditions.

Puff releases are assumed for the dispersion calculations, since a time distribution of the released quantities would require arbitrary assumptions of release duration and mass flow rate. Furthermore, puff releases lead to higher atmospheric concentrations and hence stronger effects than time-dependent releases of the same quantities.

12.2.4 Damage and Risk

The probabilities of damage are assessed using probit relations (vid. Appendix B and Sect. 2.6.2.2).

The risk is assessed by combining the elements of frequency and damage. The result then is the expected frequency for a particular type of damage, e.g. the individual risk of death, i.e. the expected frequency of death at a particular distance from the source.

12.3 Processing of Random Variables

Above a number of phenomena were mentioned whose behaviour is random (e.g. behaviour of a released gas, weather conditions etc.). The variables describing them adopt a particular value with a certain probability and are therefore described by probability distributions. Furthermore there are phenomena which can be described by several models. This points to modelling uncertainties.

In order to propagate modelling uncertainties and uncertainties stemming from the stochastic character of variables or insufficient knowledge of variables through the calculations and account for them in the final results the Monte Carlo simulation is used (cf. Example 4.5 and [14]).

As already explained, Monte Carlo simulation is based on repeating a calculation several times (N times). Each calculation is called a trial. In each trial a concrete value (realization) is generated for any random variable on the basis of its corresponding distribution. If several models for one phenomenon are available a concrete model is selected on the basis of a probability believed to represent its relevance. In order to generate random variables from different probability distributions, random variables uniformly distributed on $[0, 1]$ are transformed into random variables from the distribution in question (cf. [14] and Sect. 10.9).

The total of N results forms a histogram. For simplicity's sake this histogram is approximated by a log-normal distribution.

The procedure is shown in the schematic of Fig. 4.21.

12.4 Risk Limits and Distances on the Basis of Risk Considerations

12.4.1 Risk Limits

As already explained the results of the calculations are affected by uncertainties. They are therefore given in terms of probability or frequency distributions. Hence it makes sense to also formulate the yardstick (risk limit, safety goal) as an uncertain value.

In several countries point values are used as quantitative risk or safety targets (vid. Chap. 8). However, there is no agreement on which requirements are to be made. This becomes evident, for example, from the criteria for the individual risk, which have been set in different countries, and the question of whether the duration of exposure of a person should be accounted for or the location risk should be used instead. In addition, it must be borne in mind that risk limits have always to be

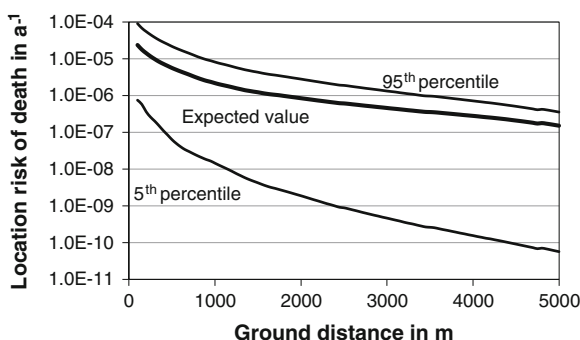
Table 12.4 Appropriate distances for process plants and storages for several plant types and covered areas of 1,000,000 and 100,000 m² (plant types according to [16])

Type of plant	Typical hazardous materials	Distance in m	Location risk in 10 ⁻⁶ a ⁻¹	Distance in m	Location risk in 10 ⁻⁶ a ⁻¹
Area		1,000,000 m ²		100,000 m ²	
Production of hydrocarbons (linear or ring shaped, saturated or unsaturated, aliphatic or aromatic)	Acetylene, benzene, ethylene, toluene, hydrogen	100	0.8	100	0.07
Storage for the above production	Acetylene, benzene, ethylene, toluene, hydrogen	150	12.5	150	1.2
Production of sulphuric hydrocarbons	Hydrogen sulphide	850	3.1	400	2.3
Storage for the above production	hydrogen sulphide	350	5.1	300	1.4
<i>After upgrading</i>					
Production of hydrocarbons (linear or ring shaped, saturated or unsaturated, aliphatic or aromatic)	Acetylene, benzene, ethylene, toluene, hydrogen	100	0.08	100	0.07
Storage for the above production	Acetylene, benzene, ethylene, toluene, hydrogen	150	1.2	100	0.1
Production of sulphuric hydrocarbons	Hydrogen sulphide	400	2.4	100	0.3
Storage for the above production	Hydrogen sulphide	300	1.3	100	0.9

valuated in relation with the procedure used for risk assessment. For example, often the number and type of scenarios to be considered are fixed. This is a restriction, because not the total but only part of the risk is then assessed and that part is compared with the risk limit. Thus risk-based procedures of decision-making also represent a convention.

Based on the information in Chap. 8 a limiting band is formulated here, which is represented by a rectangular distribution with the limits $b = 10^{-4} \text{ a}^{-1}$ and $a = 10^{-6} \text{ a}^{-1}$. This then serves as a yardstick for the calculated frequency distribution. Compliance or non-compliance is decided upon using the probability excess, W_{ex} ,

Fig. 12.3 Location risk as a function of the distance from an existing plant (including storage)



as determined according to [15]. It is fixed here that the radius is selected for which $W_{\text{ex}} < 0.4$ is true.

12.4.2 Distances

Table 12.4 contains examples resulting for different types of plants, if the land use of an area of 1,000,000 m² respectively 100,000 m² is to be planned for a plant without and with technical upgrading.

Thereafter the distance between an existing plant and the surrounding residential areas is examined. Materials of importance for risk are acrylonitrile, hydrogen and ammonia. The plant occupies 1,000 m² of ground and comprises one process unit and a storage vessel.

The calculation results in a distance of 700 m giving a location risk of $3.7 \times 10^{-6} \text{ a}^{-1}$. This distance to residential areas exists in reality so that the plant site complies with the criterion. The location risk as a function of the distance from the plant is shown in Fig. 12.3.

Figure 12.4 shows the location risk for the plant as a function of distance for the case of upgrading, which leads to a recommended appropriate distance of 150 m with a location risk of $1.8 \times 10^{-6} \text{ a}^{-1}$.

Figure 12.5 finally gives an example of the dependence of recommended appropriate distance on the size of the area subject to planning.

12.4.3 Example for Land-Use Planning

The industrial use of an area of 160,000 m² is to be planned. The distance from residential areas is 500 m. The objective is to assess the location risk. By way of example the following installations are planned on the area (the plant classification stems from [16]):

Fig. 12.4 Location risk as a function of the distance from an existing plant (including storage) (after technical upgrading)

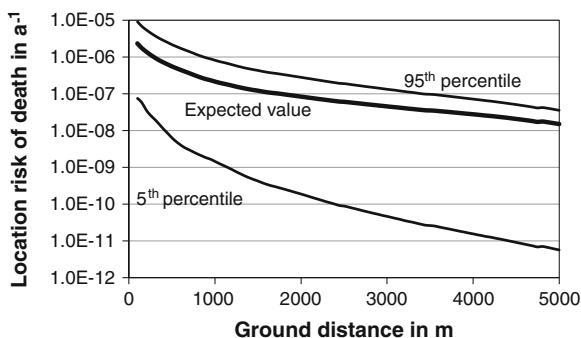
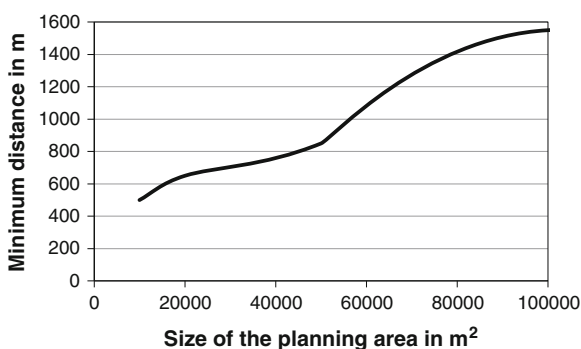


Fig. 12.5 Appropriate distance as a function of the size of the planning area for the storage of plants for producing metal-organic compounds (typical hazardous material: chlorine)



- administration building 20,000 m²
- production plant of type 4.1a (plant for the production of hydrocarbons, linear or ring shaped, saturated or unsaturated, aliphatic or aromatic) 20,000 m²
- storage of type 4.1a (hydrocarbons) 10,000 m²
- production plant of type 4.1c (plant for the production of sulphurated hydrocarbons) 10,000 m²
- storage of type 4.1c (sulphurated hydrocarbons) 10,000 m²
- production plant of type 4.1f (plant for the production of halogenated hydrocarbons) 20,000 m²
- storage of type 4.1f (halogenated hydrocarbons) 10,000 m²
- production plant of type 4.1 g (plants for the production of metal-organic compounds) 50,000 m²
- storage of type 4.1 g (metal-organic compounds) 10,000 m²

Figure 12.6 shows the result.

The total risk (sum of the location risks from all production plants and storages) amounts to: $1.6 \times 10^{-5} \text{ a}^{-1}$. This would require a larger distance according to the

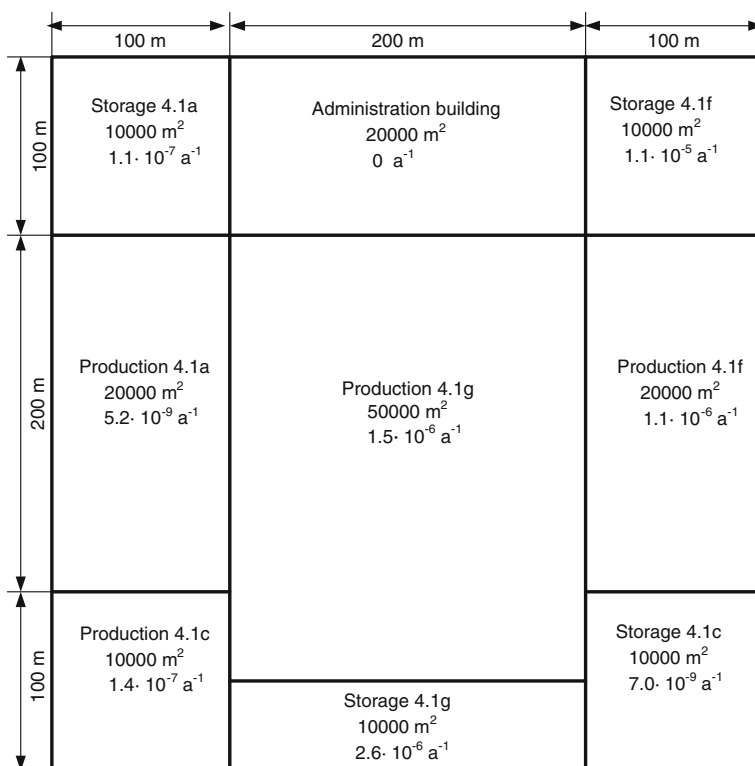


Fig. 12.6 Planning of a fictitious area for process plants with indication of the location risk (annual expected frequency of death for a person staying at a distance of 500 m for 24 h)

above mentioned risk limit criterion, namely 950 m (total risk: $4.7 \times 10^{-6} \text{ a}^{-1}$). If the possibility of upgrading were chosen a total location risk of von $1.8 \times 10^{-6} \text{ a}^{-1}$ would result for a distance of 500 m.

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Appendix A

GHS—Globally Harmonized System of Classification and Labelling of Chemicals

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) was published by the UN in 2003 [A-1] with the objective to harmonize the differing approaches of classifying and labeling chemicals in different countries. The GHS was introduced in the European Community by [A-2]. It came into force on January 20th, 2009. The regulation comprises to a large extent the provisions of [A-1] and is also known as the CLP regulation (Regulation on Classification, Labelling and Packaging of Substances and Mixtures).

The purpose of the regulation is described in [A-2] as follows: “This Regulation should ensure a high level of protection of human health and the environment as well as the free movement of chemical substances, mixtures and certain specific articles, while enhancing competitiveness and innovation”.

In order to achieve this, materials are assigned to hazard classes which describe the physical hazard, the hazards for human health or the environment. The classes are divided into hazard categories in order to characterize the severity of a hazard. In addition pictograms and signal words are introduced. Pictograms are intended to graphically convey specific information on the hazard concerned. A ‘signal word’ means a word that indicates the relative level of severity of hazards to alert the reader to a potential hazard. For example, the word ‘danger’ indicates the more severe hazard categories, whilst ‘warning’ signals the less severe hazard categories.

In Annex I of [A-2] the general principles for classification and labelling are treated in part 1. Part 2 deals with the physical hazards and uses the classes listed in Table A.1.

The subject of part 3 of Annex I are health hazards. Table A.2 lists the classes of health hazards.

Further to that part 4 of Annex I deals with substances, which constitute hazards for the aquatic environment, and part 5 with substances which are hazardous to the ozone layer.

Table A.1 Physical hazards [A-2]

Numbering according to Annex I, part 2	Description of the class
2.1	Explosives, substances and mixtures as well as articles with explosives
2.2	Flammable gases
2.3	Flammable aerosols
2.4	Oxidizing gases
2.5	Gases under pressure
2.6	Flammable liquids
2.7	Flammable solids
2.8	Self-reactive substances and mixtures
2.9	Pyrophoric liquids
2.10	Pyrophoric solids
2.11	Self-heating substances and mixtures
2.12	Substances and mixtures which in contact with water emit flammable gases
2.13	Oxidizing liquids
2.14	Oxidizing solids
2.15	Organic peroxides
2.16	Corrosive to metals

Table A.2 Health hazards [A-2]

Numbering according to Annex I, part 3	Description of the class	Differentiation according to
3.1	Acute toxicity	Acute oral toxicity
		Acute dermal toxicity
		Acute inhalation toxicity
3.2	Skin corrosion/irritation	
3.3	Serious eye damage/eye irritation	
3.4	Respiratory or skin sensitization	
3.5	Germ cell mutagenicity	
3.6	Carcinogenicity	
3.7	Reproductive toxicity	
3.8	Specific target organ toxicity—single exposure	
3.9	Specific target organ toxicity—repeated exposure	
3.10	Aspiration hazard	

References

- [A-1] United Nations (2003) Globally harmonized system of classification and labelling of chemicals (GHS), ST/SG/AC. 10/30, New York and Geneva
- [A-2] Regulation (EC) No 1272/2008 of the European parliament and of the council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. Official J Eur Union L 353/1, 31.12.2008

Appendix B

Probit Relations, Reference and Limit Values

B.1 Probit Relations

B.1.1 Fatal Toxic Effects for Selected Materials [B-1]–[B-3]

Acrolein

$$Y = -9.931 + 2.049 \cdot \ln(C \cdot t) \quad (\text{B.1})$$

Acrylonitrile

$$Y = -29.42 + 3.008 \cdot \ln(C^{1.43} \cdot t) \quad (\text{B.2})$$

Ammonia

$$Y = -30.75 + 1.385 \cdot \ln \left(\int_0^t C(t')^{2.75} \cdot dt' \right) \quad (\text{B.3a})$$

$$Y = -28.33 + 2.27 \cdot \ln \left(\int_0^t C(t')^{1.36} \cdot dt' \right) \quad (\text{B.3b})$$

$$Y = -35.9 + 1.85 \cdot \ln(C^2 \cdot t) \quad (\text{B.3c})$$

Benzene

$$Y = -109.78 + 5.3 \cdot \ln(C^2 \cdot t) \quad (\text{B.4})$$

Hydrogen cyanide

$$Y = -29.42 + 3.008 \cdot \ln(C^{1.43} \cdot t) \quad (\text{B.5})$$

Bromine

$$Y = -9.04 + 0.92 \cdot \ln(C^2 \cdot t) \quad (\text{B.6})$$

Chlorine

$$Y = -17.1 + 1.69 \cdot \ln \left(\int_0^t C(t')^{2.75} \cdot dt' \right) \quad (\text{B.7a})$$

$$Y = -36.45 + 3.13 \cdot \ln \left(\int_0^t C(t')^{2.64} \cdot dt' \right) \quad (\text{B.7b})$$

$$Y = -11.4 + 0.82 \cdot \ln \left(\int_0^t C(t')^{2.75} \cdot dt' \right) \quad (\text{B.7c})$$

$$Y = -5.04 + 0.5 \cdot \ln \left(\int_0^t C(t')^{2.75} \cdot dt' \right) \quad (\text{B.7d})$$

Hydrogen chloride

$$Y = -16.85 + 2.0 \cdot \ln(C \cdot t) \quad (\text{B.8})$$

Ethylene oxide

$$Y = -6.8 + \ln(C \cdot t)^* \quad (\text{B.9})$$

Fluorine

$$Y = -8.56 + 1.08 \cdot \ln(C^{1.85} \cdot t)^* \quad (\text{B.10})$$

Hydrogen fluoride

$$Y = -48.33 + 4.853 \cdot \ln(C \cdot t) \quad (\text{B.11a})$$

$$Y = -26.36 + 2.854 \cdot \ln(C \cdot t) \quad (\text{B.11b})$$

$$Y = -35.87 + 3.354 \cdot \ln(C \cdot t) \quad (\text{B.11c})$$

$$Y = -25.87 + 3.354 \cdot \ln(C \cdot t) \quad (\text{B.11d})$$

Formaldehyde

$$Y = -12.24 + 1.3 \cdot \ln(C^2 \cdot t) \quad (\text{B.12})$$

Carbon disulphide

$$Y = -46.56 + 4.2 \cdot \ln(C \cdot t) \quad (\text{B.13})$$

Carbon monoxide

$$Y = -37.98 + 3.7 \cdot \ln(C \cdot t) \quad (\text{B.14})$$

Methanol

$$Y = -6.34734 + 0.66358 \cdot \ln(C \cdot t) \quad (\text{B.15})$$

Fuming sulphuric acid (oleum)

$$Y = -14.2 + 1.6 \cdot \ln(C^{1.8} \cdot t)^* \quad (\text{B.16})$$

Phosgene

$$Y = -27.2 + 5.1 \cdot \ln(C \cdot t) \quad (\text{B.17a})$$

$$Y = -19.27 + 3.686 \cdot \ln(C \cdot t) \quad (\text{B.17b})$$

Phosphine

$$Y = -2.25 + \ln(C \cdot t) \quad (\text{B.18})$$

Sulphur dioxide

$$Y = -15.67 + 2.1 \cdot \ln(C \cdot t) \quad (\text{B.19})$$

Hydrogen sulphide

$$Y = -11.15 + \ln(C^{1.9} \cdot t) \quad (\text{B.20})$$

Toluene

$$Y = -6.794 + 0.408 \cdot \ln(C^{2.5} \cdot t) \quad (\text{B.21})$$

where $C(t)$ is the time-dependent concentration in ppm and the time is in minutes (exception: * in mg/m^3 and minutes).

B.1.2 Pressure and Heat Radiation Exposures [B-1, B-4]

Death from lung haemorrhage due to a blast wave

$$Y = -77.1 + 6.91 \cdot \ln p_s \quad (\text{B.22})$$

Eardrum rupture due to a blast wave

$$Y = -15.6 + 1.93 \cdot \ln p_s \quad (\text{B.23a})$$

$$Y = -12.6 + 1.524 \cdot \ln p_s \quad (\text{B.23b})$$

Death following body translation due to impulse

$$Y = -46.1 + 4.82 \cdot \ln J \quad (\text{B.24})$$

Injuries from impact

$$Y = -39.1 + 4.45 \cdot \ln J \quad (\text{B.25})$$

Serious injuries from flying fragments (particularly glass)

$$Y = -27.1 + 4.26 \cdot \ln J \quad (\text{B.26})$$

Structural damage

$$Y = -23.8 + 2.92 \cdot \ln p_s \quad (\text{B.27})$$

Glass breakage

$$Y = -18.1 + 2.79 \cdot \ln p_s \quad (\text{B.28})$$

Death due to thermal radiation

$$Y = -14.9 + 2.56 \cdot \ln \left(t_e \cdot q''^{4/3} \cdot 10^{-4} \right) \quad (\text{B.29})$$

Death due to thermal radiation (unprotected by clothing)

$$Y = -36.38 + 2.65 \cdot \ln \left(t_e \cdot q''^{4/3} \right) \quad (\text{B.30})$$

Death due to thermal radiation (protected by clothing)

$$Y = -37.23 + 2.56 \cdot \ln \left(t_e \cdot q''^{4/3} \right) \quad (\text{B.31})$$

First degree burns

$$Y = -39.83 + 3.02 \cdot \ln \left(t_e \cdot q''^{4/3} \right) \quad (\text{B.32})$$

Second degree burns

$$Y = -43.14 + 3.02 \cdot \ln \left(t_e \cdot q''^{4/3} \right) \quad (\text{B.33})$$

The symbols have the following meaning:

- p_s peak side-on overpressure in N/m^2 ;
- J impulse in Ns/m^2 ;
- t_e duration of exposure in s;
- q'' radiation intensity (heat flux) in W/m^2

B.2 Reference Values for Damage to Health, Property, and Buildings

Tables B.1, B.2, B.3 and B.4.

Table B.1 Reference values for health damage from thermal radiation [B-1]

Thermal dose in kJ/m^2	Effect
375	Third degree burns
250	Second degree burns
125	First degree burns
65	Threshold of pain, no reddening or blistering of skin

Table B.2 Reference values for property damage from thermal radiation [B-1, B-4]

Thermal radiation intensity limit in kW/m^2	Effect
37.5	Damage to process plant equipment
35	Spontaneous ignition of wood (without ignition source)
35	Textiles ignite (without ignition source)
18–20	Cable insulation degrades
12	Plastic melts

Table B.3 Reference values for damage from thermal radiation with durations of exposure >30 min [B-4]

Material	Thermal radiation intensity limit in kW/m^2	
	Damage level 1 ^a	Damage level 2 ^b
Wood	15	2
Synthetic material	15	2
Glass	4	–
Steel	100	25

^a *Damage level 1* catching of fire by surfaces of materials exposed to heat radiation as well as the rupture or other type of failure (collapse) of structural elements

^b *Damage level 2* damage caused by serious discoloration of the surface of materials, peeling-off of paint and/or substantial deformation of structural elements

Table B.4 Reference values for building damage caused by blast waves (after [B-1])

Damage type	Peak side-on overpressure in Pa
Shattering of glass windows large and small, occasional frame damage	3447.4–6894.8
Blowing in of wood siding panels	6894.8–13789.6
Shattering of concrete or cinder-block wall panels, 20 or 30 cm thick, not reinforced	10342.2–37921.4
Nearly complete destruction of houses	34500.0–48300.0
Rupture of oil storage tanks	20684.4–27579.2

B.3 Limit Values in Germany and Other European Countries for Damage Causing Loads (After [B-5])

Tables [B.5](#), [B.6](#), [B.7](#), [B.8](#) and [B.9](#).

Table B.5 Reference values for impacts on people of different forms of energy (*bold print* limit values proposed in [B-5])

Damage causing factor	Limit value	Valuation according to the Major Accident Ordinance (StörfallV)
Peak side-on overpressure	1.85 bar (lung haemorrhage)	§2 no. 4a StörfallV Threat to the life of humans
Thermal radiation	10.5 kW/m ² (lethal burns in 40 s)	Grave health damage (irreversible damage) - of concern even if only one person is affected
Peak side-on overpressure	0.175 bar (eardrum rupture)	- small ↓
Thermal radiation	2.9 kW/m ² (threshold of pain reached after 30 s)	- number of affected people large
Peak side-on overpressure	0.1 bar (destruction of brick walls)	§2 no. 4b StörfallV
Thermal radiation	1.6 kW/m² (adverse effect)	Health impairment of a large number of people (reversible damage)
Peak side-on overpressure	0.003 bar (loud bang)	Harassment
Thermal radiation	1.3 kW/m ² (maximum of solar radiation)	

Table B.6 Limit values in Belgium

	Thermal radiation in kW/m ²	Explosion pressure in mbar	Missile flight
Safety zone ^a	–	–	–
Risk zone ^b	2.5 during 30 s	20	–

^a Zone, where reversible effects are observed

^b Zone, where specific measures must be taken for limiting accident consequences with due consideration of the duration of exposure

Table B.7 Limit values in France

	Thermal radiation ^b in kW/m	Explosion pressure in mbar	Missile flight
Irreversible consequences	3	50	—
Lethal consequences	5	140	—
Risk of a Domino effect ^a	8 for unprotected structures 12 for protected structures	200 for significant damage 350 for grave damage 500 for very grave damage	—

^a these threshold values are used by *INERIS* Institut National des Risques, but are not official

^b if exposure is longer than 60 s

Table B.8 Limit values in Italy^a

	Thermal radiation in kW/m ²	Explosion pressure in mbar	Missile flight
Reversible consequences	3	30	–
Irreversible consequences	5	70	–
Start of lethality	7	140	–
High risk of lethality	12.5	300	–
Risk of a domino effect	12.5	300	–

^a In Italy the following threshold values are used as well for non-stationary thermal radiation (in case of a fireball): 125 kJ/m² for reversible effects, 200 kJ/m² for irreversible effects, 350 kJ/m² for the threshold to lethality, radius of the fireball for high lethality: 200–800 m, Domino effects. For instantaneous thermal radiation of short duration (in case of a flash fire): ½ · LFL (start of lethality) and LFL (high lethality)

Table B.9 Limit values in Spain

	Thermal radiation in kW/ m ²	Explosion pressure in mbar	Missile flight
Alarm zone ^a	3	50	99.9 % of the range of the missile flight
Intervention zone ^b	5	125	95 % of the range of the missile flight
Domino effect zone	12 for unprotected structural elements inside the plant 37 for protected elements inside the plant	100 for buildings 160 for equipment under atmospheric pressure 350 for equipment under overpressure	100 % of the range of the missile flight

^a the consequences of the accident can be perceived by the population, but do not justify an intervention except with critical groups of people

^b the consequences of the accident are so grave that an immediate intervention is justified

References

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- [B-4] The Director-General of Labour (1989) Methods for the determination of possible damage to people and objects resulting from the release of hazardous materials. Green Book, Voorburg, December 1989
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Short version of Guidance KAS-18 (2014) Recommendations for separation distances between establishments covered by the major accidents ordinance (Störfall-Verordnung) and areas worthy of protection within the framework of land-use planning implementation of Article 50 of the Federal Immission Control Act (Bundes-Immissionsschutzgesetz, BImSchG). http://www.kas-u.de/publikationen/pub_gb.htm. Last visited on 13 May 2014

Appendix C

Basics of Probability Calculations

In what follows an overview of selected results of probability calculations is given; the presentation draws upon [C-1].

C.1 Events and Random Experiments

Probability calculations deal with random events and phenomena. The underlying processes are either random like, for example, the disintegration of radioactive isotopes, or they are so complex that we are either not willing or incapable to describe them exactly in quantitative terms. For example, we could, on the basis of influenza cases of the year 2012, estimate an expected number of cases for the year 2013, although they might be counted in the year 2013. Yet this can only be done after the end of 2013. This tells us that a probability can be assigned to events which may possibly occur in the future. In retrospect we are then certain; either one or none of the prospectively considered possible events has become true.

If we throw a die, we carry out an experiment which takes place according to known physical laws. Yet its outcome cannot be predicted with certainty. Such an experiment is called a random experiment. It can be identified on the basis of the following prescriptions [C-2]

1. A prescription exists for carrying out the experiment (hence it takes place according to strict rules).
2. The experiment can be repeated as often as desired.
3. At least two outcomes are possible.
4. The outcome is not predictable.

The set of possible outcomes of a random experiment forms the so-called event space or sample space, which generally is denoted by Ω . For a die $\Omega = \{1, 2, 3, 4,$

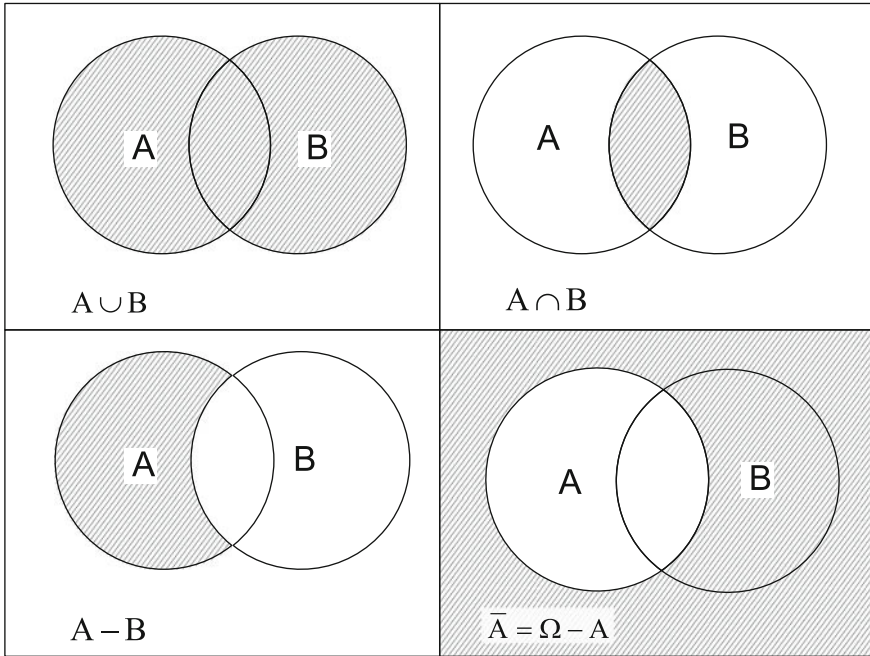


Fig C.1 Set operations represented by set or Venn diagrams

5, 6} applies. With random events we may be interested not only in a particular event, but also in a combination of several events, for example the occurrence of 3 or 4 pips on throwing a die. This is illustrated by set operations such as

- union: $A \cup B$; at least one of the two events A or B occurs
- intersection: $A \cap B$; both A and B occur
- difference: $A - B$; A, but not B occurs
- complement: $\bar{A} = \Omega - A$; A does not occur, $\bar{A}$ is the event complementary to A

The relationships are illustrated by Fig. C.1.

The universal set Ω , which contains all conceivable events, is called the certain event, its complement $\bar{\Omega}$ the impossible event. Two events for which $A \cap B = \emptyset$ is true, are called incompatible or disjunct, where $\emptyset$ denotes the empty set.

Example C.1 Quality of screws [C-2]

In a production of screws we wish to check, if the required length, which is to lie between 1.9 and 2.1 cm, is satisfied. For this purpose a screw is selected at random and its length is measured (random experiment). Let A be the event that the screw is shorter than 1.9 cm and B the event that it is longer than 2.1 cm. Then $A \cup B$ means that the screw does not have the required length and $\overline{A \cup B}$ means that it satisfies the length requirement. If C were the event that the screw is at least 2.0 cm long, then $C \cap \overline{A \cup B}$ is the event that the length of the screw is between 2.0 and 2.1 cm. $\square$

C.2 Probabilities

One cannot predict the outcome of a random experiment, but it is possible to indicate a probability for a particular outcome. Thus it is known that 5 pips show up with a probability of $1/6$ when throwing an ideal die. If this event is denoted by C we write

$$P(C) = \frac{1}{6} \quad (\text{C.1})$$

Since it is mathematically inexact to base areas of knowledge on experiments with ideal—but in reality non-existent—objects, Kolmogoroff established axioms. These axioms, however, comprise the results which would intuitively be expected if the experiment were repeated an infinite number of times. The axioms are

1.

$$P(A) \geq 0 \quad \text{for any event } A \subset \Omega \quad (\text{positivity})$$

2.

$$P(\Omega) = 1 \quad (\text{unitarity}) \quad (\text{C.2})$$

3.

$$P\left(\bigcup_{i=1}^{\infty} A_i\right) = \sum_{i=1}^{\infty} P(A_i) \quad (\sigma - \text{additivity})$$

The third property of course implies the finite additivity

$$P\left(\bigcup_{i=1}^n A_i\right) = \sum_{i=1}^n P(A_i) \quad (\text{C.3})$$

If there are just two disjunct (mutually exclusive) events, A and B , we have

$$P(A \cup B) = P(A) + P(B) \quad (\text{C.4})$$

All calculation rules for probabilities can be derived from the above properties, e.g.

$$P(A \cup B) = P(A) + P(B) - P(A \cap B) \quad \text{for any arbitrary } A \text{ and } B$$

$$P(\bar{A}) = 1 - P(A) \quad (\text{C.5})$$

$$P(A - B) = P(A) - P(B), \quad \text{if } B \subset A$$

Example C.2 Game of Dice

We are looking for the probability that when throwing a die two or four pips appear. This event is described by the set $\{2, 4\}$. According to Eq. (C.4) we have

$$\begin{aligned} P(\{2, 4\}) &= P(\{2\}) + P(\{4\}) \\ &= \frac{1}{6} + \frac{1}{6} = \frac{1}{3} \end{aligned}$$

Another way of solving the problem consists in subtracting from the certain event all events which we are not looking for, i.e.

$$\begin{aligned} P(\{2, 4\}) &= P(\{1, 2, 3, 4, 5, 6\}) - P(\{1, 3, 5, 6\}) \\ &= 1 - P(\{1\}) - P(\{3\}) - P(\{5\}) - P(\{6\}) \\ &= 1 - \frac{1}{6} - \frac{1}{6} - \frac{1}{6} - \frac{1}{6} = \frac{1}{3}. \end{aligned}$$

□

C.3 Conditional Probabilities and Independence

Often we are interested in the probability of the occurrence of an event A under the condition that a particular event B has already occurred. For example, the failure of a pump in a process plant under the condition that the plant has been flooded. Such a probability is called conditional probability. It is explained below using examples from [C-2].

Example C.3 Relative risk

Those who are exposed to a particular risk factor are called exposed persons and those who are not, unexposed or control persons (members of the control group). The probability of falling ill of disease K, if the risk factor R prevails is denoted by $P(K|R)$. Then we obtain the possibilities and probabilities of falling ill or not listed in Table C.1.

The parameter $\delta = P(K|R) - P(K|\bar{R})$ is called the risk which can be attributed to the risk factor R. □

Example C.4 Probability of survival

The probability for a male newborn baby to reach his 70th birthday and to survive until his 71st is $P(A) = 0.95$. The probability of living until the 72nd

Table C.1 Possibilities and probabilities for exposed and unexposed persons to fall ill or not

	K	$\bar{K}$	
R	$P(K R)$	$P(\bar{K} R)$	$P(R)$
$\bar{R}$	$P(K \bar{R})$	$P(\bar{K} \bar{R})$	$P(\bar{R})$
	$P(K)$	$P(\bar{K})$	1

birthday after having reached the 71st is $P(B|A) = 0.945$. Hence, we obtain the probability of reaching the 72nd birthday after having lived until 70 years as

$$P(A \cap B) = P(A) \cdot P(B|A) = 0.950 \cdot 0.945 = 0.898$$

□

The conditional probability for B to occur under the condition that A has occurred is understood to be

$$P(B|A) = \frac{P(A \cap B)}{P(A)} \quad (\text{C.6})$$

where $P(A) \neq 0$ has to hold. In this way we obtain the rule for multiplication, i.e.

$$P(A \cap B) = P(B|A) \cdot P(A) = P(A|B) \cdot P(B) = P(B \cap A) \quad (\text{C.7})$$

Equation (C.7) can be extended analogously to more than two events. Events are stochastically independent, if

$$P(A \cap B) = P(B) \cdot P(A) = P(A) \cdot P(B) = P(B \cap A) \quad (\text{C.8})$$

holds. Stochastic dependence has to be distinguished from causal dependence. The latter is directed, i.e. the cause produces the consequence. Stochastic dependence, on the other hand, is symmetric. Two quantities depend on each other. Causal dependence implies stochastic dependence. However, the inverse argument is not true.

C.4 Total Probability and Bayes' Theorem

If K denotes a particular disease, F a woman and M a man, then we obtain as probability for a randomly chosen person of being ill

$$P(K) = P(F) \cdot P(K|F) + P(M) \cdot P(K|M) \quad (\text{C.9})$$

Using Eqs. (C.7) and (C.9) is written as follows

$$P(K) = P(F \cap K) + P(M \cap K) \quad (\text{C.10})$$

or generalized

$$P(K) = \sum_i P(A_i \cap K) \quad (\text{C.11})$$

Equation (C.11) is known as the total probability of event K.

Combining Eqs. (C.9) and (C.10) in such a way that we can answer the question whether a person suffering from disease K is a man, we obtain the probability

$$P(M|K) = \frac{P(M \cap K)}{P(K)} \quad (\text{C.12})$$

In Eq. (C.12) we ask for a particular circumstance related to an event. In the present context the question is if a person affected by the disease K (event) is a man (circumstance).

Inserting Eq. (C.10) in Eq. (C.12) and using Eq. (C.9), one obtains

$$P(M|K) = \frac{P(K|M) \cdot P(M)}{P(F) \cdot P(K|F) + P(M) \cdot P(K|M)} \quad (C.13)$$

In this way we obtain Bayes' theorem, which in generalized form reads

$$P(A_k|K) = \frac{P(A_k) \cdot P(K|A_k)}{\sum_{i=1}^n P(A_i) \cdot P(K|A_i)} \quad (C.14)$$

The following example from [C-2] shows an application of Bayes' theorem.

Example C.5 Terrorism and air traffic

As a precaution all passengers in an airport are controlled. A terrorist is detained with a conditional probability of $P(F|T) = 0.98$, a non-terrorist with probability $P(F|\bar{T}) = 0.001$. Every one hundred thousandth tourist is assumed to be a terrorist, i.e. $P(T) = 0.00001$. What is the probability that a detained person really is a terrorist? The solution is

$$\begin{aligned} P(T|F) &= \frac{P(F|T) \cdot P(T)}{P(F|T) \cdot P(T) + P(F|\bar{T}) \cdot P(\bar{T})} = \frac{0.98 \cdot 0.00001}{0.98 \cdot 0.00001 + 0.001 \cdot 0.99999} \\ &= 0.0097 \end{aligned}$$

Despite the quality (reliability) of the controls (probability of success: 0.98) the detention of 99.03 % of the passengers is unjustified, they are not terrorists. $\square$

C.5 Random Variables and Distributions

Variables which adopt a particular value with a certain probability are called random variables. They may result, for example, from an experiment. Thus the probability of having six pips when throwing a die is $1/6$. In general such a process can be described as follows. An experiment was carried out in which a random variable X adopted a value x ; x is called a realization of X . The universal set is the set of all possible realizations of X (here: $x = 1, 2, 3, 4, 5, 6$). A sample is understood to be the n -fold realization of X .

In case of a die the random variable is discrete. It can at most adopt countably many values x_i . A probability $P(X = x_i)$ is assigned to each of these values, the sum of all of them is equal to 1.

If we are dealing with a continuous variable, for example the weights of fragments after the explosion of a vessel, we use a distribution function for its description. This function indicates the probability for $X \leq x$. Hence we have

$$F(x) = P(X \leq x) \quad (C.15)$$

$F(x)$ is thus defined for all real numbers. $F(x)$ is also called the cumulative distribution function. If $F(x)$ is differentiable, which normally is the case, we obtain its probability density function (pdf)

$$f(t) = P(t \leq X \leq t + dt) \quad (C.16)$$

Equation (C.16) is the probability for X lying between t and $t + dt$.

By combining Eqs. (C.15) and (C.16) we obtain

$$F(x) = \int_{-\infty}^x f(t)dt \quad \text{with} \quad \int_{-\infty}^{\infty} f(t)dt = 1 \quad (C.17)$$

Probability distributions are characterised by so-called moments. The first moment is the expected value. In case of discrete variables we have

$$E(X) = \sum_{i=1}^n x_i \cdot P(X = x_i) \quad (C.18)$$

and for continuous variables

$$E(X) = \int_{-\infty}^{\infty} t \cdot f(t)dt \quad (C.19)$$

Furthermore the variance is used. It is obtained from

$$V(X) = E[(X - E(X))^2] \quad (C.20)$$

Using Steiner's theorem Eq. (C.20) becomes

$$V(X) = E(X^2) - E(X)^2 \quad (C.21)$$

where $E(X^2)$ is the second moment. The square root of the variance is called standard deviation, i.e.

$$S(X) = \sqrt{V(X)} \quad (C.22)$$

Example C.6 Expected value and variance

The expected values and the variance for throws of an ideal die and for an exponential distribution with parameter $\lambda = 1/6$ are to be calculated.

Note: the probability density function of the exponential distribution is

$$f(t) = \lambda \cdot \exp(-\lambda t) \quad \lambda, t \geq 0$$

*Solution***Die**

- Expected value according to Eq. (C.18)

$$E(X) = \sum_{i=1}^6 i \cdot \frac{1}{6} = 3.5$$

- Second moment in analogy with Eq. (C.18)

$$E(X^2) = \sum_{i=1}^6 i^2 \cdot \frac{1}{6} = 15.1667$$

- Variance according to Eq. (C.21)

$$V(X) = E(X^2) - E(X)^2 = 15.1667 - 3.5^2 = 2.9167$$

Exponential distribution

- Expected value according to Eq. (C.19)

$$E(X) = \int_0^{\infty} t \cdot \lambda \cdot e^{-\lambda t} dt = \frac{1}{\lambda} = 6$$

- Second moment in analogy with Eq. (C.19)

$$E(X^2) = \int_0^{\infty} t^2 \cdot \lambda \cdot e^{-\lambda t} dt = \frac{2}{\lambda^2} = 72$$

- Variance according to Eq. (C.21)

$$V(X) = E(X^2) - E(X)^2 = \frac{2}{\lambda^2} - \frac{1}{\lambda^2} = \frac{1}{\lambda^2} = 36$$

□

In addition to expected value and variance the distribution percentiles are used to characterize a distribution. The percentiles are values below which a certain fraction of the distribution lies. In use are the 5th, 50th (median) and 95th percentiles. Using Eq. (C.17) we obtain for continuous random variables

$$F(x^*) = \int_{-\infty}^{x^*} f(t) dt = \frac{1 \pm \gamma}{2} \quad (C.23)$$

Equation (C.23) gives for $\gamma = 0.9$ the 5th respectively the 95-th percentiles and for $\gamma = 0$ the median.

C.6 Selected Types of Distributions

The exponential distribution was presented in the preceding Section. This distribution is a one-parameter distribution (λ). Mathematical statistics uses a large number of distributions, which may serve, for example, to describe empirical data or random processes. Below the probability density functions of several two-parameter distributions are listed, some of which also exist in versions with three parameters. Details are found in [C-1–C-5].

- Normal distribution

$$f_X(x) = \frac{1}{\sigma_x \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{x - \bar{x}_x}{\sigma_x} \right)^2 \right] \quad -\infty < x < \infty \quad (\text{C.24})$$

- Truncated normal distribution

$$f_X(x) = \frac{1}{r \cdot \sigma_x \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{x - \bar{x}_x}{\sigma_x} \right)^2 \right] \quad 0 < x < \infty \quad (\text{C.25})$$

with

$$r = 1 - \phi \left(-\frac{\bar{x}_x}{\sigma_x} \right)$$

and ϕ denoting the standard normal distribution

- Inverse Gaussian distribution

$$f_X(x) = \left(\frac{a}{2 \cdot \pi \cdot x^3} \right)^{\frac{1}{2}} \cdot \exp \left(\frac{-a \cdot (x - s)^2}{2 \cdot s^2 \cdot x} \right) \quad 0 \leq x \leq \infty \quad (\text{C.26})$$

- Logarithmic normal (lognormal) distribution

$$f_X(x) = \frac{1}{x s_x \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\ln x - \mu_x}{s_x} \right)^2 \right] \quad 0 < x < \infty \quad (\text{C.27})$$

- Gamma distribution

$$f_X(x) = \frac{\eta^b}{\Gamma(b)} \cdot x^{b-1} \cdot \exp(-\eta \cdot x) \quad x, b, \eta > 0 \quad (\text{C.28})$$

- Inverse gamma distribution

$$f_X(x) = \frac{\eta^b}{\Gamma(b)} \cdot \left(\frac{1}{x} \right)^{b+1} \cdot \exp \left(-\frac{\eta}{x} \right) \quad x, b, \eta > 0 \quad (\text{C.29})$$

- Weibull distribution

$$f_X(x) = \eta \cdot b \cdot (\eta \cdot x)^{b-1} \cdot \exp(-\eta \cdot x)^b \quad x, b, \eta > 0 \quad (\text{C.30})$$

- Log-logistic distribution

$$f_X(x) = \frac{\delta \cdot e^{-\gamma} \cdot x^{-\delta-1}}{(1 + e^{-\gamma} \cdot x^{-\delta})^2} \quad x, \delta > 0 \quad (\text{C.31})$$

- Beta distribution

$$f_X(x) = \frac{\Gamma(a+b)}{\Gamma(a) \cdot \Gamma(b)} x^{a-1} \cdot (1-x)^{b-1} \quad a > 0, b > 0, \quad x \in [0, 1] \quad (\text{C.32})$$

- Rectangular distribution (constant probability density function)

$$f_X(x) = \begin{cases} \frac{1}{b-a} & \text{if } b \geq x \geq a \\ 0 & \text{otherwise} \end{cases} \quad (\text{C.33})$$

- Right-sided triangular distribution

$$f_X(x) = \begin{cases} \frac{2b}{(b-a)^2} - \frac{2x}{(b-a)^2} & \text{if } b \geq x \geq a \\ 0 & \text{if } b \geq x \geq a \end{cases} \quad (\text{C.34})$$

- Bivariate lognormal distribution

$$f_{X,Y}(x,y) = \frac{\exp\left\{-\frac{1}{2 \cdot (1-\rho^2)} \cdot \left[\left(\frac{\ln X - \mu_1}{s_1}\right)^2 - 2 \cdot \rho \left(\frac{\ln X - \mu_1}{s_1}\right) \cdot \left(\frac{\ln Y - \mu_2}{s_2}\right) + \left(\frac{\ln Y - \mu_2}{s_2}\right)^2\right]\right\}}{2 \cdot \pi \cdot s_1 \cdot s_2 \cdot \sqrt{(1-\rho^2)} \cdot x \cdot y}$$

$$0 \leq x, y < \infty; \quad s_1, s_2 > 0; \quad |\rho| < 1 \quad (\text{C.35})$$

C.7 Estimation of Parameters

Let the sequence of observations $x_1, x_2, \dots, x_n$ of a random sample be realizations of n independent random variables $X_1, X_2, \dots, X_n$, all of which possess the same distribution; n is called the sample size. The expected value of the distribution is $E(X) = \mu$. $E(X)$ is estimated by the mean or average value

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (\text{C.36})$$

and the variance $V(X)$ by

$$\sigma^2 = \frac{1}{n-1} \left(\sum_{i=1}^n x_i^2 - n\bar{x}^2 \right) \quad (\text{C.37})$$

Equations (C.36) and (C.37) result from applying the maximum-likelihood estimation (MLE) to normally distributed variables. The estimation of the parameters of other distributions leads to more complicated systems of equations. Details are found, for example in [C-1, C-3]. An application is given in the next Example.

Example C.7 Estimation of the parameters of a discrete and a continuous distribution

In a die game the following numbers of pips appeared:

3, 5, 4, 5, 6, 5, 1, 1, 4, 3, 1, 2, 4, 6, 5, 2, 3, 2, 2, 3

Calculate the mean value and the variance and compare them with the theoretical results of Example C.6.

According to Eq. (C.36) the mean value is

$$\hat{\bar{x}} = \frac{1}{n} \sum_{i=1}^n x_i = \frac{1}{20} \cdot 67 = 3.35$$

The variance results from Eq. (C.37)

$$\hat{\sigma}^2 = \frac{1}{n-1} \left(\sum_{i=1}^n x_i^2 - n\bar{x}^2 \right) = 2.6605$$

The corresponding theoretical values are 3.5 and 2.9167. The standard deviation is $\sigma = 1.6311$. The circumflex above $\bar{x}$ and σ^2 indicates that we are dealing with an empirical estimator. These estimators take the places in the relationships of the corresponding true but unknown parameters.

When observing the lifetimes of gas vessels the following values were found:

$t_1 = 800,000$ h, $t_2 = 1,000,000$ h, $t_3 = 650,000$ h and $t_4 = 1,200,000$ h

Calculate the failure rate assuming exponentially distributed lifetimes. The failure rate is determined using the maximum-likelihood method, which requires the probability density function

$$f(t) = \lambda \cdot e^{-\lambda t} \quad \lambda, t \geq 0$$

The likelihood function then is

$$L = f(t_1) \cdot f(t_2) \cdot f(t_3) \cdot f(t_4)$$

Usually the logarithm of function L is formed and derived with respect to the parameter, λ in this case. If the result is set equal to zero, we have the necessary

condition for the maximum of the function, from which λ is determined.

$$\frac{d \ln L}{d \lambda} = \frac{4}{\lambda} - (t_1 + t_2 + t_3 + t_4)$$

where from

$$\lambda = \frac{4}{t_1 + t_2 + t_3 + t_4} = 1.1 \cdot 10^{-6} \text{ h}^{-1}$$

results. □

C.8 Probability Trees

Based on the methods described above probability calculations for sequences of events can be performed, as shown in the following example from [C-2].

Example C.8 Engine damage of a jet plane

A rickety jet aeroplane has three engines (A, B, C), which would survive an overseas flight with the probabilities of $P(A) = 0.95$, $P(B) = 0.96$ and $P(C) = 0.97$. For being capable of flying, the plane needs at least two functioning engines ('success criterion'). What is the probability that the aeroplane survives the overseas flight? The corresponding tree structure is shown in Fig. C.2.

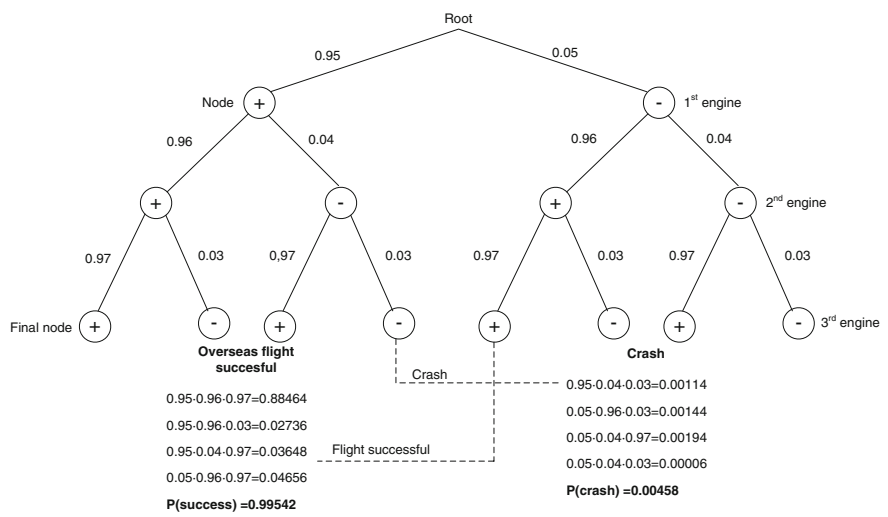


Fig C.2 Tree structure for treating engine failures of an aeroplane with probabilities (after [C-2])

The flight is successful if any one of the following situations occurs:

- engines A and B survive, C fails

$$P(A \cap B \cap \bar{C}) = P(A) \cdot P(B) \cdot (1 - P(C)) = 0.02736$$

- engines B and C survive, A fails

$$P(B \cap C \cap \bar{A}) = P(B) \cdot P(C) \cdot (1 - P(A)) = 0.04656$$

- engines A and C survive, B fails

$$P(A \cap C \cap \bar{B}) = P(A) \cdot P(C) \cdot (1 - P(B)) = 0.03686$$

- all engines survive

$$P(A \cap C \cap B) = P(A) \cdot P(B) \cdot P(C) = 0.88464$$

Since we are dealing with mutually exclusive events the total probability of a successful flight is calculated according to Eq. (C.4), which gives

$$P(\text{successful flight}) = 0.99542 \text{ and hence } P(\text{crash}) = 0.00458.$$

□

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Appendix D

Coefficients for the TNO Multienergy Model and the BST Model

Tables [D.1](#) and [D.2](#).

Table D.1 Coefficients for the TNO multienergy model Eq. (10.163) [D-1–D-3]

Explosion strength	Range	a	b	c	d
Curve 1	$0.23 \leq x \leq 0.53$	$1.00 \cdot 10^{-2}$			
	$x > 0.53$	$6.23 \cdot 10^{-3}$	−0.95		
Curve 2	$0.23 \leq x \leq 0.60$	$1.00 \cdot 10^{-2}$			
	$x > 0.60$	$1.22 \cdot 10^{-2}$	−0.98		
Curve 3	$0.23 \leq x \leq 0.60$	$5.00 \cdot 10^{-2}$			
	$x > 0.60$	$3.05 \cdot 10^{-2}$	−0.97		
Curve 4	$0.23 \leq x \leq 0.55$	$1.00 \cdot 10^{-1}$			
	$x > 0.55$	$6.20 \cdot 10^{-2}$	−0.97		
Curve 5	$0.23 \leq x \leq 0.55$	$2.00 \cdot 10^{-1}$			
	$x > 0.55$	$1.10 \cdot 10^{-1}$	−0.99		
Curve 6	$0.23 \leq x \leq 0.56$	$5.00 \cdot 10^{-1}$			
	$0.56 < x \leq 3.50$	$3.00 \cdot 10^{-1}$	−1.10		
	$x > 3.50$			1.1188	0.5120
Curve 7	$0.23 \leq x \leq 0.50$	$1.00 \cdot 10^{-0}$			
	$0.50 < x \leq 1.00$	$4.60 \cdot 10^{-1}$	−1.20		
	$1.00 < x \leq 2.50$			1.5236	0.3372
	$x > 2.50$			1.1188	0.5120
Curve 8	$0.23 \leq x \leq 0.50$	$2.00 \cdot 10^{-0}$			
	$0.50 < x \leq 0.60$	$4.67 \cdot 10^{-1}$	−2.08		
	$0.60 < x \leq 1.0$			2.3721	0.3372
	$1.00 < x \leq 2.50$			1.5236	0.3372
	$x > 2.50$			1.1188	0.5120
Curve 9	$0.23 \leq x \leq 0.35$	$5.00 \cdot 10^{-0}$			
	$0.35 < x \leq 1.00$			2.3721	0.3372
	$1.00 < x \leq 2.50$			1.5236	0.3372
	$x > 2.50$			1.1188	0.5120
Curve 10	$0.23 \leq x \leq 1.00$			2.3721	0.3372
	$1.00 < x \leq 2.50$			1.5236	0.3372
	$x > 2.50$			1.1188	0.5120

Table D.2 Constants for the BST model Eq. (10.169) [D-1, D-4]

Mf	x range	a	b	c	d	e	f	g	h	p	q
0.07	$x \leq 0.15$	0.01	—	—	—	—	—	—	—	—	—
	$0.15 < x \leq 2.10$	—	−0.933128	−2.888832	−1.737895	0.920042	0.087748	−1.005685	−2.377646	—	—
	$x > 2.10$	—	—	—	—	—	—	—	—	−1.011736	−2.365616
0.12	$x \leq 0.15$	0.028	—	—	—	—	—	—	—	—	—
	$0.15 < x \leq 2.10$	—	−0.933128	−2.888832	−1.737895	0.920042	0.087748	−1.005685	−1.930488	—	—
	$x > 2.10$	—	—	—	—	—	—	—	—	−1.011736	−1.918458
0.20	$x \leq 0.15$	0.065739	—	—	—	—	—	—	—	—	—
	$0.15 < x \leq 2.10$	—	−0.933128	−2.888832	−1.737895	0.920042	0.087748	−1.005685	−1.559823	—	—
	$x > 2.10$	—	—	—	—	—	—	—	—	−1.011736	−1.547793
0.35	$x \leq 0.16$	0.218	—	—	—	—	—	—	—	—	—
	$0.16 < x \leq 1.70$	—	−0.058243	−1.513539	−1.509913	0.602095	0.106104	−1.005685	−0.962616	—	—
	$x > 1.70$	—	—	—	—	—	—	—	—	−0.996587	−1.037988
0.70	$x \leq 0.19$	0.68	—	—	—	—	—	—	—	—	—
	$0.19 < x \leq 2.37$	—	3.14094	4.025197	−0.520525	−1.615733	−0.553277	−0.724239	−0.523105	—	—
	$x > 2.37$	—	—	—	—	—	—	—	—	−1.160157	−0.494153
1.00	$x \leq 0.12$	1.24	—	—	—	—	—	—	—	—	—
	$0.12 < x \leq 2.26$	—	−2.650731	−5.975678	−2.655464	1.920581	0.417161	−1.408333	−0.488746	—	—
	$x > 2.26$	—	—	—	—	—	—	—	—	−1.113825	−0.535492
1.40	$x \leq 0.17$	2.00	—	—	—	—	—	—	—	—	—
	$0.17 < x \leq 2.21$	—	−2.318816	−8.107616	−6.830475	1.070003	1.567781	−1.353722	−0.492033	—	—
	$x > 2.21$	—	—	—	—	—	—	—	—	−1.138989	−0.475584
2.00	$x \leq 0.12$	5.00	—	—	—	—	—	—	—	—	—
	$0.12 < x \leq 2.27$	—	14.12624	22.55578	2.850864	−5.885056	−0.10116	−0.954886	−0.418265	—	—
	$x > 2.27$	—	—	—	—	—	—	—	—	−1.174514	−0.415406
3.00	$x \leq 0.18$	10.00	—	—	—	—	—	—	—	—	—
	$0.18 < x \leq 1.86$	—	−21.67565	−11.63587	7.95783	1.56914	−0.57778	−1.267661	−0.396133	—	—
	$x > 1.86$	—	—	—	—	—	—	—	—	−1.174514	−0.415406
4.00	$x \leq 0.16$	15.2	—	—	—	—	—	—	—	—	—
	$0.16 < x \leq 2.25$	—	−14.87262	−12.50994	2.727597	1.731734	0.159062	−1.319884	−0.405275	—	—
	$x > 2.25$	—	—	—	—	—	—	—	—	−1.174514	−0.415406
5.20	$x \leq 0.17$	20.0	—	—	—	—	—	—	—	—	—
	$0.17 < x \leq 2.27$	—	18.600175	19.416571	0.730754	−4.407614	−0.063184	−1.089879	−0.399327	—	—
	$x > 2.27$	—	—	—	—	—	—	—	—	−1.174514	−0.415406

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