PEARSON
Education

Applied Thermodynamics

for Engineering Technologists

Fifth Edition

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Preface to the Fifth Edition

This book aims to give students of engineering a thorough grounding in the subject of thermodynamics and the design of thermal plant. The book is comprehensive in its coverage without sacrificing the necessary theoretical rigour; the emphasis throughout is on the applications of the theory to real processes and plant. The objectives have remained unaltered through four previous editions and continuing interest in the book not only in the UK but also in most other countries in the English-speaking world has confirmed these objectives as suitable for students on a wide range of courses.

The book is designed as a complete course text for degree courses in mechanical, aeronautical, chemical, environmental, and energy engineering, engineering science, and combined studies courses in which thermodynamics and related topics are an important part of the curriculum. Students on technician diploma and certificate courses in engineering will also find the book suitable although the coverage is more extensive than they might require.

A number of lecturers in universities and polytechnics in the UK were asked for comments on the book before the fifth edition was prepared; the consensus was that the balance of the book was broadly correct with only minor changes needed, but a more modern format was thought to be desirable.

The fifth edition has therefore been completely recast in a new style which will make it more attractive, and easier to use. The opportunity has also been taken to rearrange the chapters in what seems to be a more logical order. Throughout the book the emphasis is now on the effective use of energy resources and the need to protect the environment. The chapter on energy sources, use and management (Ch. 17), has been improved and extended; it now includes a more extensive coverage of combined heat and power and a new section on energy recovery, including a brief mention of pinch technology. The material on gas turbines, steam turbines, nozzles, and propulsion (Chs 8–10) has been rewritten in a more logical format giving a more general treatment of blade design while still stressing the differences in design procedures for steam and gas turbines. In the chapter on refrigeration (Ch. 14) more emphasis is given to the heat pump and to vapour-absorption plant. A new section on refrigerants discusses the vitally important question of the thinning of the ozone layer due to CFCs; examples and problems in this chapter now use refrigerant 134a instead of refrigerant 12, and tables and a reduced scale chart for R134a are included by permission of ICI. Analysis of exhaust gases, emission control for IC engines, and the greenhouse effect are also included.

A new sign convention for energy transfer across a system boundary has come into general use in recent years and has therefore been introduced in this book. The convention is to treat both work and heat crossing a boundary as positive when it is transferred from the surroundings to the system. Also, there has been an international agreement to standardize symbols used for heat and mass transfer and the symbols in this text have been chosen accordingly. For example, the symbol for heat transfer coefficient is α, that for thermal conductivity λ, that for dynamic viscosity η, and that for thermal diffusivity κ. Molar quantities are now distinguished by the overscript, $\tilde{}$. Thanks are due to Dr Y.R. Mayhew for many helpful discussions on the use of physical quantities, units, and nomenclature. In the chapter on combustion (Ch. 7) the section on dissociation has been rewritten to conform with the use of a standard thermal equilibrium constant as tabulated in the latest edition of Rogers and Mayhew's *Thermodynamic and Transport Properties of Fluids.*

While preparing this new edition I have been ever conscious of the loss of my co-author and colleague for so many years, Allan McConkey, who died just after the publication of the previous edition in 1986. I would like to dedicate this edition to Allan with deep affection and gratitude for a long and fruitful collaboration.

TDE 1992

Acknowledgements

We are grateful to Blackwell Publishers for permission to include extracts from the Rogers and Mayhew *Thermodynamic and Transport Properties of Fluids* (*SI Units*) (4th ed.), 1988. Figure 15.4 is reproduced by permission of the Chartered Institution of Building Services Engineers, copies of the chart (size A3) for record purposes may be obtained from CIBSE, 222 Balham High Road, London SW12 9BS. Figure 14.14 is reproduced by permission of ICI; Table 14.1 is an extract with some interpolated values of thermodynamic properties of HFA 134a by permission of ICI, Runcorn, Cheshire.

The following sources have been drawn on for information: Figures 13.21 and 13.22 are adapted from *The Internal Combustion Engine in Theory and Practice* by C.F. Taylor, MIT Press. Section 13.13 includes material adapted from *Exhaust Emissions Handbook* published by Cussons Ltd. The data for Fig. 12.30 was provided by J.S. Milne of the Department of Mechanical and Industrial Engineering, Dundee College of Technology, from an original test carried out by him.

Nomenclature

A	air–fuel ratio; area
a	velocity of sound; acceleration; non-flow specific exergy
BDC	bottom dead centre
BS	British Standard
Bi	Biot number
b	steady-flow specific exergy
bmep	brake mean effective pressure
bp	brake power
C	velocity; constant; thermal capacity
CHP	combined heat and power
CI	compression ignition
COP	coefficient of performance
CV	calorific value
C_d	discharge coefficient
c	specific heat capacity
$\tilde{c}$	molar heat capacity
c_p	specific heat capacity at constant pressure
c_{pma}	specific heat capacity of air per unit mass of dry air
c_v	specific heat capacity at constant volume
$\tilde{c}_p$	molar heat capacity at constant pressure
$\tilde{c}_v$	molar heat capacity at constant volume
D, d	bore; diameter
E	emissive power; energy
e	eccentricity
F	force; geometric factor
FI	fuel injection
Fo	Fourier number
f	friction factor; frequency
fp	friction power
$\dot{G}$	irradiation
GCV	gross calorific value
Gr	Grashof number
g	gravitational acceleration

H	enthalpy; fundamental dimension of heat
HC	hydrocarbons
ΔH	enthalpy of reaction
h	specific enthalpy
Δh	specific enthalpy of reaction
$\tilde{h}$	molar enthalpy
$\Delta \tilde{h}$	molar enthalpy of reaction
h_f	specific enthalpy of a saturated liquid
h_{fg}	specific enthalpy of vaporization
h_g	specific enthalpy of a saturated vapour
I	electric current
IC	internal combustion
i	intensity of radiation
imep	indicated mean effective pressure
ip	indicated power
J	current density
$\dot{J}$	radiosity
j	Colburn factor for heat transfer
K	equilibrium constant
$K^{\ominus}$	standardized equilibrium constant
k	isentropic index for steam; blade velocity coefficient
L	stroke; fundamental dimension of length
l	length; characteristic linear dimension
M	fundamental dimension of mass
Ma	Mach number
m	mass
$\tilde{m}$	molar mass
$\dot{m}$	mass flow rate
N	rotational speed
NCV	net calorific value
NDIR	non-dispersive infra-red
Nu	Nusselt number
N_{tu}	number of transfer units
n	polytropic index; amount of substance; number of cylinders; nozzle arc length
ON	octane number
P	perimeter
PN	performance number
Pr	Prandtl number
p	absolute pressure; blade pitch
p_m	mean effective pressure
p_b	brake mean effective pressure
p_i	indicated mean effective pressure
Δp	pressure loss
Q	heat
$\dot{Q}$	rate of heat transfer
$\dot{q}$	rate of heat transfer per unit area
$\dot{q}_g$	rate of heat transfer per unit volume

R	specific gas constant; thermal resistance; radius; ratio of thermal capacities
$\tilde{R}$	molar gas constant
RF	reheat factor
Re	Reynolds number
r	radius; expansion ratio
r_p	pressure ratio
r_v	compression ratio
S	entropy; steam consumption
SI	spark ignition
St	Stanton number
s	specific entropy
sfc	specific fuel consumption
T	absolute temperature; torque; fundamental dimension of time
TDC	top dead centre
t	temperature; fundamental dimension of temperature; blade thickness
Δt	temperature difference
$\Delta \bar{t}$	true mean temperature difference
$\Delta \bar{t}_a$	arithmetic mean temperature difference
$\Delta \bar{t}_{ln}$	logarithmic mean temperature difference
U	internal energy; overall heat transfer coefficient
ΔU	internal energy of reaction
u	specific internal energy
Δu	specific internal energy of reaction
$\tilde{u}$	molar internal energy
$\Delta \tilde{u}$	molar internal energy of reaction
V	volume
$\dot{V}$	rate of volume flow
v	specific volume
W	work; brake load
$\dot{W}$	rate of work transfer, power
X	temperature on any arbitrary scale
x	dryness fraction; nozzle pressure ratio; length
Z	height above a datum level
z	number of stages

Greek symbols

α	angle of absolute velocity; heat transfer coefficient; absorptivity for radiation
β	blade angle; coefficient of cubical expansion
γ	ratio of specific heats, c_p/c_v
δ	film thickness
Λ	degree of reaction
ε	emissivity; effectiveness of a heat exchanger

η	efficiency; dynamic viscosity
κ	thermal diffusivity
λ	thermal conductivity; wavelength
ν	kinematic viscosity
ρ	density; reflectivity
σ	Stefan–Boltzmann constant
τ	time; shear stress in a fluid; transmissivity
ϕ	relative humidity; angle
ω	specific humidity; solid angle
ψ	percentage saturation

Subscripts

AS	air standard
a	dry air; atmospheric; aircraft; absolute velocity
ai	absolute velocity at inlet
ae	absolute velocity at exit
B	black body
BT	brake thermal
b	blade velocity
C	cold fluid; compressor
c	condensate; convective; critical value; clearance
d	dew point; diagram
DB	dry bulb
e	exit; exhaust
F	fin; fluid
f	saturated liquid; fuel; film; flow velocity
fg	change of phase at constant pressure
g	saturated vapour; gases
gr	gross
H	hot fluid; high-pressure stage
hp	heat pump
I	intercooler
IT	indicated thermal
i	inlet; a constituent in a mixture; inside surface; intermediate; indicated; mesh point; injector
j	mesh point; jet
L	low-pressure stage
M	mechanical
m	mean
max	maximum
min	minimum
N	normal
net	net
0	stagnation condition; overall; outside; zero or reference condition

P	product of combustion
p	constant pressure
R	reactant
r	radiation; relative velocity
ref	refrigeration
re	relative velocity at exit
ri	relative velocity at inlet
s	isentropic
s	vapour; swept volume; stage; steam
T	throat; turbine; total
V	volumetric
v	constant volume
WB	wet bulb
w	water; wall; whirl
λ	monochromatic value at wavelength, λ
ϕ	radiation at angle, ϕ
∞_c	polytropic compression
∞_e	polytropic expansion

1

Introduction and the First Law of Thermodynamics

All living things depend on energy for survival, and modern civilizations will continue to thrive only if existing sources of energy can be developed to meet the growing demands. Energy exists in many forms, from the energy locked in the atoms of matter itself to the intense radiant energy emitted by the sun. Many sources of energy exist; many are known, some perhaps unknown; but when an energy source exists means must first be found to transform the energy into a form convenient to our purpose.

The chemical energy of combustion of fossil fuels (oil, coal, gas), and waste (agricultural, industrial, domestic), is used to produce heat which in turn is used to provide mechanical energy in turbines or reciprocating engines; uranium atoms are bombarded asunder and the nuclear energy released is used as heat; the potential energy of large masses of water is converted into electrical energy as it passes through water turbines on its way from the mountains to the sea; the kinetic energy of the wind is harnessed by windmills to produce electricity; the energy of the waves of the sea is converted into electrical power in floating turbines; the tides produced by the rotation of the moon produce electrical energy by flowing through turbines in large river estuaries; hot rocks and trapped liquids in the depths of the earth are made to release their energy to be converted to electricity; the immense radiant energy of the sun is tapped to heat water or by suitable device is converted directly into electricity. Figure 1.1 shows the various energy sources and the possible conversion paths with the more important transfers shown as bold lines; more information can be found in Chapter 4 of ref. 1.1 and the bibliography therein.

Applied thermodynamics is the science of the relationship between heat, work, and the properties of systems. It is concerned with the means necessary to convert heat energy from available sources such as fossil fuels into mechanical work. A *heat engine* is the name given to a system which by operating in a cyclic manner produces net work from a supply of heat. The laws of thermodynamics are natural hypotheses based on observations of the world in which we live. It is observed that heat and work are two mutually convertible forms of energy, and this is the basis of the First Law of Thermodynamics. It is also observed that heat never flows unaided from an object at a low temperature to one at a high temperature, in the same way that a river never

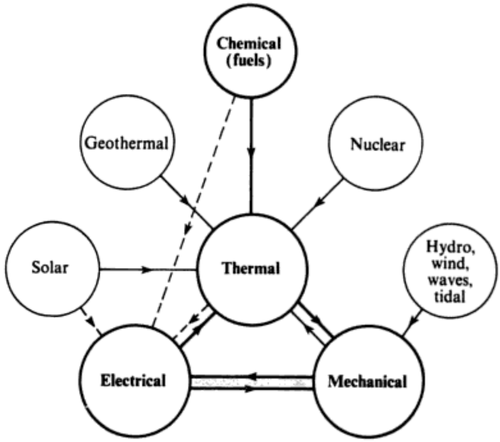


Fig. 1.1 Energy conversion diagram

flows unaided uphill. This observation is the basis of the Second Law of Thermodynamics, which can be used to show that a heat engine cannot convert all the heat supplied to it into mechanical work but must always reject some heat at a lower temperature. These ideas will be discussed and developed in due course, but first some fundamental definitions must be made.

1.1 Heat, work, and the system

In order to deal with the subject of applied thermodynamics rigorously it is necessary to define the concepts used.

Heat is a form of energy which is transferred from one body to another body at a lower temperature, by virtue of the temperature difference between the bodies.

For example, when a body A at a certain temperature, say 20 °C, is brought into contact with a body B at a higher temperature, say 21 °C, then there will be a transfer of heat from B to A until the temperatures of A and B are equal (Fig. 1.2). When the temperature of A is the same as the temperature of B no heat transfer takes place between the bodies, and they are said to be in *thermal equilibrium*. Heat is apparent during the process only and is therefore transitory energy. Since heat energy flows from B to A there is a reduction in the intrinsic energy possessed by B and an increase in the intrinsic energy possessed by A. This intrinsic energy of a body, which is a function of temperature at least, must not be confused with heat. Heat can never be contained in a body or possessed by a body.

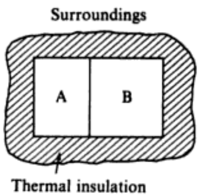


Fig. 1.2 Two isolated bodies in contact

A *system* may be defined as a collection of matter within prescribed and identifiable boundaries (Fig. 1.3). The boundaries are not necessarily inflexible; for instance the fluid in the cylinder of a reciprocating engine during the

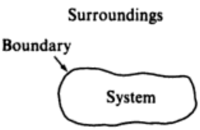


Fig. 1.3 Definition of a system

expansion stroke may be defined as a system whose boundaries are the cylinder walls and the piston crown. As the piston moves so do the boundaries move (Fig. 1.4). This type of system is known as a *closed* system.

An *open* system is one in which there is a transfer of mass across the boundaries; for instance, the fluid in a turbine at any instant may be defined as an open system whose boundaries are as shown in Fig. 1.5.

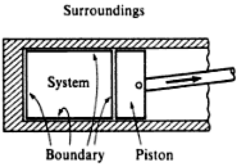


Fig. 1.4 Fluid in a cylinder as a closed system

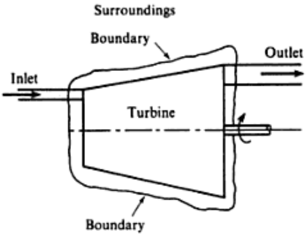


Fig. 1.5 Fluid in a turbine as an open system

The *pressure* of a system is the force exerted by the system on unit area of its boundaries. Units of pressure are, for example, pascal, Pa (where 1 Pa = 1 N/m^2), or bar; the symbol p will be used for pressure. Pressure as defined here is called *absolute pressure.* A gauge for measuring pressure (e.g. as shown in Fig. 1.6(a) and 1.6(b)), records the pressure above atmospheric. This is called *gauge pressure*, i.e. absolute pressure equals gauge pressure plus atmospheric pressure.

The gauge shown in Fig. 1.6(b) is called a Bourdon gauge. The absolute pressure of the system in a closed elliptical section tube forces the tube out of

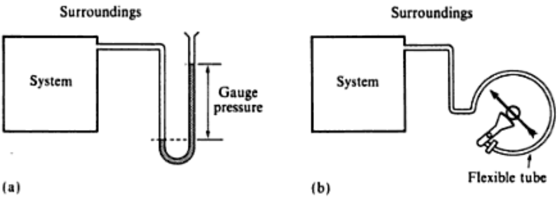


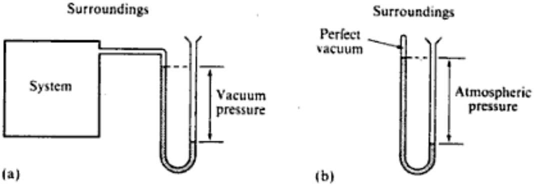
Fig. 1.6 Two different pressure gauges

position against the pressure of the atmosphere. The tube's displacement is recorded by a pointer on a circular scale, which can be calibrated directly in bars.

When the pressure of a system is below atmospheric, it is called *vacuum pressure* (Fig. 1.7(a)).

When one side of a U-tube is completely evacuated and then sealed, the gauge will act as a *barometer* and the atmospheric pressure can be measured (Fig. 1.7(b)).

Fig. 1.7 Vacuum pressure and barometric pressure



The gauges shown in Figs 1.6(a) and 1.7(a) measure gauge pressure in mm of a liquid of known relative density, and are called manometers.

For example, when water is the liquid, then

$$1 \text{ mm of water} = \frac{1}{10^3} \times 9806.65 \text{ N/m}^2 = 9.81 \text{ N/m}^2 = 9.81 \text{ Pa}$$

where 1 m^3 of water weighs 9810 N, say.

Mercury (Hg) is very often used in gauges. Taking the relative density of mercury as 13.6, then

$$1 \text{ mm Hg} = \frac{1}{10^3} \times 13.6 \times 9810 \text{ N/m}^2 = 133.4 \text{ N/m}^2 = 133.4 \text{ Pa}$$

For a simple introduction to manometers and pressure measurement, see ref. 1.2.

The *specific volume* of a system is the volume occupied by unit mass of the system. The symbol used is v and the units are, for example, m^3/kg. The symbol V will be used for volume. (Note that the specific volume is the reciprocal of density.)

Work is defined as the product of a force and the distance moved in the direction of the force. When a boundary of a closed system moves in the direction of the force acting on it, then the surroundings do work on the system. When the boundary is moved outwards the work is done by the system on its surroundings. The units of work are, for example, N m. If work is done on unit mass of a fluid, then the work done per kilogram of fluid has units of N m/kg.

Work is observed to be energy in transition. It is never contained in a body or possessed by a body.

Heat and work are both transitory energies and must not be confused with the intrinsic energy possessed by a system. For example, when a gas contained in a well-lagged cylinder (Fig. 1.8(a)) is compressed by moving the piston to the left, the pressure and temperature of the gas are observed to increase, and

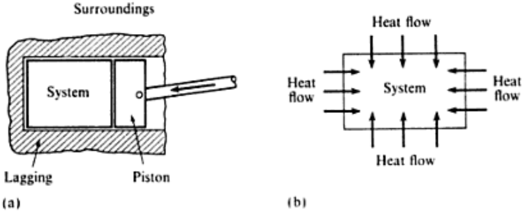


Fig. 1.8 Intrinsic energy increase by work or heat input

hence the intrinsic energy of the gas increases. Since the cylinder is well lagged, no heat can flow into or out of the gas. The increase in intrinsic energy of the gas has therefore been caused by the work done by the piston on the gas.

As another example, consider a gas contained in a rigid container and heated (Fig. 1.8(b)). Since the boundaries of the system are rigidly fixed then no work is done on or by the system. The pressure and temperature of the gas are observed to increase, and hence the intrinsic energy of the gas will increase. The increase in intrinsic energy has been caused by the heat flow to the system.

In the example of Fig. 1.8(a) the work done on the system is energy which is apparent only during the actual process of compression. There is an intrinsic energy of the system initially and an intrinsic energy finally, but the work done appears only in transition from the initial to the final condition. Similarly, in the example of Fig. 1.8(b), the heat supplied appears only in transition from one state of the gas to another.

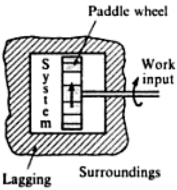


Fig. 1.9 Paddle wheel work input

Another way in which work may be transferred to a system is illustrated in Fig. 1.9. The paddle wheel imparts a change of momentum to the fluid and a work input is required to turn the shaft. The kinetic energy attained by the fluid is dissipated by internal fluid friction, and friction between the fluid and the container. When the container is well lagged, all the work input goes to increasing the intrinsic energy of the system.

Convention

The sign convention used in this book assumes that all external inputs to a system are positive. That is

Heat supplied to a system, Q, is positive.
Work input to a system, W, is positive.

When a system boundary is drawn to define the system then it follows that heat supplied, Q, and work input, W, will always be shown by arrows pointing into the system. In algebraic equations it will be quite clear when numbers are substituted whether the value of Q and/or W is positive or negative; a negative value for Q will indicate that heat is rejected from the system; a negative value for W will indicate that work is done by the system on its surroundings.

In many cases it would cause unnecessary confusion by referring throughout to negative quantities; for example, it is clear that for a device designed to produce power, such as an internal combustion engine or turbine, the work input to the system is always negative. Although the above sign convention will be used for all algebraic equations it will be made clear in the wording that the system is producing a work output. For example

Work done *by* the system $= -W$

Similarly, for the case of a system designed specifically to cool a fluid, such as a condenser for example, it is clear that the heat supplied to the system is always negative. Hence we can write

Heat *rejected by* the system $= -Q$

1.2 Units

Throughout this book SI units will be used. The International System of Units (Système International d'Unités, abbreviation SI) was adopted by the General Conference of Weights and Measures in 1960 and subsequently endorsed by the International Organization for Standardization. It is a *coherent* system. In a coherent system all derived unit quantities are formed by the product or quotient of other unit quantities. In SI units six physical quantities are arbitrarily assigned unit value and hence all other physical quantities are derived from these. The six quantities chosen and their units are as follows: length (metre, m); mass (kilogram, kg); time (second, s); electric current (ampere, A); thermodynamic temperature (degree kelvin, K); luminous intensity (candela, cd).

Thus, for example, velocity = length/time has units of m/s; acceleration = velocity/time has units of m/s^2; volume = length × length × length has units of m^3; specific volume = volume/mass has units of m^3/kg.

Force, energy, and power

Newton's second law may be written as force ∝ mass × acceleration for a body of constant mass, i.e.

$$F = kma \tag{1.1}$$

where m is the mass of a body accelerated with an acceleration a, by a force F; k is a constant.

In a coherent system of units such as SI, $k = 1$, hence

$$F = ma$$

The SI unit of force is therefore $kg\,m/s^2$. This composite unit is called the *newton*, N, i.e. 1 N is the force required to give a mass of 1 kg an acceleration of 1 m/s^2.

It follows that the SI unit of work (= force × distance) is the newton metre, N m. As stated earlier heat and work are both forms of energy, and hence both can have the units of $kg\,m^2/s^2$ or N m. A general unit for energy is introduced by giving the newton metre the name *joule*, J, i.e. 1 joule, J = 1 newton × 1 metre

or 1 J = 1 N m

The use of additional names for composite units is extended further by introducing the *watt*, W, as the unit of power,

i.e. 1 watt, W = 1 J/s = 1 N m/s

Pressure

The unit of pressure (force per unit area) is N/m^2 and this unit is sometimes called the *pascal*, Pa. For most cases occurring in thermodynamics the pressure expressed in pascals would be a very small number; a new unit is defined as follows:

$$1 \text{ bar} = 10^5 \text{ N/m}^2 = 10^5 \text{ Pa}$$

The advantage of using a unit such as the bar is that it is approximately equal to atmospheric pressure. In fact the standard atmospheric pressure is exactly 1.013 25 bar.

As indicated in section 1.1, it is often convenient to express a pressure as a head of a liquid. We have:

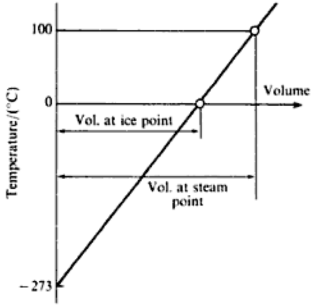
Standard atmospheric pressure = 1.013 25 bar = 0.76 m Hg

Temperature

The variation of an easily measurable property of a substance with temperature can be used to provide a temperature-measuring instrument. For example, the length of a column of mercury will vary with temperature due to the expansion and contraction of the mercury. The instrument can be calibrated by marking the length of the column when it is brought into thermal equilibrium with the vapour of boiling water at atmospheric pressure and again when it is in thermal equilibrium with ice at atmospheric pressure. On the Celsius (or Centigrade) scale 100 divisions are made between the two fixed points and the zero is taken at the ice point.

The change in volume at constant pressure, or the change in pressure at constant volume, of a fixed mass of gas which is not easily liquefied (e.g. oxygen, nitrogen, helium, etc.) can be used as a measure of temperature. Such an instrument is called a *gas thermometer*. It is found for all gases used in such thermometers that if the graph of temperature against volume in the constant pressure gas thermometer is extrapolated beyond the ice point to the point at which the volume of the gas would become zero, then the temperature at this point is −273 °C approximately (Fig. 1.10). Similarly if the graph of temperature against pressure in the constant volume gas thermometer is extrapolated to zero pressure, then the same zero of temperature is found. An absolute zero of temperature has therefore been fixed, and an absolute scale of temperature can be defined. Temperature on the absolute Celsius scale can be

Fig. 1.10 Graph of temperature against volume for a gas



obtained by adding 273 to all temperatures on the Celsius scale; this scale is called the *Kelvin* scale. The unit of temperature is the degree kelvin and is given the symbol K, but since the Celsius scale which is used in practice has a different zero the temperature in degrees Celsius is given the symbol C (e.g. 20 °C = 293 K approximately; also, 30 °C − 20 °C = 10 K). In this text capital T is used for absolute temperature and small t for other temperatures.

In Chapter 5 an absolute scale of temperature will be introduced as a direct consequence of the Second Law of Thermodynamics. It is found that the gas thermometer absolute scales approach the ideal scale as a limit. Also, with regard to the practical absolute temperature scale, there is an internationally agreed working scale which gives temperatures in terms of more practicable and more accurate instruments than the gas thermometer (see ref. 1.3).

Multiples and sub-multiples

Multiples and sub-multiples of the basic units are formed by means of prefixes, and the ones most commonly used are shown in the following table:

Multiplying factor	*Prefix*	*Symbol*
One million million	tera	T
One thousand million	giga	G
One million, 10^6	mega	M
One thousand, 10^3	kilo	k
One thousandth, 10^{-3}	milli	m
One millionth, 10^{-6}	micro	μ
One thousand millionth	nano	n
One million millionth	pico	p

For most purposes the multiplying factors shown in the above table are sufficient. For example, power can be expressed in either megawatts, MW, or kilowatts, kW, or watts, W. In the measurement of length the millimetre, mm, the metre, m, and the kilometre, km, are usually adequate. For areas, the difference in size between the square millimetre, mm^2, and the square metre, m^2, is large (a factor of 10^6), and an intermediate size is useful; the square centimetre, cm^2, is recommended for limited use only. For volumes, the difference between the cubic millimetre, mm^3, and the cubic metre, m^3, is much too great (a factor of 10^9), and the most commonly used intermediate unit is the cubic decimetre, dm^3, which is equal to one-thousandth of a cubic metre (i.e. $1\ dm^3 = 10^{-3}\ m^3$). The cubic decimetre can also be called the *litre*, l,

i.e. $\quad 1\ \text{litre},\ l = 1\ dm^3 = 10^{-3}\ m^3$

(Note, for very precise measurements, 1 litre = $1.000028\ dm^3$.)

Certain exceptions to the general rule of multiplying factors are inevitable. The most obvious example is in the case of the unit of time. Instead of the centisecond, kilosecond, or megasecond, for instance, the minute, hour, day, etc. are used. Similarly, a mass flow rate may be expressed in kilograms per hour, kg/h, if this gives a more convenient number than when expressed in kilograms per second, kg/s. Also the speed of road vehicles is expressed in kilometres per hour, km/h, since this is more convenient than the normal unit of velocity which is metres per second, m/s.

1.3 The state of the working fluid

In all problems in applied thermodynamics we are concerned with energy transfers to or from a system. In practice the matter contained within the boundaries of the system can be liquid, vapour, or gas, and is known as the *working fluid*. At any instant the *state* of the working fluid may be defined by certain characteristics called its *properties*. Many properties have no significance in thermodynamics (e.g. electrical resistance), and will not be considered. The thermodynamic properties introduced in this book are pressure, temperature, specific volume, specific internal energy, specific enthalpy, and specific entropy. It has been found that, for any pure working fluid, only two independent properties are necessary to define completely the state of the fluid. Since any two independent properties suffice to define the state of a system, it is possible to represent the state of a system by a point situated on a diagram of properties. For example, a cylinder containing a certain fluid at pressure p_1 and specific volume v_1 is at state 1, defined by point 1 on a diagram of p against v (Fig. 1.11(a)). Since the state is defined, then the temperature of the fluid, T, is

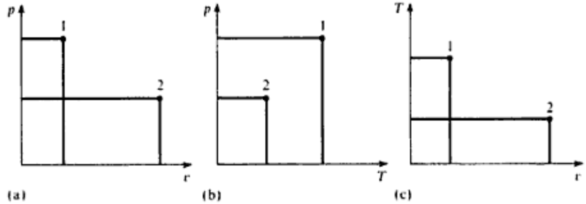


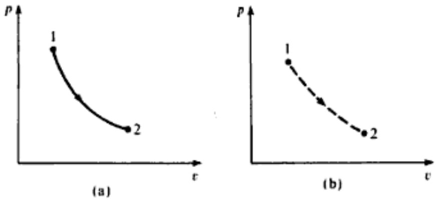
Fig. 1.11 State of a working fluid on a property diagram

fixed and the state point can be located on a diagram of p against T and T against v (Figs 1.11(b) and 1.11(c)). At any other instant the piston may be moved in the cylinder such that the pressure and specific volume are changed to p_2 and v_2. State 2 can then be marked on the diagrams. Diagrams of properties are used continually in applied thermodynamics to plot state changes. The most important are the pressure–volume and temperature–entropy diagrams, but enthalpy–entropy and pressure–enthalpy diagrams are also used frequently.

1.4 Reversibility

In section 1.3 it was shown that the state of a fluid can be represented by a point located on a diagram using two properties as coordinates. When a system changes state in such a way that at any instant during the process the state point can be located on the diagram, then the process is said to be *reversible*. The fluid undergoing the process passes through a continuous series of equilibrium states. A reversible process between two states can therefore be drawn as a line on any diagram of properties (Fig. 1.12(a)). In practice, the fluid undergoing a process cannot be kept in equilibrium in its intermediate states and a continuous path cannot be traced on a diagram of properties. Such real processes are called *irreversible processes*. An irreversible process is usually represented by a dotted line joining the end states to indicate that the intermediate states are indeterminate (Fig. 1.12(b)).

Fig. 1.12 Reversible and irreversible processes



A more rigorous definition of reversibility is as follows:

When a fluid undergoes a reversible process, both the fluid and its surroundings can always be restored to their original state.

The criteria of reversibility are as follows:

(a) The process must be frictionless. The fluid itself must have no internal friction and there must be no mechanical friction (e.g. between cylinder and piston).
(b) The difference in pressure between the fluid and its surroundings during the process must be infinitely small. This means that the process must take place infinitely slowly, since the force to accelerate the boundaries of the system is infinitely small.

(c) The difference in temperature between the fluid and its surroundings during the process must be infinitely small. This means that the heat supplied or rejected to or from the fluid must be transferred infinitely slowly.

It is obvious from the above criteria that no process in practice is truly reversible. However, in many practical processes a very close approximation to an *internal reversibility* may be obtained. In an internally reversible process, although the surroundings can never be restored to their original state, the fluid itself is at all times in an equilibrium state and the path of the process can be exactly retraced to the initial state. In general, processes in cylinders with a reciprocating piston are assumed to be internally reversible as a reasonable approximation, but processes in rotary machinery (e.g. turbines) are known to be irreversible due to the high degree of turbulence and scrubbing of the fluid.

1.5 Reversible work

Consider an ideal frictionless fluid contained in a cylinder behind a piston. Assume that the pressure and temperature of the fluid are uniform and that there is no friction between the piston and the cylinder walls. Let the cross-sectional area of the piston be A, let the pressure of the fluid be p, let the pressure of the surroundings be $(p + dp)$ (Fig. 1.13). The force exerted by the piston on the fluid is pA. Let the piston move under the action of the force exerted a distance dl to the left. Then work done on the fluid by the piston is given by force times the distance moved,

i.e. Work done, $dW = -(pA) \times dl = -p\,dV$

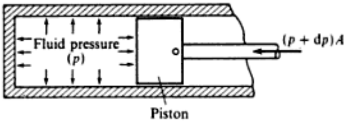


Fig. 1.13 Fluid in a cylinder undergoing a compression

where dV is a small increase in volume. The negative sign is necessary because the volume is decreasing.

Or for a mass, m,

$$dW = -mp\,dv$$

where v is the specific volume. This is only true when criteria (a) and (b) hold as stated in section 1.4.

When a fluid undergoes a reversible process a series of state points can be joined up to form a line on a diagram of properties. The work done on the fluid during any reversible process, W, is therefore given by the area under the line of the process plotted on a p–v diagram (Fig. 1.14),

i.e. $$W = -m\int_1^2 p\,dv = m\int_2^1 p\,dv = m\,(\text{shaded area on Fig. 1.14}) \qquad (1.2)$$

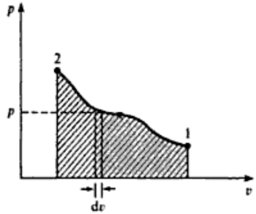


Fig. 1.14 Work done in a compression process

When p can be expressed in terms of v then the integral, $m\int_1^2 p\,dv$, can be evaluated.

Example 1.1 Unit mass of a fluid at a pressure of 3 bar, and with a specific volume of 0.18 m^3/kg, contained in a cylinder behind a piston expands reversibly to a pressure of 0.6 bar according to a law $p = c/v^2$, where c is a constant. Calculate the work done during the process.

Solution Referring to Fig. 1.15

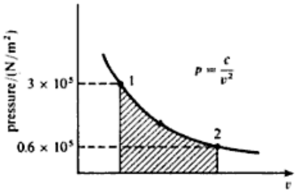


Fig. 1.15 Pressure-specific volume diagram for Example 1.1

$$W = -m\int_1^2 p\,dv = -m\text{ (shaded area)}$$

i.e. $$W = -cm\int_{v_1}^{v_2}\frac{dv}{v^2} = -cm\left[-\frac{1}{v}\right]_{v_1}^{v_2}$$

also $$c = pv^2 = 3 \times 0.18^2 = 0.0972 \text{ bar } (m^3/kg)^2$$

and $$v_2 = \sqrt{\frac{c}{p_2}} = \sqrt{\frac{0.0972}{0.6}} = 0.402 \text{ m}^3/\text{kg}$$

therefore

$$W = -0.0972 \times 10^5\left(\frac{1}{0.18} - \frac{1}{0.402}\right)\text{ N m/kg}$$

$$= -29\,840 \text{ N m/kg}$$

i.e. Work done *by* the fluid = +29 840 N m/kg

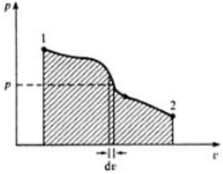


Fig. 1.16 Reversible expansion process on a p–v diagram

When an expansion process takes place reversibly (see Fig. 1.16), the integral, $\int_1^2 p\,dv$, is positive, i.e.

$$W = -m\int_1^2 p\,dv = -m\text{ (shaded area on Fig. 1.16)}$$

A process from right to left on the p–v diagram is one in which there is a work input to the fluid (i.e. W is positive). Conversely, a process from left to right is one in which there is a work output from the fluid (i.e. W is negative).

When a fluid undergoes a series of process and finally returns to its initial state, then it is said to have undergone a thermodynamic *cycle*. A cycle which consists only of reversible processes is a reversible cycle. A cycle plotted on a diagram of properties forms a closed figure, and a reversible cycle plotted on a p–v diagram forms a closed figure the area of which represents the net work of the cycle. For example, a reversible cycle consisting of four reversible processes 1 to 2, 2 to 3, 3 to 4, and 4 to 1 is shown in Fig. 1.17. The net work input is equal to the shaded area. If the cycle were described in the reverse direction (i.e. 1 to 4, 4 to 3, 3 to 2, and 2 to 1), then the shaded area would represent net work output from the system. The rule is that the enclosed area of a reversible cycle represents net work input (i.e. net work done on the system) when the cycle is described in an anticlockwise manner, and the enclosed area represents work output (i.e. work done by the system) when the cycle is described in a clockwise manner.

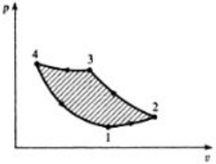


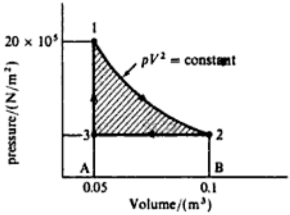
Fig. 1.17 Reversible cycle on a p–v diagram

Example 1.2 Unit mass of a certain fluid is contained in a cylinder at an initial pressure of 20 bar. The fluid is allowed to expand reversibly behind a piston according to a law pV^2 = constant until the volume is doubled. The fluid is then cooled reversibly at constant pressure until the piston regains its original position; heat is then supplied reversibly with the piston firmly locked in position until the pressure rises to the original value of 20 bar. Calculate the net work done by the fluid, for an initial volume of 0.05 m³.

Solution Referring to Fig. 1.18

$$p_1 V_1^2 = p_2 V_2^2$$

Fig. 1.18 Figure for Example 1.2



therefore

$$p_2 = p_1\left(\frac{V_1}{V_2}\right)^2 = \frac{20}{2^2} = 5 \text{ bar}$$

$$W_{12} = -\int_1^2 p\,dV \text{ from equation (1.2)} = -\text{area 12BA1}$$

i.e. $$W_{12} = -\int_{V_1}^{V_2} \frac{c}{V^2}\,dV \quad \text{where} \quad c = p_1 V_1^2 = 20 \times 0.05^2 \text{ bar m}^6$$

therefore

$$W_{12} = -10^5 \times 20 \times 0.0025\left[-\frac{1}{V}\right]_{0.05}^{0.1}$$

$$= -10^5 \times 20 \times 0.0025\left(\frac{1}{0.05} - \frac{1}{0.1}\right) = -50\,000 \text{ N m}$$

$$W_{23} = \text{area 32BA3} = p_2(V_2 - V_3) = 10^5 \times 5 \times (0.1 - 0.05)$$

$$= 25\,000 \text{ N m}$$

Work done from 3 to 1 is zero since the piston is locked in position. Therefore

$$\text{Net work done} = W_{12} + W_{23} = -(\text{enclosed area 1231})$$

$$= -50\,000 + 25\,000 = -25\,000 \text{ N m}$$

Hence the net work done by the fluid is +25 000 N m.

It has been stated above that work is given by $-\int p\,dv$ for a reversible process only. It can easily be shown that $-\int p\,dv$ is not equal to the work done if a

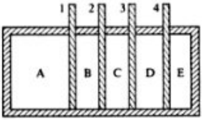


Fig. 1.19 Compartments with sliding partitions

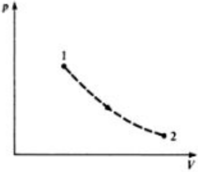


Fig. 1.20 Irreversible process on a p–v diagram

process is irreversible. For example, consider a cylinder, divided into a number of compartments by sliding partitions (Fig. 1.19). Initially, compartment A is filled with a mass of fluid at pressure p_1. When the sliding partition 1 is removed quickly, then the fluid expands to fill compartments A and B. When the system settles down to a new equilibrium state the pressure and volume are fixed and the state can be marked on the p–V diagram (Fig. 1.20). Sliding partition 2 is now removed and the fluid expands to occupy compartments A, B, and C. Again the equilibrium state can be marked on the diagram. The same procedure can be adopted with partitions 3 and 4 until finally the fluid is at p_2 and occupies a volume V_2 when filling compartments A, B, C, D, and E. The area under the curve 1–2 on Fig. 1.20 is given by $\int_1^2 p\,dV$, but no work has been done (apart from the negligible work required to move the partitions). No piston has been moved, no turbine wheel has been revolved; in other words, no external force has been moved through a distance. This is the extreme case of an irreversible process in which $\int p\,dV$ has a value and yet the work done is zero. When a fluid expands without a restraining force being exerted by the surroundings, as in the example above, the process is known as *free expansion*. Free expansion is highly irreversible by criterion (b), section 1.4. In many practical expansion processes some work is done by the fluid which is less than $\int p\,dv$ and in many practical compression processes work is done which is greater than $\int p\,dv$. It is important to represent all irreversible processes by dotted lines on a p–v diagram as a reminder that the area under the dotted line does not represent work.

1.6 Conservation of energy and the First Law of Thermodynamics

The concept of energy and the hypothesis that it can neither be created nor destroyed were developed by scientists in the early part of the nineteenth century, and became known as the *Principle of the Conservation of Energy*. The First Law of Thermodynamics is merely one statement of this general principle with particular reference to thermal energy, (i.e. heat), and mechanical energy, (i.e. work).

When a system undergoes a complete thermodynamic cycle the intrinsic energy of the system is the same at the beginning and end of the cycle. During the various processes that make up the cycle work is done on or by the fluid and heat is supplied or rejected; the network input can be defined as $\sum W$, and the net heat supplied as $\sum Q$, where the symbol $\sum$ represents the sum for a complete cycle.

Since the intrinsic energy of the system is unchanged the First Law of Thermodynamics states that:

> *When a system undergoes a thermodynamic cycle then the net heat supplied to the system from its surroundings plus the net work input to the system from its surroundings must equal zero.*

That is

$$\sum Q + \sum W = 0 \quad (1.3)$$

Example 1.3 In a certain steam plant the turbine develops 1000 kW. The heat supplied to the steam in the boiler is 2800 kJ/kg, the heat rejected by the steam to the cooling water in the condenser is 2100 kJ/kg and the feed-pump work required to pump the condensate back into the boiler is 5 kW. Calculate the steam flow rate.

Solution The cycle is shown diagrammatically in Fig. 1.21. A boundary is shown which encompasses the entire plant. Strictly, this boundary should be thought of as encompassing the working fluid only. For unit mass flow rate

$$\sum dQ = 2800 - 2100 = 700 \text{ kJ/kg}$$

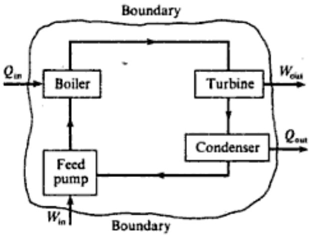
Let the steam flow be $\dot{m}$ kg/s. Therefore

$$\sum dQ = 700m \text{ kW}$$

and

$$\sum dW = 5 - 1000 = -995 \text{ kW}$$

Fig. 1.21 Steam plant for Example 1.3



Then in equation (1.3)

$$\sum \mathrm{d}Q + \sum \mathrm{d}W = 0$$

i.e. $700\,\dot{m} - 995 = 0$

therefore

$$\dot{m} = 995/700 = 1.421 \text{ kg/s}$$

i.e. Steam mass flow rate required = 1.421 kg/s

1.7 The non-flow equation

In section 1.6 it is stated that when a system possessing a certain intrinsic energy is made to undergo a cycle by heat and work transfer, then the net heat supplied plus the net work input is zero.

This is true for a complete cycle when the final intrinsic energy of the system is equal to its initial value. Consider now a process in which the intrinsic energy of the system is finally greater than the initial intrinsic energy. The sum of the net heat supplied and the net work input has increased the intrinsic energy of the system, i.e.

Gain in intrinsic energy = Net heat supplied + net work input

When the net effect is to transfer energy from the system, then there will be a loss in the intrinsic energy of the system.

When a fluid is not in motion then its intrinsic energy per unit mass is known as the *specific internal energy* of the fluid and is given the symbol u. The specific internal energy of a fluid depends on its pressure and temperature, and is itself a property. The simple proof that specific internal energy is a property is given in ref. 1.4. The internal energy of mass, m, of a fluid is written as U, i.e. $mu = U$. The units of internal energy, U, are usually written as kJ.

Since internal energy is a property, then gain in internal energy in changing from state 1 to state 2 can be written $U_2 - U_1$.

Also, gain in internal energy = net heat supplied + net work input,

i.e. $$U_2 - U_1 = \sum_1^2 \mathrm{d}Q + \sum_1^2 \mathrm{d}W$$

This equation is true for a process or series of processes between state 1 and state 2 provided there is no flow of fluid into or out of the system. In any one non-flow process there will be either heat supplied or heat rejected, but not both; similarly there will be either work input or work output, but not both. Hence,

$$U_2 - U_1 = Q + W \quad \text{for a non-flow process}$$

or, for unit mass

$$Q + W = u_2 - u_1 \tag{1.4}$$

This equation is known as the *non-flow energy equation*. Equation (1.4) is very often written in differential form. For a small amount of heat supplied dQ, a small amount of work done on the fluid dW, and a small gain in specific internal energy du, then

$$dQ + dW = du \tag{1.5}$$

Example 1.4 In the compression stroke of an internal-combustion engine the heat rejected to the cooling water is 45 kJ/kg and the work input is 90 kJ/kg. Calculate the change in specific internal energy of the working fluid stating whether it is a gain or a loss.

Solution

$$Q = -45\ \text{kJ/kg}$$

(−ve sign since heat is rejected).

$$W = 90\ \text{kJ/kg}$$

Using equation (1.4)

$$Q + W = u_2 - u_1$$

$$-45 + 90 = u_2 - u_1$$

therefore

$$u_2 - u_1 = 45\ \text{kJ/kg}$$

i.e. Gain in internal energy = 45 kJ/kg

Example 1.5 In the cylinder of an air motor the compressed air has a specific internal energy of 420 kJ/kg at the beginning of the expansion and a specific internal energy of 200 kJ/kg after expansion. Calculate the heat flow to or from the cylinder when the work done by the air during the expansion is 100 kJ/kg.

Solution From equation (1.4)

$$Q + W = u_2 - u_1$$

i.e. $Q - 100 = 200 - 420$

therefore

$$Q = -120\ \text{kJ/kg}$$

i.e. Heat rejected by the air = +120 kJ/kg

It is important to note that equations (1.3), (1.4), and (1.5) are true whether or not the process is reversible. These are energy equations.

For reversible non-flow processes we have, from equation (1.2)

$$W = -m\int_1^2 p\,dv$$

or in differential form

$$dW = -m\,p\,dv$$

Hence for any reversible non-flow process for unit mass, substituting in equation (1.5)

$$dQ = du + p\,dv \tag{1.6}$$

or substituting in equation (1.4)

$$Q = (u_2 - u_1) + \int_1^2 p\,dv \tag{1.7}$$

Equations (1.6) and (1.7) can only be used for ideal reversible non-flow processes.

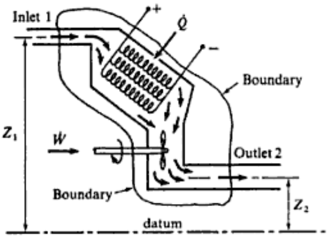
1.8 The steady-flow equation

In section 1.7, the specific internal energy of a fluid was said to be the intrinsic energy of the fluid due to its thermodynamic properties. When unit mass of a fluid with specific internal energy, u, is moving with velocity C and is a height Z above a datum level, then it possesses a total energy of $u + (C^2/2) + Zg$, where $C^2/2$ is the kinetic energy of unit mass of the fluid and Zg is the potential energy of unit mass of the fluid.

In most practical problems the rate at which the fluid flows through a machine or piece of apparatus is constant. This type of flow is called *steady flow*.

Consider a fluid flowing in steady flow with a mass flow rate, $\dot{m}$, through a piece of apparatus (Fig. 1.22). This constitutes an open system as defined in section 1.2. The boundary is shown cutting the inlet pipe at section 1 and the outlet pipe at section 2. This boundary is sometimes called a *control surface*, and the system encompassed, a *control volume*.

Fig. 1.22 Steady-flow open system



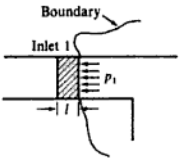


Fig. 1.23 Section at inlet to the system

Let it be assumed that a steady rate of flow of heat $\dot{Q}$ units is supplied, and that $\dot{W}$ is the rate of work input on the fluid as it passes through the apparatus. Now in order to introduce the fluid across the boundary an expenditure of energy is required; similarly in order to push the fluid across the boundary at exit, an expenditure of energy is required. The inlet section is shown enlarged in Fig. 1.23. Consider an element of fluid, length l, and let the cross-sectional area of the inlet pipe be A_1. Then we have

Energy required to push element across boundary

$$= (p_1 A_1) \times l = p_1 \times (\text{volume of fluid element})$$

therefore

Energy required for unit mass flow rate of fluid $= p_1 v_1$

where v_1 is the specific volume of the fluid at section 1.

Similarly it can be shown that

Energy required at exit to push unit mass flow rate of fluid across the boundary $= p_2 v_2$

Consider now the energy entering and leaving the system. The energy entering the system consists of the energy of the flowing fluid at inlet

$$\dot{m}\left(u_1 + \frac{C_1^2}{2} + Z_1 g\right)$$

the energy term $\dot{m}p_1 v_1$, the heat supplied $\dot{Q}$, and the rate of work input, $\dot{W}$. The energy leaving the system consists of the energy of the flowing fluid at the outlet section

$$\dot{m}\left(u_2 + \frac{C_2^2}{2} + Z_2 g\right)$$

and the energy term $\dot{m}p_2 v_2$. Since there is steady flow of fluid into and out of the system, and there are steady flows of heat and work, then the energy entering must exactly equal the energy leaving.

$$\dot{m}\left(u_1 + \frac{C_1^2}{2} + Z_1 g + p_1 v_1\right) + \dot{Q} + \dot{W} = \dot{m}\left(u_2 + \frac{C_2^2}{2} + Z_2 g + p_2 v_2\right) \tag{1.8}$$

In nearly all problems in applied thermodynamics, changes in height are negligible and the potential energy terms can be omitted from the equation. The terms in u and pv occur on both sides of the equation and always will do so in a flow process, since a fluid always possesses a certain internal energy, and the term pv always occurs at inlet and outlet as seen in the above proof. The sum of specific internal energy and the pv term is given the symbol h, and is called *specific enthalpy*,

i.e. Specific enthalpy, $h = u + pv$ (1.9)

The specific enthalpy of a fluid is a property of the fluid, since it consists of the sum of a property and the product of two properties. Since specific enthalpy is a property like specific internal energy, pressure, specific volume, and temperature, it can be introduced into any problem whether the process is a flow process or a non-flow process. The enthalpy of mass, m, of a fluid can be written as H (i.e. $mh = H$). The units of h are the same as those of internal energy.

Substituting equation (1.9) in equation (1.8)

$$\dot{m}\left(h_1 + \frac{C_1^2}{2} + Z_1 g\right) + \dot{Q} + \dot{W} = \dot{m}\left(h_2 + \frac{C_2^2}{2} + Z_2 g\right) \tag{1.10}$$

Equation (1.10) is known as the *steady-flow energy equation*. In steady flow the rate of mass flow of fluid at any section is the same as at any other section.

Consider any section of cross-sectional area A, where the fluid velocity is C, then the rate of volume flow past the section is CA. Also, since mass flow is volume flow divided by specific volume

$$\text{Mass flow rate, } \dot{m} = \frac{CA}{v} = \rho CA \tag{1.11}$$

where v is the specific volume at the section and ρ the density at the section. This equation is known as the *continuity of mass equation.*

With reference to Fig. 1.22

$$\dot{m} = \frac{C_1 A_1}{v_1} = \frac{C_2 A_2}{v_2}$$

Example 1.6 In the turbine of a gas turbine unit the gases flow through the turbine at 17 kg/s and the power developed by the turbine is 14 000 kW. The specific enthalpies of the gases at inlet and outlet are 1200 kJ/kg and 360 kJ/kg respectively, and the velocities of the gases at inlet and outlet are 60 m/s and 150 m/s respectively. Calculate the rate at which heat is rejected from the turbine. Find also the area of the inlet pipe given that the specific volume of the gases at inlet is 0.5 m^3/kg.

Solution A diagrammatic representation of the turbine is shown in Fig. 1.24. From equation (1.10), neglecting changes in height

$$\dot{m}\left(h_1 + \frac{C_1^2}{2}\right) + \dot{Q} + \dot{W} = \dot{m}\left(h_2 + \frac{C_2^2}{2}\right)$$

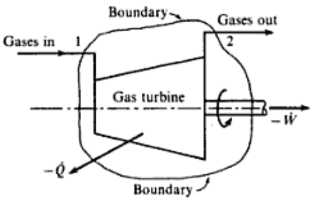


Fig. 1.24 Gas turbine for Example 1.6

For unit mass flow rate:

$$\text{Kinetic energy at inlet} = \frac{C_1^2}{2} = \frac{60^2}{2}\,\text{m}^2/\text{s}^2 = \frac{60^2}{2}\frac{\text{kg m}^2}{\text{s}^2\,\text{kg}}$$

$$= 1800\ \text{N m/kg} = 1.8\ \text{kJ/kg}$$

$$\text{Kinetic energy at outlet} = \frac{C_2^2}{2} = 2.5^2 \times (\text{kinetic energy at inlet})$$

$$= 11.25\ \text{kJ/kg (since } C_2 = 2.5C_1)$$

Also $\quad W = -14\,000$ kW

Substituting in equation (1.10)

$$17(1200 + 1.8) + \dot{Q} - 14\,000 = 17(360 + 11.25)$$

therefore

$$Q = -119.3 \text{ kW}$$

i.e. $\quad$ Heat rejected $= +119.3$ kW

To find the inlet area, use equation (1.11), i.e.

$$\dot{m} = \frac{CA}{v} \quad \text{or } A = \frac{\dot{m}v}{C}$$

therefore

$$\text{Inlet area, } A_1 = \frac{17 \times 0.5}{60} = 0.142 \text{ m}^2$$

Example 1.7 Air flows steadily at the rate of 0.4 kg/s through an air compressor, entering at 6 m/s with a pressure of 1 bar and a specific volume of 0.85 m^3/kg, and leaving at 4.5 m/s with a pressure of 6.9 bar and a specific volume of 0.16 m^3/kg. The specific internal energy of the air leaving is 88 kJ/kg greater than that of the air entering. Cooling water in a jacket surrounding the cylinder absorbs heat from the air at the rate of 59 kW. Calculate the power required to drive the compressor and the inlet and outlet pipe cross-sectional areas.

Solution In this problem it is more convenient to write the flow equation as in equation 1.8, omitting the Z terms,

i.e.
$$\dot{m}\left(u_1 + \frac{C_1^2}{2} + p_1 v_1\right) + \dot{Q} + \dot{W} = \dot{m}\left(u_2 + \frac{C_2^2}{2} + p_2 v_2\right)$$

A diagrammatic representation of the compressor is shown in Fig. 1.25. Note that the heat rejected across the boundary is equivalent to the heat removed by the cooling water from the compressor. For unit mass flow rate:

$$\frac{C_1^2}{2} = \frac{6 \times 6}{2} \text{ J/kg} = 18 \text{ J/kg} = 0.018 \text{ kJ/kg}$$

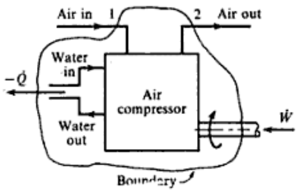


Fig. 1.25 Air compressor for Example 1.7

$$\frac{C_2^2}{2} = \frac{4.5 \times 4.5}{2}\ \text{J/kg} = 10.1\ \text{J/kg} = 0.0101\ \text{kJ/kg}$$

$$p_1 v_1 = 1 \times 10^5 \times 0.85 = 85\,000\ \text{J/kg} = 85\ \text{kJ/kg}$$

$$p_2 v_2 = 6.9 \times 10^5 \times 0.16 = 110\,400\ \text{J/kg} = 110.4\ \text{kJ/kg}$$

$$u_2 - u_1 = 88\ \text{kJ/kg}$$

Also $\dot{Q} = -59\ \text{kW}$

Now $\dot{Q} + \dot{W} = \dot{m}\left\{(u_2 - u_1) + (p_2 v_2 - p_1 v_1) + \left(\frac{C_2^2}{2} - \frac{C_1^2}{2}\right)\right\}$

i.e. $-59 + \dot{W} = 0.4(88 + 110.4 - 85 + 0.0101 - 0.018)$

therefore

$$\dot{W} = 104.4\ \text{kW}$$

(Note that the change in kinetic energy is negligibly small in comparison with the other terms.)

i.e. Power input required = 104.4 kW

From equation (1.11)

$$\dot{m} = \frac{CA}{v}$$

$$A_1 = \frac{0.4 \times 0.85}{6} = 0.057\ \text{m}^2$$

i.e. Inlet pipe cross-sectional area = $0.057\ \text{m}^2$

Similarly

$$A_2 = \frac{0.4 \times 0.16}{4.5} = 0.014\ \text{m}^2$$

i.e. Outlet pipe cross-sectional area = $0.014\ \text{m}^2$

In Example 1.7 the steady-flow energy equation has been used, despite the fact that the compression consists of suction of air, compression in a closed cylinder, and discharge of air. The steady-flow equation can be used because the cycle of processes takes place many times in a minute, and therefore the average effect is steady flow of air through the machine.

Problems

1.1 A certain fluid at 10 bar is contained in a cylinder behind a piston, the initial volume being $0.05\ \text{m}^3$. Calculate the work done by the fluid when it expands reversibly:
(i) at constant pressure to a final volume of $0.2\ \text{m}^3$;
(ii) according to a linear law to a final volume of $0.2\ \text{m}^3$ and a final pressure of 2 bar;

(iii) according to a law pV = constant to a final volume of 0.1 m^3;
(iv) according to a law pv^3 = constant to a final volume of 0.06 m^3;
(v) according to a law, $p = (A/V^2) - (B/V)$, to a final volume of 0.1 m^3 and a final pressure of 1 bar, where A and B are constants.

Sketch all processes on a p–v diagram.

(150 000 N m; 90 000 N m; 34 700 N m; 7640 N m; 19 200 N m)

1.2 1 kg of a fluid is compressed reversibly according to a law $pv = 0.25$, where p is in bar and v is in m^3/kg. The final volume is $\frac{1}{4}$ of the initial volume. Calculate the work done on the fluid and sketch the process on a p–v diagram.

(34 660 N m)

1.3 0.05 m^3 of a gas at 6.9 bar expands reversibly in a cylinder behind a piston according to the law $pv^{1.2}$ = constant, until the volume is 0.08 m^3. Calculate the work done by the gas and sketch the process on a p–V diagram.

(15 480 N m)

1.4 1 kg of a fluid expands reversibly according to a linear law from 4.2 bar to 1.4 bar; the initial and final volumes are 0.004 m^3 and 0.02 m^3. The fluid is then cooled reversibly at constant pressure, and finally compressed reversibly according to a law pv = constant back to the initial conditions of 4.2 bar and 0.004 m^3. Calculate the work done in each process and the net work of the cycle. Sketch the cycle on a p–v diagram.

(−4480 N m; +1120 N m; +1845 N m; −1515 N m)

1.5 A fluid at 0.7 bar occupying 0.09 m^3 is compressed reversibly to a pressure of 3.5 bar according to a law pv^n = constant. The fluid is then heated reversibly at constant volume until the pressure is 4 bar; the specific volume is then 0.5 m^3/kg. A reversible expansion according to a law pv^2 = constant restores the fluid to its initial state. Sketch the cycle on a p–v diagram and calculate:
(i) the mass of fluid present;
(ii) the value of n in the first process;
(iii) the net work of the cycle.

(0.0753 kg; 1.847; −640 N m)

1.6 A fluid is heated reversibly at a constant pressure of 1.05 bar until it has a specific volume of 0.1 m^3/kg. It is then compressed reversibly according to a law pv = constant to a pressure of 4.2 bar, then allowed to expand reversibly according to a law $pv^{1.7}$ = constant, and is finally heated at constant volume back to the initial conditions. The work done in the constant pressure process is −515 N m, and the mass of fluid present is 0.2 kg. Calculate the net work of the cycle and sketch the cycle on a p–v diagram.

(+781 N m)

1.7 In an air compressor the compression takes place at a constant internal energy and 50 kJ of heat are rejected to the cooling water for every kilogram of air. Calculate the work input for the compression stroke per kilogram of air.

(50 kJ/kg)

1.8 In the compression stroke of a gas engine the work done on the gas by the piston is 70 kJ/kg and the heat rejected to the cooling water is 42 kJ/kg. Calculate the change of specific internal energy stating whether it is a gain or a loss.

(28 kJ/kg gain)

1.9 A mass of gas at an initial pressure of 28 bar, and with an internal energy of 1500 kJ, is contained in a well-insulated cylinder of volume 0.06 m^3. The gas is allowed to

expand behind a piston until its internal energy is 1400 kJ; the law of expansion is pv^2 = constant. Calculate:
(i) the work done;
(ii) the final volume;
(iii) the final pressure.

(−100 kJ; 0.148 m^3; 4.59 bar)

1.10 The gases in the cylinder of an internal combustion engine have a specific internal energy of 800 kJ/kg and a specific volume of 0.06 m^3/kg at the beginning of expansion. The expansion of the gases may be assumed to take place according to a reversible law, $pv^{1.5}$ = constant, from 55 bar to 1.4 bar. The specific internal energy after expansion is 230 kJ/kg. Calculate the heat rejected to the cylinder cooling water per kilogram of gases during the expansion stroke.

(104 kJ/kg)

1.11 A steam turbine receives a steam flow of 1.35 kg/s and the power output is 500 kW. The heat loss from the casing is negligible. Calculate:
(i) the change of specific enthalpy across the turbine when the velocities at entrance and exit and the difference in elevation are negligible;
(ii) the change of specific enthalpy across the turbine when the velocity at entrance is 60 m/s, the velocity at exit is 360 m/s, and the inlet pipe is 3 m above the exhaust pipe.

(370 kJ/kg; 433 kJ/kg)

1.12 A steady flow of steam enters a condenser with a specific enthalpy of 2300 kJ/kg and a velocity of 350 m/s. The condensate leaves the condenser with a specific enthalpy of 160 kJ/kg and a velocity of 70 m/s. Calculate the heat transfer to the cooling fluid per kilogram of steam condensed.

(−2199 kJ/kg)

1.13 A turbine operating under steady-flow conditions receives steam at the following state: pressure, 13.8 bar; specific volume 0.143 m^3/kg, specific internal energy 2590 kJ/kg, velocity 30 m/s. The state of the steam leaving the turbine is as follows: pressure 0.35 bar, specific volume 4.37 m^3/kg, specific internal energy 2360 kJ/kg, velocity 90 m/s. Heat is rejected to the surroundings at the rate of 0.25 kW and the rate of steam flow through the turbine is 0.38 kg/s. Calculate the power developed by the turbine.

(102.7 kW)

1.14 A nozzle is a device for increasing the velocity of a steadily flowing fluid. At the inlet to a certain nozzle the specific enthalpy of the fluid is 3025 kJ/kg and the velocity is 60 m/s. At the exit from the nozzle the specific enthalpy is 2790 kJ/kg. The nozzle is horizontal and there is a negligible heat loss from it. Calculate:
(i) the velocity of the fluid at exit;
(ii) the rate of flow of fluid when the inlet area is 0.1 m^2 and the specific volume at inlet is 0.19 m^3/kg;
(iii) the exit area of the nozzle when the specific volume at the nozzle exit is 0.5 m^3/kg.

(688 m/s; 31.6 kg/s; 0.0229 m^2)

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1.2 DOUGLAS J F, GASIOREK J M and SWAFFIELD J A 1986 *Fluid Mechanics* 2nd edn Longman

1.3 BS 1041 *Temperature Measurement* HMSO; Section 2.1 1985 *Guide to Selection and Use of Liquid-in-glass Thermometers*; Part 3 1989 *Guide to Selection and Use of Industrial Resistance Thermometers*; Part 4 1966 *Thermocouples*; Part 5 1972 *Radiation Pyrometers*; Part 7 1988 *Guide to Selection and Use of Temperature-time Records*

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2

The Working Fluid

In section 1.3 the matter contained within the boundaries of a system is defined as the working fluid, and it is stated that when two independent properties of the fluid are known then the thermodynamic state of the fluid is defined. In thermodynamic systems the working fluid can be in the liquid, vapour, or gaseous phase. All substances can exist in any one of these phases, but we tend to identify all substances with the phase in which they are in equilibrium at atmospheric pressure and temperature. For instance, substances such as oxygen and nitrogen are thought of as gases; H_2O is thought of as liquid or vapour (i.e. water or steam); mercury is thought of as a liquid. All these substances can exist in different phases: oxygen and nitrogen can be liquefied; H_2O can become a gas at very high temperatures; mercury can be vaporized and will act as a gas if the temperature is raised high enough.

2.1 Liquid, vapour, and gas

Consider a p–v diagram for any substance. The solid phase is not important in engineering thermodynamics, being more the province of the metallurgist or physicist. When a liquid is heated at any one constant pressure there is one fixed temperature at which bubbles of vapour form in the liquid; this phenomenon is known as boiling. The higher the pressure of the liquid then the higher the temperature at which boiling occurs. It is also found that the volume occupied by 1 kg of a boiling liquid at a higher pressure is slightly larger than the volume occupied by 1 kg of the same liquid when it is boiling at a low pressure. A series of boiling-points plotted on a p–v diagram will appear as a sloping line, as shown in Fig. 2.1. The points P, Q, and R represent the boiling-points of a liquid at pressure p_P, p_Q, and p_R respectively.

When a liquid at boiling-point is heated further at constant pressure the additional heat supplied changes the phase of the substance from liquid to vapour; during this change of phase the pressure and temperature remain constant. The heat supplied is called the *specific enthalpy of vaporization*. It is found that the higher the pressure then the smaller is the amount of heat required. There is a definite value of specific volume of the vapour at any one

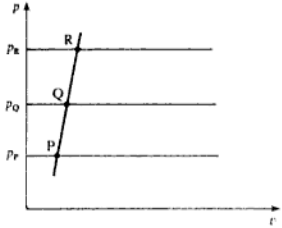


Fig. 2.1 Boiling-points plotted on a p–v diagram

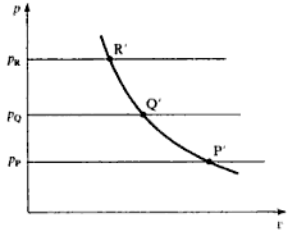


Fig. 2.2 Points of complete vaporization plotted on a p–v diagram

pressure, at the point at which vaporization is complete; hence a series of points such as P′, Q′, R′ can be plotted and joined to form a line as shown in Fig. 2.2.

When the two curves already drawn are extended to higher pressures they form a continuous curve, thus forming a loop (see Fig. 2.3). The pressure at which the turning point occurs is called the *critical pressure* and the turning point itself is called the *critical point* (point C on Fig. 2.3). It can be seen that at the critical point the specific enthalpy of vaporization is zero. The substance existing at a state point inside the loop consists of a mixture of liquid and dry vapour and is known as a *wet vapour*. A *saturation state* is defined as a state at which a change of phase may occur without change of pressure or temperature. Hence the boiling-points P, Q, and R are saturation states, and a series of such boiling-points joined up is called the *saturated liquid line*. Similarly the points P′, Q′, and R′, at which the liquid is completely changed into vapour, are saturation states, and a series of such points joined up is called the *saturated vapour line*. The word 'saturation' as used here refers to energy saturation. For example, a slight addition of heat to a boiling liquid changes some of it into a vapour, and it is no longer a liquid but is now a wet vapour. Similarly when a substance just on the saturated vapour line is cooled slightly, droplets of liquid will begin to form, and the saturated vapour becomes a wet vapour. A saturated vapour is usually called *dry saturated* to emphasize the fact that no liquid is present in the vapour in this state.

Lines of constant temperature, called isothermals, can be plotted on a p–v diagram as shown in Fig. 2.4. The temperature lines become horizontal between

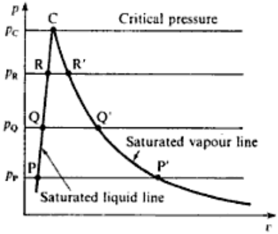


Fig. 2.3 Wet loop plotted on a p–v diagram

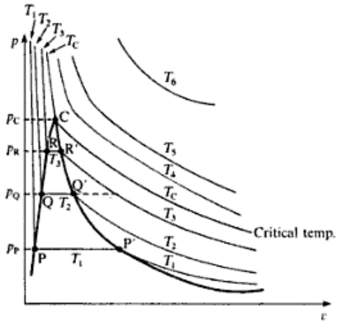


Fig. 2.4 Isothermals for a vapour plotted on a p–v diagram

the saturated liquid line and the saturated vapour line (e.g. between P and P′, Q and Q′, R and R′). Thus there is a corresponding *saturation temperature* for each *saturation pressure*. At pressure p_P the saturation temperature is T_1, at pressure p_Q the saturation temperature is T_2, and at pressure p_R the saturation temperature is T_3. The critical temperature line T_C just touches the top of the loop at the critical point C.

When a dry saturated vapour is heated at constant pressure its temperature rises and it becomes *superheated*. The difference between the actual temperature of the superheated vapour and the saturation temperature at the pressure of the vapour is called the *degree of superheat*. For example, the vapour at point S (Fig. 2.4) is superheated at p_Q and T_3, and the degree of superheat is $T_3 - T_2$.

In section 1.5 it is stated that two independent properties are sufficient to define the state of a substance. Now between P and P′, Q and Q′, R and R′ the temperature and pressure are not independent since they remain constant for a range of values of v. For example, a substance at p_Q and T_2 (Fig. 2.4) could be a saturated liquid, a wet vapour, or a dry saturated vapour. The state cannot be defined until one other property (e.g. specific volume) is given. The condition or quality of a wet vapour is most frequently defined by its *dryness* *fraction*, and when this is known as well as the pressure or temperature then the state of the wet vapour is fully defined.

Dryness fraction, x = the mass of dry vapour in 1 kg of the mixture

(Sometimes a wetness fraction is defined as the mass of liquid in 1 kg of the mixture, i.e. wetness fraction = $1 - x$.)

Note that for a dry saturated vapour $x = 1$, and that for a saturated liquid $x = 0$.

The distinction between a gas and a superheated vapour is not rigid. However, at very high degrees of superheat an isothermal line on the p–v diagram tends to become a hyperbola (i.e. pv = constant). For example the isothermal T_6 on Fig. 2.4 is almost a hyperbola. An idealized substance called a *perfect gas* is assumed to have an equation of state pv/T = constant. It can be seen that when a line of constant temperature follows a hyperbolic law then the equation pv/T = constant is satisfied. All substances tend to obey the equation pv/T = constant at very high degrees of superheat. Substances which are thought of as gases (e.g. oxygen, nitrogen, hydrogen, etc.) are highly superheated at normal atmospheric conditions. For example, the critical temperatures of oxygen, nitrogen, and hydrogen are approximately −119, −147, and −240 °C respectively. Substances normally existing as vapours must be raised to high temperatures before they begin to act as a perfect gas. For example, the critical temperatures of ammonia, sulphur dioxide, and water vapour are 130, 157, and 374.15 °C respectively.

The working fluid in practical engineering problems is either a substance which is approximately a perfect gas, or a substance which exists mainly as liquid and vapour, such as steam and the refrigerant vapours. For the substances which approximate to perfect gases certain laws relating the properties can be assumed. For the substances in the liquid and vapour phases the properties are not related by definite laws, and values of the properties are determined empirically and tabulated in a convenient form.

2.2 The use of vapour tables

Tables are available for a wide variety of substances which normally exist in the vapour phase. The tables which will be used in this book are those arranged by Rogers and Mayhew (ref. 2.1), which are suitable for student use. For more comprehensive tables for steam, ref. 2.2 should be consulted. The tables of Rogers and Mayhew are mainly concerned with steam, but some properties of refrigerants are also given.

Saturation state properties

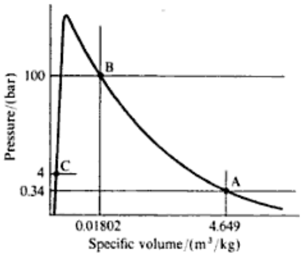
The saturation pressures and corresponding saturation temperatures of steam are tabulated in parallel columns in the first table, for pressures ranging from 0.006 112 bar to the critical pressure of 221.2 bar. The specific volume, internal energy, enthalpy, and entropy are also tabulated for the dry saturated vapour

Table 2.1 Extract from tables of properties of wet steam

p	t	v_g	u_f	u_g	h_f	h_{fg}	h_g	s_f	s_{fg}	s_g
(bar)	(°C)	(m³/kg)	(kJ/kg)		(kJ/kg)			(kJ/kg K)		
0.34	72	4.649	302	2472	302	2328	2630	0.980	6.745	7.725

at each pressure and corresponding saturation temperature. The suffix g is used to denote the dry saturated stage. A specimen row from the tables is shown in Table 2.1. For example at 0.34 bar the saturation temperature is 72 °C, the specific volume of dry saturated vapour, v_g, at this pressure is 4.649 m³/kg, the internal energy of dry saturated vapour, u_g, is 2472 kJ/kg, and the enthalpy of dry saturated vapour, h_g, is 2630 kJ/kg. The steam is in the state represented by point A on Fig. 2.5. At point B dry saturated steam at a pressure of 100 bar and saturation temperature 311 °C has a specific volume, v_g, of 0.01802 m³/kg, internal energy, u_g, of 2545 kJ/kg and enthalpy, h_g, of 2725 kJ/kg.

Fig. 2.5 Points identified on a p–v diagram for steam



The specific internal energy, specific enthalpy, and specific entropy of saturated liquid are also tabulated, the suffix f being used for this state. For example at 4 bar and the corresponding saturation temperature 143.6 °C, saturated water has a specific internal energy, u_f, of 605 kJ/kg, and a specific enthalpy, h_f, of 605 kJ/kg. This state corresponds to point C on Fig. 2.5. The specific volume of saturated water, v_f, is tabulated in a separate table, but it is usually negligibly small in comparison with the specific volume of the dry saturated vapour, and its variation with temperature is very small; the saturated liquid line on a p–v diagram is very nearly coincident with the pressure axis in comparison with the width of the wet loop (see Fig. 2.5). As seen from the table, values of v_f vary from about 0.001 m³/kg at 0.01 °C to about 0.0011 m³/kg at 160 °C; as the pressure approaches the critical value, the increase of v_f is more marked, and at the critical temperature of 374.15 °C the value of v_f is 0.00317 m³/kg.

The change in specific enthalpy from h_f to h_g is given the symbol h_{fg}. When saturated water is changed to dry saturated vapour, from equation (1.4),

$$Q + W = u_2 - u_1 = u_g - u_f$$

Also $-W$ is represented by the area under the horizontal line on the p–v diagram,

i.e. $\quad W = -(v_g - v_f)p$

therefore

$$Q = (u_g - u_f) + p(v_g - v_g)$$
$$= (u_g + pv_g) - (u_f + pv_f)$$

From equation (1.9)

$$h = u + pv$$

therefore

$$Q = h_g - h_f = h_{fg}$$

The heat required to change a saturated liquid to a dry saturated vapour is called the specific enthalpy of vaporization, h_{fg}.

In the case of steam tables, the specific internal energy of saturated liquid is taken to be zero at the triple point (i.e. at 0.01 °C and 0.006 112 bar). Then since, from equation (1.9), $h = u + pv$, we have

$$h \text{ at } 0.01\ ^\circ\text{C and } 0.006\,112 \text{ bar} = 0 + \frac{0.006\,112 \times 10^5 \times 0.001\,000\,2}{10^3}$$

where v_f at 0.01 °C is 0.001 000 2 m^3/kg,

i.e. $\quad h = 6.112 \times 10^{-4}$ kJ/kg

This is negligibly small and hence the zero for enthalpy may be taken at 0.01 °C.

Note that at the other end of the pressure range tabulated in the first table the pressure of 221.2 bar is the critical pressure, 374.15 °C is the critical temperature, and the specific enthalpy of vaporization, h_{fg}, is zero.

Properties of wet vapour

For a wet vapour the total volume of the mixture is given by the volume of liquid present plus the volume of dry vapour present. Therefore the specific volume is given by

$$v = \frac{\text{volume of liquid} + \text{volume of dry vapour}}{\text{total mass of wet vapour}}$$

Now for 1 kg of wet vapour there are x kg of dry vapour and $(1 - x)$ kg of liquid, where x is the dryness fraction as defined earlier. Hence,

$$v = v_f(1 - x) + v_g x$$

The volume of the liquid is usually negligibly small compared to the volume of dry saturated vapour, hence for most practical problems

$$v = xv_g \qquad (2.1)$$

The enthalpy of a wet vapour is given by the sum of the enthalpy of the liquid plus the enthalpy of the dry vapour,

i.e. $$h = (1 - x)h_f + xh_g$$

therefore

$$h = h_f + x(h_g - h_f)$$

i.e. $$h = h_f + xh_{fg} \tag{2.2}$$

Similarly, the internal energy of a wet vapour is given by the internal energy of the liquid plus the internal energy of the dry vapour,

i.e. $$u = (1 - x)u_f + xu_g \tag{2.3}$$

or $$u = u_f + x(u_g - u_f) \tag{2.4}$$

Equation (2.4) can be expressed in a form similar to equation (2.2), but equations (2.3) and (2.4) are more convenient since u_g and u_f are tabulated and the difference, $u_g - u_f$, is not tabulated in ref. 2.1.

Example 2.1 Calculate the specific volume, specific enthalpy, and specific internal energy of wet steam at 18 bar, dryness fraction 0.9.

Solution From equation (2.1)

$$v = xv_g$$

therefore

$$v = 0.9 \times 0.1104 = 0.0994 \text{ m}^3/\text{kg}$$

From equation (2.2)

$$h = h_f + xh_{fg}$$

therefore

$$h = 885 + (0.9 \times 1912) = 2605.8 \text{ kJ/kg}$$

From equation (2.3)

$$u = (1 - x)u_f + xu_g$$

therefore

$$u = (1 - 0.9)883 + (0.9 \times 2598) = 2426.5 \text{ kJ/kg}$$

Example 2.2 Calculate the dryness fraction, specific volume and specific internal energy of steam at 7 bar and specific enthalpy 2600 kJ/kg.

Solution At 7 bar, $h_g = 2764$ kJ/kg, hence since the actual enthalpy is given as 2600 kJ/kg, the steam must be in the wet vapour state. From equation (2.2), $h = h_f + xh_{fg}$,

i.e. $$2600 = 697 + x2067$$

therefore

$$x = \frac{2600 - 697}{2067} = 0.921$$

Then from equation (2.1)

$$v = xv_g = 0.921 \times 0.2728 = 0.2515\ \text{m}^3/\text{kg}$$

From equation (2.3)

$$u = (1 - x)u_f + xu_g$$

therefore

$$u = (1 - 0.921)696 + (0.921 \times 2573) = 55 + 2365$$

i.e. $u = 2420\ \text{kJ/kg}$

Properties of superheated vapour

For steam in the superheat region, temperature and pressure are independent properties. When the temperature and pressure are given for superheated steam then the state is defined and all the other properties can be found. For example, steam at 2 bar and 200 °C is superheated since the saturation temperature at 2 bar is 120.2 °C, which is less than the actual temperature. The steam in this state has a degree of superheat of 200 − 120.2 = 79.8 K. The tables of properties of superheated steam (ref. 2.1) range in pressure from 0.006 112 bar to the critical pressure of 221.2 bar, and there is an additional table of supercritical pressures up to 1000 bar. At each pressure there is a range of temperatures up to high degrees of superheat, and the values of specific volume, internal energy, enthalpy, and entropy are tabulated at each pressure and temperature for pressures up to and including 70 bar; above this pressure the specific internal energy is not tabulated. For reference the saturation temperature is inserted in brackets under each pressure in the superheat tables and values of v_g, u_g, h_g and s_g are also given. A specimen row of values is shown in Table 2.2. For example, from superheat tables at 20 bar and 400 °C the specific volume is 0.1511 m³/kg and the enthalpy is 3248 kJ/kg.

For pressures above 70 bar the internal energy can be found when required using equation (1.9). For example, steam at 80 bar, 400 °C has an enthalpy, *h*,

Table 2.2 Extract from tables of properties of superheated steam at 20 bar (saturation temperature 212.4 °C)

	Temperature/(°C)						
	250	300	350	400	450	500	600
$v/(\text{m}^3/\text{kg})$	0.1115	0.1255	0.1386	0.1511	0.1634	0.1756	0.1995
$u/(\text{kJ/kg})$	2681	2774	2861	2946	3030	3116	3291
$h/(\text{kJ/kg})$	2904	3025	3138	3248	3357	3467	3690
$s/(\text{kJ/kg K})$	6.547	6.768	6.957	7.126	7.283	7.431	7.701

of 3139 kJ/kg and a specific volume, v, of 3.428×10^{-2} m³/kg, therefore

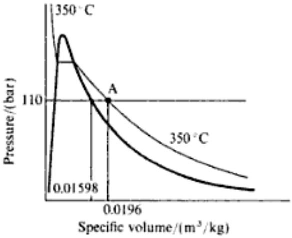
$$u = h - pv = 3139 - \frac{80 \times 10^5 \times 0.034\,28}{10^3}$$

i.e. $u = 3139 - 274.2 = 2864.8$ kJ/kg

Example 2.3 Steam at 110 bar has a specific volume of 0.0196 m³/kg, calculate the temperature, the specific enthalpy, and the specific internal energy.

Solution First it is necessary to decide whether the steam is wet, dry saturated, or superheated. At 110 bar, $v_g = 0.015\,98$ m³/kg, which is less than the actual specific volume of 0.0196 m³/kg, and hence the steam is superheated. The state of the steam is shown as point A of Fig. 2.6.

Fig. 2.6
Pressure-specific volume diagram for Example 2.3



From the superheat tables at 110 bar, the specific volume is 0.0196 m³/kg at a temperature of 350 °C. Hence this is the isothermal which passes through point A as shown. The degree of superheat in this case is 350 − 318 = 32 K. From tables the enthalpy, h, is 2889 kJ/kg. Then using equation (1.9), we have

$$u = h - pv = 2889 - \frac{110 \times 10^5 \times 0.0196}{10^3}$$

i.e. $u = 2889 - 215.6 = 2673.4$ kJ/kg

Example 2.4 Steam at 150 bar has a specific enthalpy of 3309 kJ/kg. Calculate the temperature, the specific volume, and the specific internal energy.

Solution At 150 bar, $h_g = 2611$ kJ/kg, which is less than the actual enthalpy of 3309 kJ/kg, and hence the steam is superheated. From superheat tables at 150 bar, $h = 3309$ kJ/kg at a temperature of 500 °C. The specific volume is $v = 0.020\,78$ m³/kg. Using equation (1.9)

$$u = h - pv = 3309 - \frac{150 \times 10^5 \times 0.02078}{10^3} = 2997.3 \text{ kJ/kg}$$

Interpolation

For properties which are not tabulated exactly in the tables it is necessary to interpolate between the values tabulated. For example, to find the temperature, specific volume, internal energy, and enthalpy of dry saturated steam at 9.8 bar, it is necessary to interpolate between the values given in the tables.

$$t_g \text{ at } 9.8 \text{ bar} = (t_g \text{ at } 9 \text{ bar}) + \left(\frac{9.8 - 9}{10 - 9}\right) \times \{(t_g \text{ at } 10 \text{ bar}) - (t_g \text{ at } 9 \text{ bar})\}$$

Note that this assumes a linear variation between the two values (see Fig. 2.7),

i.e. $$t_g = 175.4 + \left(\frac{9.8 - 9}{10 - 9}\right) \times (179.9 - 175.4)$$

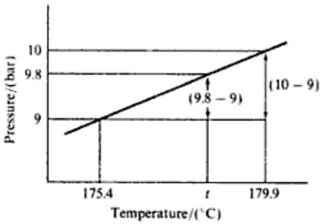


Fig. 2.7 Interpolation for Example 2.4

therefore

$$t_g = 175.4 + 0.8 \times 4.5 = 179\,^\circ\text{C}$$

Similarly,

$$h_g \text{ at } 9.8 \text{ bar} = (h_g \text{ at } 9 \text{ bar}) + 0.8 \times (h_g \text{ at } 10 \text{ bar} - h_g \text{ at } 9 \text{ bar})$$

i.e. $$h_g \text{ at } 9.8 \text{ bar} = 2774 + 0.8 \times (2778 - 2774)$$

$$= 2774 + 0.8 \times 4 = 2777.2 \text{ kJ/kg}$$

Also, $$u_g \text{ at } 9.8 \text{ bar} = 2581 + 0.8(2584 - 2581)$$

$$= 2581 + (0.8 \times 3) = 2583.4 \text{ kJ/kg}$$

As another example consider steam at 5 bar and 320 °C. The steam is superheated since the saturation temperature at 5 bar is 151.8 °C, but to find the specific volume and enthalpy an interpolation is necessary,

$$v = (v \text{ at } 5 \text{ bar and } 300\,^\circ\text{C})$$

$$+ \frac{20}{50}(v \text{ at } 5 \text{ bar and } 350\,^\circ\text{C} - v \text{ at } 5 \text{ bar and } 300\,^\circ\text{C})$$

therefore

$$v = 0.5226 + 0.4(0.5701 - 0.5226)$$
$$= 0.5226 + 0.019 = 0.5416\ \mathrm{m^3/kg}$$

Similarly,

$$h = 3065 + 0.4(3168 - 3065) = 3065 + 41.2$$

i.e. $h = 3106.2\ \mathrm{kJ/kg}$

In some cases a double interpolation is necessary. For example, to find the enthalpy of superheated steam at 18.5 bar and 432 °C an interpolation between 15 bar and 20 bar is necessary, and interpolation between 400 °C and 450 °C is also necessary. A tabular presentation is usually better in such cases (Table 2.3). First find the enthalpy at 15 bar and 432 °C,

$$h = 3256 + \frac{32}{50}(3364 - 3256) = 3256 + 0.64 \times 108$$

i.e. $h = 3325.1\ \mathrm{kJ/kg}$

Table 2.3 Table showing a double interpolation

Pressure (bar)		Temperature/(°C) 400	432	450
15.0	h/(kJ/kg)	3256	?	3364
18.5	h/(kJ/kg)		?	
20.0	h/(kJ/kg)	3248	?	3357

Now find the enthalpy at 20 bar, 432 °C,

$$h = 3248 + 0.64(3357 - 3248) = 3248 + 0.64 \times 109$$

i.e. $h = 3317.8\ \mathrm{kJ/kg}$

Now interpolate between h at 15 bar, 432 °C, and h at 20 bar, 432 °C in order to find h at 18.5 bar, 432 °C,

i.e. $$h = 3325.1 - \frac{3.5}{5}(3325.1 - 3317.8)$$

(Note the negative sign in this case since h at 15 bar, 432 °C is larger than h at 20 bar, 432 °C.) Then

$$h \text{ at } 18.5\ \text{bar, } 432\,°\text{C} = 3325.1 - (0.7 \times 7.3) = 3320\ \mathrm{kJ/kg}$$

Example 2.5 Sketch a pressure–volume diagram for steam and mark on it the following points, labelling clearly the pressure, specific volume and temperature of each point.

(a) $p = 20$ bar, $t = 250\,°\mathrm{C}$

(b) $t = 212.4\,^\circ\mathrm{C}$, $v = 0.09957\ \mathrm{m^3/kg}$
(c) $p = 10$ bar, $h = 2650$ kJ/kg
(d) $p = 6$ bar, $h = 3166$ kJ/kg

Solution *Point* (*a*): At 20 bar the saturation temperature is 212.4 °C, hence the steam is superheated at 250 °C. Then from tables, $v = 0.1115\ \mathrm{m^3/kg}$.
Point (*b*): At 212.4 °C the saturation pressure is 20 bar and v_g is $0.09957\ \mathrm{m^3/kg}$. Therefore the steam is just dry saturated since $v = v_g$.
Point (*c*): At 10 bar, h_g is 2778 kJ/kg, therefore the steam is wet since $h = 2650$ kJ/kg. Since the steam is wet, the temperature is the saturation temperature at 10 bar, i.e. $t = 179.9\,^\circ\mathrm{C}$. The dryness fraction can be found from equation (2.2),

$$h = h_f + xh_{fg}$$

therefore

$$x = \frac{2650 - 763}{2015} = \frac{1887}{2015} = 0.937$$

Then from equation (2.1)

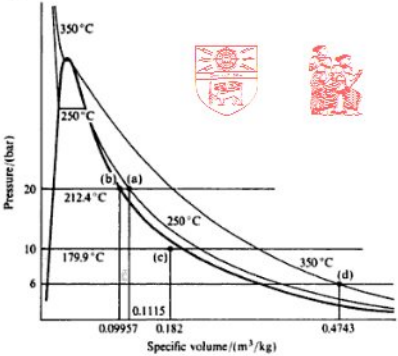
$$v = xv_g$$

$$v = 0.937 \times 0.1944 = 0.182\ \mathrm{m^3/kg}$$

Point (*d*): At 6 bar, h_g is 2757 kJ/kg, therefore the steam is superheated, since it is given that $h = 3166$ kJ/kg. Hence from tables at 6 bar and $h = 3166$ kJ/kg the temperature is 350 °C, and the specific volume is $0.4743\ \mathrm{m^3/kg}$.

The points (a), (b), (c), and (d) can now be marked on a p–v diagram as shown in Fig. 2.8.

Fig. 2.8 Solution for Example 2.5



Example 2.6 Calculate the internal energy for each of the four states given in Example 2.5.

Solution (a) The steam is superheated at 20 bar, 250 °C,

i.e. $u = 2681 \text{ kJ/kg}$

(b) The steam is dry saturated at 20 bar,

i.e. $u = u_g = 2600 \text{ kJ/kg}$

(c) The steam is wet at 10 bar with $x = 0.937$. Therefore

$$u = (1 - x)u_f + xu_g \quad \text{from equation (2.3)}$$

i.e. $u = (1 - 0.937)762 + (0.937 \times 2584) = 2470 \text{ kJ/kg}$

(d) The steam is superheated at 6 bar, 350 °C,

i.e. $u = 2881 \text{ kJ/kg}$

Example 2.7 Using the properties of ammonia given in ref. 2.1, calculate:

(i) the enthalpy at 1.902 bar, dryness fraction 0.95;
(ii) the enthalpy at 8.57 bar, 60 °C.

Solution (i) From equation (2.2)

$$h = h_f + xh_{fg}$$

Therefore, at 1.902 bar,

$$h = 89.8 + 0.95(1420.0 - 89.8)$$
$$= 1353.5 \text{ kJ/kg}$$

(ii) At 8.570 bar the saturation temperature is 20 °C so the ammonia at 60 °C is superheated by $(60 - 20) = 40$ K. It is therefore necessary to interpolate to find the enthalpy,

i.e. $$h = 1462.6 + \frac{40}{50} \times (1597.2 - 1462.6)$$
$$= 1570.3 \text{ kJ/kg}$$

2.3 The perfect gas

The characteristic equation of state

At temperatures that are considerably in excess of the critical temperature of a fluid, and also at very low pressures, the vapour of the fluid tends to obey the equation

$$\frac{pv}{T} = \text{constant} = R$$

No gases in practice obey this law rigidly, but many gases tend towards it. An imaginary ideal gas which obeys the law is called a *perfect gas*, and the equation, $pv/T = R$, is called the characteristic equation of state of a perfect gas. The constant, R, is called the *specific gas constant*. The units of R are N m/kg K or kJ/kg K. Each perfect gas has a different specific gas constant.

The characteristic equation is usually written

$$pv = RT \tag{2.5}$$

or for a mass, m, occupying a volume, V,

$$pV = mRT \tag{2.6}$$

Another form of the characteristic equation can be derived using the *amount of substance* (sometimes called the mole). The amount of substance is defined by the 1971 General Conference of Weights and Measures (CGPM) as follows:

The amount of substance of a system is that quantity which contains as many elementary entities as there are atoms in 0.012 kg of carbon-12; the elementary entities must be specified and may be atoms, molecules, ions, electrons, or other particles, or specific groups of such particles.

The normal unit symbol used for the amount of substance is 'mol'. In SI it is convenient to use 'kmol'.

The mass of any substance per amount of substance is known as the *molar mass*, $\tilde{m}$, i.e.

$$\tilde{m} = \frac{m}{n} \tag{2.7}$$

where m is the mass and n is the amount of substance. The normal units used for m and n are kg and kmol, therefore the normal unit for $\tilde{m}$ is kg/kmol.

Relative masses of the various elements are commonly used, and physicists and chemists agreed in 1960 to give the value of 12 to the isotope 12 of carbon (this led to the definition of the amount of substance as above). A scale is thus obtained of *relative atomic mass* or *relative molecular mass* (e.g. the relative atomic mass of the element oxygen is approximately 16; the relative molecular mass of oxygen gas, O_2, is approximately 32).

The relative molecular mass is numerically equal to the molar mass, $\tilde{m}$, but is dimensionless.

Substituting for m from equation (2.7) in equation (2.6) gives

$$pV = n\tilde{m}RT \quad \text{or} \quad \tilde{m}R = \frac{pV}{nT}$$

Now *Avogadro's hypothesis* states that the volume of 1 mol of any gas is the same as the volume of 1 mol of any other gas, when the gases are at the same temperature and pressure. Therefore V/n is the same for all gases at the same value of p and T. That is, the quantity pV/nT is a constant for all gases. This constant is called the *molar gas constant*, and is given the symbol, $\tilde{R}$,

i.e. $$\tilde{m}R = \tilde{R} = \frac{pV}{nT} \quad \text{or} \quad pV = n\tilde{R}T \tag{2.8}$$

or since $\tilde{m}R = \tilde{R}$ then

$$R = \frac{\tilde{R}}{\tilde{m}} \tag{2.9}$$

The value of $\tilde{R}$ has been shown to be 8314.5 N m/kmol K.

From equation (2.9) the specific gas constant for any gas can be found when the molar mass is known, e.g. for oxygen of molar mass 32 kg/kmol, the specific gas constant

$$R = \frac{\tilde{R}}{\tilde{m}} = \frac{8314.5}{32} = 259.83 \text{ N m/kg K}$$

Example 2.8 A vessel of volume 0.2 m³ contains nitrogen at 1.013 bar and 15 °C. If 0.2 kg of nitrogen is now pumped into the vessel, calculate the new pressure when the vessel has returned to its initial temperature. The molar mass of nitrogen is 28 kg/kmol, and it may be assumed to be a perfect gas.

Solution From equation (2.9)

$$\text{Specific gas constant, } R = \frac{\tilde{R}}{\tilde{m}} = \frac{8314.5}{28} = 296.95 \text{ N m/kg K}$$

From equation (2.6), for the initial conditions

$$p_1 V_1 = m_1 R T_1$$

therefore

$$m_1 = \frac{p_1 V_1}{R T_1} = \frac{1.013 \times 10^5 \times 0.2}{296.95 \times 288} = 0.237 \text{ kg}$$

where $T_1 = 15 + 273 = 288$ K

The mass of nitrogen added is 0.2 kg, hence $m_2 = 0.2 + 0.237 = 0.437$ kg. Then from equation (2.6), for the final conditions

$$p_2 V_2 = m_2 R T_2$$

but $V_2 = V_1$ and $T_2 = T_1$, therefore

$$p_2 = \frac{m_2 R T_2}{V_2} = \frac{0.437 \times 296.95 \times 288}{10^5 \times 0.2}$$

i.e. $p_2 = 1.87$ bar

Example 2.9 A certain perfect gas of mass 0.01 kg occupies a volume of 0.003 m³ at a pressure of 7 bar and a temperature of 131 °C. The gas is allowed to expand until the pressure is 1 bar and the final volume is 0.02 m³. Calculate:

(i) the molar mass of the gas;
(ii) the final temperature.

Solution (i) From equation (2.6)

$$p_1 V_1 = mRT_1$$

therefore

$$R = \frac{p_1 V_1}{mT_1} = \frac{7 \times 10^5 \times 0.003}{0.01 \times 404} = 520 \text{ N m/kg K}$$

where $T_1 = 131 + 273 = 404$ K.

Then from equation (2.9)

$$R = \frac{\tilde{R}}{\tilde{m}}$$

therefore

$$\tilde{m} = \frac{\tilde{R}}{R} = \frac{8314.5}{520} = 16 \text{ kg/kmol}$$

i.e. Molar mass = 16 kg/kmol

(ii) From equation (2.6)

$$p_2 V_2 = mRT_2$$

therefore

$$T_2 = \frac{p_2 V_2}{mR} = \frac{1 \times 10^5 \times 0.02}{0.01 \times 520} = 384.5 \text{ K}$$

i.e. Final temperature = 384.5 − 273 = 111.5 °C

Specific heat capacity

The specific heat capacity of a solid or liquid is usually defined as the heat required to raise unit mass through one degree temperature rise. We have $dQ = mc\,dT$, where m is the mass, dT is the increase in temperature, and c is the specific heat capacity. For a gas there are an infinite number of ways in which heat may be added between two temperatures, and hence a gas could have an infinite number of specific heat capacities. However, only two specific heat capacities for gases are defined; the specific heat capacity at constant volume, c_v, and the specific heat capacity at constant pressure, c_p.

The definition must be restricted to reversible non-flow processes, since irreversibilities can cause temperature changes which are indistinguishable from those due to reversible heat and work quantities. Specific heat capacities can be introduced more rigorously as properties of a fluid. We have in the limit

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \quad \text{and} \quad c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

A more rigorous treatment is given in ref. 2.3.

We can write:

$$dQ = mc_p\,dT \quad \text{for a reversible non-flow process at constant pressure} \qquad (2.10)$$

and

$$dQ = mc_v\,dT \quad \text{for a reversible non-flow process at constant volume} \qquad (2.11)$$

For a perfect gas the values of c_p and c_v are constant for any one gas at all pressures and temperatures. Hence integrating equations (2.10) and (2.11) we have for a reversible constant pressure process

$$Q = mc_p(T_2 - T_1) \qquad (2.12)$$

for a reversible constant volume process

$$Q = mc_v(T_2 - T_1) \qquad (2.13)$$

For real gases, c_p and c_v vary with temperature, but for most practical purposes a suitable average value may be used.

Joule's law

Joule's law states that the internal energy of a perfect gas is a function of the absolute temperature only, i.e. $u = f(T)$. To evaluate this function let unit mass of a perfect gas be heated at constant volume. From the non-flow energy equation, (1.5),

$$dQ + dW = du$$

Since the volume remains constant then no work is done, i.e. $dW = 0$, therefore

$$dQ = du$$

At constant volume for a perfect gas, from equation (2.11), for unit mass,

$$dQ = c_v\,dT$$

Therefore, $dQ = du = c_v\,dT$, and integrating

$$u = c_vT + K$$

where K is a constant.

Joule's law states that $u = f(T)$, hence it follows that the internal energy varies linearly with absolute temperature. Internal energy can be made zero at any arbitrary reference temperature. For a perfect gas it can be assumed that $u = 0$ when $T = 0$, hence the constant K is zero,

i.e. Specific internal energy, $u = c_vT$ for a perfect gas (2.14)

or for mass, m, of a perfect gas,

Internal energy, $U = mc_vT$ (2.15)

In any process for a perfect gas, between states 1 and 2, we have from equation (2.15),

$$\text{Gain in internal energy, } U_2 - U_1 = mc_v(T_2 - T_1) \tag{2.16}$$

The gain of internal energy for a perfect gas between two states is always given by equation (2.16), for any process, reversible or irreversible.

Relationship between the specific heat capacities

Let a perfect gas be heated at constant pressure from T_1 to T_2. From the non-flow equation (1.4), $Q + W = (U_2 - U_1)$. Also, for a perfect gas, from equation (2.16), $U_2 - U_1 = mc_v(T_2 - T_1)$. Hence,

$$Q + W = mc_v(T_2 - T_1)$$

In a constant pressure process the work done is given by the pressure times the change in volume, i.e. $W = -p(V_2 - V_1)$. Then using equation (2.6), $pV_2 = mRT_2$ and $pV_1 = mRT_1$, we have

$$W = -mR(T_2 - T_1)$$

Therefore substituting

$$Q - mR(T_2 - T_1) = mc_v(T_2 - T_1)$$

therefore

$$Q = m(c_v + R)(T_2 - T_1)$$

But for a constant pressure process from equation (2.12)

$$Q = mc_p(T_2 - T_1)$$

Hence by equating the two expressions for the heat flow, Q, we have

$$m(c_v + R)(T_2 - T_1) = mc_p(T_2 - T_1)$$

therefore

$$c_v + R = c_p$$

or
$$c_p - c_v = R \tag{2.17}$$

Specific enthalpy of a perfect gas

From equation (1.9), specific enthalpy, $h = u + pv$.

For a perfect gas, from equation (2.5), $pv = RT$. Also for a perfect gas, from Joule's law, equation (2.14), $u = c_v T$. Hence, substituting

$$h = c_v T + RT = (c_v + R)T$$

But from equation (2.17)

$$c_p - c_v = R \quad \text{or} \quad c_v + R = c_p$$

Therefore, specific enthalpy, h, for a perfect gas is given by

$$h = c_p T \tag{2.18}$$

For mass, m, of a perfect gas

$$H = mc_p T \tag{2.19}$$

(Note that, since it has been assumed that $u = 0$ at $T = 0$, then $h = 0$ at $T = 0$.)

Ratio of specific heat capacities

The ratio of the specific heat capacity at constant pressure to the specific heat capacity at constant volume is given the symbol γ (gamma),

i.e. $$\gamma = \frac{c_p}{c_v} \tag{2.20}$$

Note that since $c_p - c_v = R$, from equation (2.17), it is clear that c_p must be greater than c_v for any perfect gas. It follows therefore that the ratio, $c_p/c_v = \gamma$, is always greater than unity. In general, γ is about 1.4 for diatomic gases such as carbon monoxide (CO), hydrogen (H_2), nitrogen (N_2), and oxygen (O_2). For monoatomic gases such as argon (A), and helium (He), γ is about 1.6, and for triatomic gases such as carbon dioxide (CO_2), and sulphur dioxide (SO_2), γ is about 1.3. For some hydrocarbons the value of γ is quite low (e.g. for ethane (C_2H_6), $\gamma = 1.22$, and for isobutane (C_4H_{10}), $\gamma = 1.11$).

Some useful relationships between c_p, c_v, R, and γ can be derived. From equation (2.17)

$$c_p - c_v = R$$

Dividing through by c_v

$$\frac{c_p}{c_v} - 1 = \frac{R}{c_v}$$

Therefore using equation (2.17), $\gamma = c_p/c_v$, then,

$$\gamma - 1 = \frac{R}{c_v}$$

therefore

$$c_v = \frac{R}{(\gamma - 1)} \tag{2.21}$$

Also from equation (2.20), $c_p = \gamma c_v$, hence, substituting in equation (2.21),

$$c_p = \gamma c_v = \frac{\gamma R}{(\gamma - 1)} \tag{2.22}$$

Example 2.10 A certain perfect gas has specific heat capacities as follows:

$$c_p = 0.846 \text{ kJ/kg K} \quad \text{and} \quad c_v = 0.657 \text{ kJ/kg K}$$

Calculate the gas constant and the molar mass of the gas.

Solution From equation (2.17)

$$c_p - c_v = R$$

i.e. $R = 0.846 - 0.657 = 0.189 \text{ kJ/kg K} = 189 \text{ N m/kg K}$

From equation (2.9)

$$R = \frac{\tilde{R}}{\tilde{m}}$$

i.e. $\tilde{m} = \dfrac{8314.5}{189} = 44 \text{ kg/kmol}$

Example 2.11 A perfect gas has a molar mass of 26 kg/kmol and a value of $\gamma = 1.26$. Calculate the heat rejected:

(i) when unit mass of the gas is contained in a rigid vessel at 3 bar and 315 °C, and is then cooled until the pressure falls to 1.5 bar;
(ii) when unit mass flow rate of the gas enters a pipeline at 280 °C, and flows steadily to the end of the pipe where the temperature is 20 °C. Neglect changes in velocity of the gas in the pipeline.

Solution From equation (2.9)

$$R = \frac{\tilde{R}}{\tilde{m}} = \frac{8314.5}{26} = 319.8 \text{ N m/kg K}$$

From equation (2.21)

$$c_v = \frac{R}{(\gamma - 1)} = \frac{319.8}{10^3(1.26 - 1)} = 1.229 \text{ kJ/kg K}$$

Also from equation (2.20)

$$\frac{c_p}{c_v} = \gamma$$

therefore

$$c_p = \gamma c_v = 1.26 \times 1.229 = 1.548 \text{ kJ/kg K}$$

(i) The volume remains constant for the mass of gas present, and hence the specific volume remains constant. From equation (2.5),

$$p_1 v_1 = RT_1 \quad \text{and} \quad p_2 v_2 = RT_2$$

Therefore since $v_1 = v_2$ we have

$$T_2 = T_1 \frac{p_2}{p_1} = 588 \times \frac{1.5}{3} = 294 \text{ K}$$

where $T_1 = 315 + 273 = 588$ K.
Then from equation (2.13)

$$\text{Heat supplied per kg of gas} = c_v(T_2 - T_1) = 1.229(294 - 588)$$
$$= -1.229 \times 294 = -361 \text{ kJ/kg}$$

i.e. Heat rejected per kilogram of gas = +361 kJ/kg

(ii) From the steady-flow energy equation, (1.10),

$$\dot{m}\left(h_1 + \frac{C_1^2}{2}\right) + \dot{Q} + \dot{W} = \dot{m}\left(h_2 + \frac{C_2^2}{2}\right)$$

In this case we are told that changes in velocity are negligible; also there is no work done.
Therefore we have

$$\dot{m}h_1 + \dot{Q} = \dot{m}h_2$$

For a perfect gas, from equation (2.18)

$$h = c_p T$$

therefore

$$\dot{Q} = \dot{m}c_p(T_2 - T_1) = 1 \times 1.548(20 - 280) = -403 \text{ kW}$$

i.e. Heat rejected per kilogram per second = +403 kW

Note that it is not necessary to convert $t_1 = 280\,°\text{C}$ and $t_2 = 20\,°\text{C}$ into degrees Kelvin, since the temperature difference $(t_1 - t_2)$ is numerically the same as the temperature difference $(T_1 - T_2)$.

Problems

[Note: the answers to these problems have been evaluated using the tables of Rogers and Mayhew (ref. 2.1). The values of R, c_p, c_v, and γ for air may be assumed to be as given in the tables (i.e. $R = 0.287$ kJ/kg K; $c_p = 1.005$ kJ/kg K; $c_v = 0.718$ kJ/kg K; and $\gamma = 1.4$). For any other perfect gas the values of R, c_p, c_v, and γ, if required, must be calculated from the information given in the problem; the value of $\tilde{R}$ is given in the tables (ref. 2.1).]

2.1 Complete Table 2.4 (p. 48) using steam tables. Insert a dash for irrelevant items, and interpolate where necessary.

(see Table 2.6, p. 50)

2.2 A vessel of volume 0.03 m³ contains dry saturated steam at 17 bar. Calculate the mass of steam in the vessel and the enthalpy of this mass.

(0.257 kg; 718 kJ)

Table 2.4 Data for Problem 2.1

p (bar)	t (°C)	v (m³/kg)	x	Degree of superheat	h (kJ/kg)	u (kJ/kg)
	90	2.361				
20					2799	
5		0.3565				
	188					2400
34			0.9			
	81.3		0.85			
3	200					
15		0.152				
130					3335	
	250	1.601				
38.2			0.8			
	297		0.95			
2.3	300					
44	420					

The completed table is given on p. 50 as Table 2.6.

2.3 Steam at 7 bar and 250 °C enters a pipeline and flows along it at constant pressure. If the steam rejects heat steadily to the surroundings, at what temperature will droplets of water begin to form in the vapour? Using the steady-flow energy equation, and neglecting changes in velocity of the steam, calculate the heat rejected per kilogram of steam flowing.

(165 °C; 191 kJ/kg)

2.4 0.05 kg of steam at 15 bar is contained in a rigid vessel of volume 0.0076 m³. What is the temperature of the steam? If the vessel is cooled, at what temperature will the steam be just dry saturated? Cooling is continued until the pressure in the vessel is 11 bar; calculate the final dryness fraction of the steam, and the heat rejected between the initial and the final states.

(250 °C; 191.4 °C; 0.857; 18.5 kJ)

2.5 Using the tables for ammonia given in ref. 2.1, calculate:
(i) the specific enthalpy and specific volume of ammonia at 0.7177 bar, dryness fraction 0.9;
(ii) the specific enthalpy and specific volume of ammonia at 13 °C saturated;
(iii) the specific enthalpy of ammonia at 7.529 bar, 30 °C.

(1251 kJ/kg, 1.397 m³/kg; 1457 kJ/kg, 0.1866 m³/kg; 1496.5 kJ/kg)

2.6 Using the property values for refrigerant HFA 134a given in Table 2.5, calculate:
(i) the specific enthalpy and specific volume of HFA 134a at −8 °C, dryness fraction 0.85;
(ii) the specific enthalpy of HFA 134a at 5.7024 bar, 35 °C.

(259.96 kJ/kg, 0.0775 m³/kg; 323.25 kJ/kg)

Table 2.5 Data for Problem 2.6

Saturation values					Superheat values degree of superheat 20 K
t_g	p_g	v_g	h_f	h_g	h
(°C)	(bar)	(m³/kg)	(kJ/kg)		(kJ/kg)
−10	2.0051	0.098	86.98	288.86	308.64
−5	2.4371	0.081	93.46	291.77	312.05
20	5.7024	0.036	126.92	306.22	328.93

2.7 The relative molecular mass of carbon dioxide, CO_2, is 44. In an experiment the value of γ for CO_2 was found to be 1.3. Assuming that CO_2 is a perfect gas, calculate the specific gas constant, R, and the specific heat capacities at constant pressure and constant volume, c_p and c_v.

(0.189 kJ/kg K; 0.819 kJ/kg K; 0.63 kJ/kg K)

2.8 Calculate the internal energy and enthalpy of 1 kg of air occupying 0.05 m³ at 20 bar. If the internal energy is increased by 120 kJ as the air is compressed to 50 bar, calculate the new volume occupied by 1 kg of the air.

(250.1 kJ/kg; 350.1 kJ/kg; 0.0296 m³)

2.9 Oxygen, O_2, at 200 bar is to be stored in a steel vessel at 20 °C. The capacity of the vessel is 0.04 m³. Assuming that O_2 is a perfect gas, calculate the mass of oxygen that can be stored in the vessel. The vessel is protected against excessive pressure by a fusible plug which will melt if the temperature rises too high. At what temperature must the plug melt to limit the pressure in the vessel to 240 bar? The molar mass of oxygen is 32 kg/kmol.

(10.5 kg; 78.6 °C)

2.10 When a certain perfect gas is heated at constant pressure from 15°C to 95 °C, the heat required is 1136 kJ/kg. When the same gas is heated at constant volume between the same temperatures the heat required is 808 kJ/kg. Calculate c_p, c_v, γ, R and the molar mass of the gas.

(14.2 kJ/kg K; 10.1 kJ/kg K; 1.405; 4.1 kJ/kg K; 2.028 kg/kmol)

2.11 In an air compressor the pressures at inlet and outlet are 1 bar and 5 bar respectively. The temperature of the air at inlet is 15 °C and the volume at the beginning of compression is three times that at the end of compression. Calculate the temperature of the air at outlet and the increase of internal energy per kg of air.

(207 °C; 138 kJ/kg)

2.12 A quantity of a certain perfect gas is compressed from an initial state of 0.085 m³, 1 bar to a final state of 0.034 m³, 3.9 bar. The specific heat at constant volume is 0.724 kJ/kg K, and the specific heat at constant pressure is 1.020 kJ/kg K. The observed temperature rise is 146 K. Calculate the specific gas constant, R, the mass of gas present, and the increase of internal energy of the gas.

(0.296 kJ/kg K; 0.11 kg; 11.63 kJ)

Table 2.6 Solution to Problem 2.1 on p. 47

p (bar)	t (°C)	v (m^3/kg)	x	Degree of superheat	h (kJ/kg)	u (kJ/kg)
0.70	90	2.361	1	0	2660	2494
20	212.4	0.09957	1	0	2799	2600
5	151.8	0.3565	0.951	—	2646	2471
12	188	0.1461	0.895	—	2576	2400
34	240.9	0.0529	0.9	—	2627	2447
0.5	81.3	2.75	0.85	—	2300	2165
3	200	0.7166	—	66.5	2866	2651
15	250	0.152	—	51.7	2925	2697
130	500	0.02447	—	169.2	3335	3017
1.5	250	1.601	—	138.6	2973	2733
38.2	247.6	0.04175	0.8	—	2456	2296
82.38	297	0.0216	0.95	—	2683	2505
2.3	300	1.184	—	175.8	3071	2808
44	420	0.0696	—	164.3	3254	2952

References

2.1 ROGERS G F C and MAYHEW Y R 1987 *Thermodynamic and Transport Properties of Fluids* 4th edn Blackwell

2.2 NATIONAL ENGINEERING LABORATORY *Steam Tables 1964* HMSO

2.3 ROGERS G F C and MAYHEW Y R 1992 *Engineering Thermodynamics, Work and Heat Transfer* 4th edn Longman

3

Reversible and Irreversible Processes

In the previous chapters the energy equations for non-flow and flow processes are derived, the concepts of reversibility and irreversibility introduced, and the properties of vapours and perfect gases discussed. It is the purpose of this chapter to consider processes in practice, and to combine this with the work of the previous chapters.

3.1 Reversible non-flow processes

Constant volume process

In a constant volume process the working substance is contained in a rigid vessel, hence the boundaries of the system are immovable and no work can be done on or by the system, other than paddle-wheel work input. It will be assumed that 'constant volume' implies zero work unless stated otherwise.

From the non-flow energy equation, (1.4), for unit mass,

$$Q + W = u_2 - u_1$$

Since no work is done, we therefore have

$$Q = u_2 - u_1 \quad (3.1)$$

or for mass, m, of the working substance

$$Q = U_2 - U_1 \quad (3.2)$$

All the heat supplied in a constant volume process goes to increasing the internal energy.

A constant volume process for a vapour is shown on a p–v diagram in Fig. 3.1(a). The initial and final states have been chosen to be in the wet region and superheat region respectively. In Fig. 3.1(b) a constant volume process is shown on a p–v diagram for a perfect gas. For a perfect gas we have from equation (2.13)

$$Q = mc_v(T_2 - T_1)$$

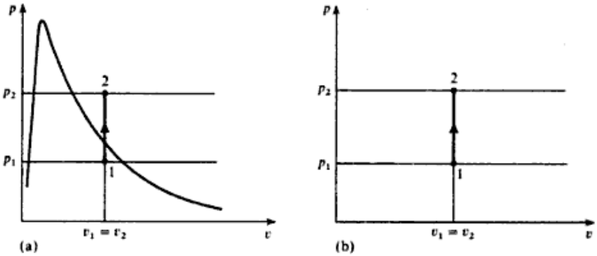


Fig. 3.1 Constant volume process for a vapour and a perfect gas

Constant pressure process

It can be seen from Figs 3.1(a) and 3.1(b) that when the boundary of the system is inflexible as in a constant volume process, then the pressure rises when heat is supplied. Hence for a constant pressure process the boundary must move against an external resistance as heat is supplied; for instance a fluid in a cylinder behind a piston can be made to undergo a constant pressure process. Since the piston is pushed through a certain distance by the force exerted by the fluid, then work is done by the fluid on its surroundings.

From equation (1.2) for unit mass

$$W = -\int_{v_1}^{v_2} p \, dv \quad \text{for any reversible process}$$

Therefore, since p is constant,

$$W = -p\int_{v_1}^{v_2} dv = -p(v_2 - v_1)$$

From the non-flow energy equation, (1.4),

$$Q + W = u_2 - u_1$$

Hence for a reversible constant pressure process

$$Q = (u_2 - u_1) + p(v_2 - v_1) = (u_2 + pv_2) - (u_1 + pv_1)$$

Now from equation (1.9), enthalpy, $h = u + pv$, hence,

$$Q = h_2 - h_1 \tag{3.3}$$

or for mass, m, of a fluid,

$$Q = H_2 - H_1 \tag{3.4}$$

A constant pressure process for a vapour is shown on a p–v diagram in Fig. 3.2(a). The initial and final states have been chosen to be in the wet region and the superheat region respectively. In Fig. 3.2(b) a constant pressure process for a perfect gas is shown on a p–v diagram. For a perfect gas we have from

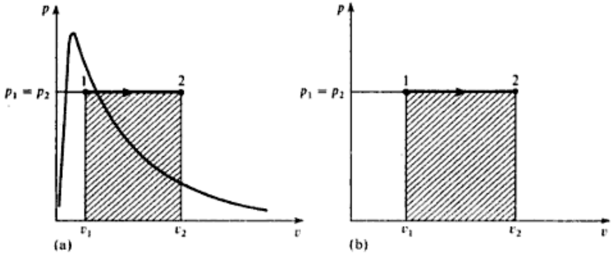


Fig. 3.2 Constant pressure process for a vapour and a perfect gas

equation (2.12),

$$Q = mc_p(T_2 - T_1)$$

Note that in Figs 3.2(a) and 3.2(b) the shaded areas represent the work done *by* the fluid, $p(v_2 - v_1)$.

Example 3.1 A mass of 0.05 kg of a fluid is heated at a constant pressure of 2 bar until the volume occupied is 0.0658 m^3. Calculate the heat supplied and the work done:

(i) when the fluid is steam, initially dry saturated;
(ii) when the fluid is air, initially at 130 °C.

Solution (i) Initially the steam is dry saturated at 2 bar, hence,

$$h_1 = h_g \text{ at 2 bar} = 2707 \text{ kJ/kg}$$

Finally the steam is at 2 bar and the specific volume is given by

$$v_2 = \frac{0.0658}{0.05} = 1.316 \text{ m}^3/\text{kg}$$

Hence the steam is superheated finally. From superheat tables at 2 bar and 1.316 m^3/kg the temperature of the steam is 300 °C, and the enthalpy is $h_2 = 3072$ kJ/kg.

Then from equation (3.4)

$$Q = H_2 - H_1 = m(h_2 - h_1) = 0.05(3072 - 2707)$$

i.e. Heat supplied $= 0.05 \times 365 = 18.25$ kJ

The process is shown on a p–v diagram in Fig. 3.3,

$$-W = p(v_2 - v_1) = \text{shaded area}$$

Now $v_1 = v_g$ at 2 bar $= 0.8856$ m^3/kg, and $v_2 = 1.316$ m^3/kg. Therefore

$$W = -2 \times 10^5(1.316 - 0.8856) = -86\,080 \text{ N m/kg}$$

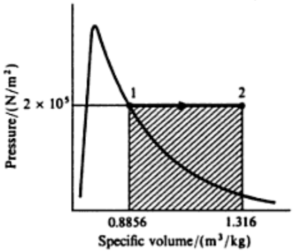


Fig. 3.3 Process for a vapour for Example 3.1 on a p–v diagram

i.e. Work done *by* the total mass present = 0.05 × 86080

= 4304 N m = 4.304 kJ

(ii) Using equation (2.6),

$$T_2 = \frac{p_2 V_2}{mR} = \frac{2 \times 10^5 \times 0.0658}{0.05 \times 0.287 \times 10^3} = 917 \text{ K}$$

For a perfect gas undergoing a constant pressure process we have, from equation (2.12),

$$Q = mc_p(T_2 - T_1)$$

i.e. Heat supplied = 0.05 × 1.005(917 − 403)

where $T_1 = 130 + 273 = 403$ K,

i.e. Heat supplied = 0.05 × 1.005 × 514 = 25.83 kJ

The process is shown on a p–v diagram in Fig. 3.4, i.e.

$$-W = p(v_2 - v_1) = \text{shaded area}$$

From equation (2.5), $pv = RT$, therefore

$$\text{Work done} = -R(T_2 - T_1) = -0.287(917 - 403) \text{ kJ/kg}$$

i.e. Work done *by* the mass of gas present = 0.05 × 0.287 × 514

= 7.38 kJ

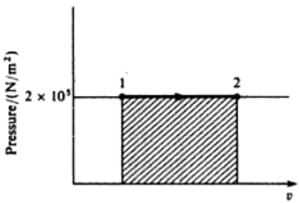


Fig. 3.4 Process for a perfect gas for Example 3.1 on a p–v diagram

Constant temperature or isothermal process

A process at constant temperature is called an isothermal process. When a fluid in a cylinder behind a piston expands from a high pressure to a low pressure there is a tendency for the temperature to fall. In an isothermal expansion heat must be added continuously in order to keep the temperature at the initial value. Similarly in an isothermal compression heat must be removed from the fluid continuously during the process. An isothermal process for a vapour is shown on a p–v diagram in Fig. 3.5. The initial and final states have been chosen in the wet region and superheat region respectively. From state 1 to state A the pressure remains at p_1, since in the wet region the pressure and temperature are the corresponding saturation values. It can be seen therefore that an isothermal process for wet steam is also at constant pressure and equations (3.3) and (3.4) can be used (e.g. heat supplied from state 1 to state A per kilogram of steam = $h_A - h_1$). In the superheat region the pressure falls to p_2 as shown in Fig. 3.5, and the procedure is not so simple. When states 1 and 2 are fixed then the internal energies u_1 and u_2 may be obtained from tables. When the property entropy, s, is introduced in Chapter 4, a convenient way of evaluating the heat supplied will be shown. When the heat flow is calculated the work done can then be obtained using the non-flow energy equation, (1.4), for unit mass

$$Q + W = u_2 - u_1$$

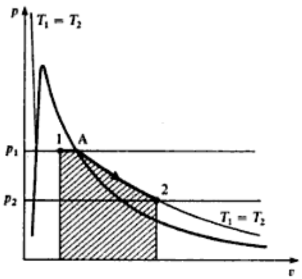


Fig. 3.5 Isothermal process for a vapour on a p–v diagram

Example 3.2 Steam at 7 bar and dryness fraction 0.9 expands in a cylinder behind a piston isothermally and reversibly to a pressure of 1.5 bar. Calculate the change of internal energy and the change of enthalpy per kg of steam. The heat supplied during the process is found to be 547 kJ/kg, by the method of Chapter 4. Calculate the work done per kilogram of steam.

Solution The process is shown in Fig. 3.6. The saturation temperature corresponding to 7 bar is 165 °C. Therefore the steam is superheated at state 2. The internal energy at state 1 is found by using equation 2.3,

i.e. $u_1 = (1 - x)u_f + xu_g = (1 - 0.9) \times 696 + (0.9 \times 2573)$

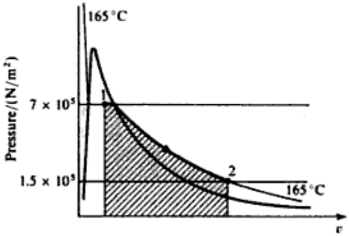


Fig. 3.6 Isothermal process on a p–v diagram for Example 3.2

therefore

$$u_1 = 69.6 + 2315.7 = 2385.3 \text{ kJ/kg}$$

Interpolating from superheat tables at 1.5 bar and 165 °C, we have

$$u_2 = 2580 + \frac{15}{50}(2656 - 2580) = 2580 + 22.8$$

i.e. $\quad u_2 = 2602.8 \text{ kJ/kg}$

Therefore

$$\text{Gain in internal energy} = u_2 - u_1 = 2602.8 - 2385.3$$
$$= 217.5 \text{ kJ/kg}$$

$$h_1 = h_f + xh_{fg} = 697 + (0.9 \times 2067)$$

therefore

$$h_1 = 697 + 1860.3 = 2557.3 \text{ kJ/kg}$$

Interpolating from superheat tables at 1.5 bar and 165 °C, we have

$$h_2 = 2773 + \frac{15}{50}(2873 - 2773) = 2773 + 30$$
$$= 2803 \text{ kJ/kg}$$

i.e. $\quad h_2 - h_1 = 2803 - 2557.3 = 245.7 \text{ kJ/kg}$

From the non-flow energy equation, (1.4),

$$Q + W = u_2 - u_1$$

therefore

$$W = (u_2 - u_1) - Q = 217.5 - 547 = -329.5 \text{ kJ/kg}$$

i.e. $\quad$ Work done *by* the system = 329.5 kJ/kg

(The work output is also given by the area on Fig. 3.6, $\int_{v_1}^{v_2} p\,dv$; this could onl be evaluated graphically in this case.)

An isothermal process for a perfect gas is more easily dealt with than an isothermal process for a vapour, since there are definite laws for a perfect gas relating p, v, and T, and the internal energy u. We have, from equation (2.5),

$$pv = RT$$

Now when the temperature is constant as in an isothermal process then we have

$$pv = RT = \text{constant}$$

Therefore for an isothermal process for a perfect gas

$$pv = \text{constant} \tag{3.5}$$

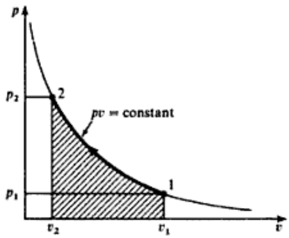
i.e. $$p_1 v_1 = p_2 v_2$$

In Fig. 3.7 an isothermal compression process for a perfect gas is shown on a p–v diagram. The equation of the process is $pv = \text{constant}$, which is the equation of a hyperbola. It must be stressed that an isothermal process is only of the form $pv = \text{constant}$ for a perfect gas, because it is only for a perfect gas that an equation of state, $pv = RT$, can be applied.

From equation (1.2) we have for unit mass

$$W = -\int_1^2 p\,dv = (\text{shaded area in Fig. 3.7})$$

Fig. 3.7 Isothermal process for a perfect gas on a p–v diagram



In this case, $pv = \text{constant}$, or $p = c/v$, where $c = \text{constant}$. Therefore

$$W = -\int_{v_1}^{v_2} c\frac{dv}{v} = -c[\ln v]_{v_1}^{v_2} = c\ln\left(\frac{v_1}{v_2}\right)$$

The constant c can either be written as $p_1 v_1$ or as $p_2 v_2$, since $p_1 v_1 = p_2 v_2 = \text{constant}, c$,

i.e. $$W = p_1 v_1 \ln\left(\frac{v_1}{v_2}\right) \text{ per unit mass of gas} \tag{3.6}$$

or $$W = p_2 v_2 \ln\left(\frac{v_1}{v_2}\right) \text{ per unit mass of gas}$$

For mass, m, of the gas

$$W = p_1 V_1 \ln\left(\frac{v_1}{v_2}\right) \quad (3.7)$$

Also, since $p_1 v_1 = p_2 v_2$, then

$$\frac{v_1}{v_2} = \frac{p_2}{p_1}$$

Hence, substituting in equation (3.6)

$$W = p_1 v_1 \ln\frac{p_2}{p_1} \text{ per unit mass of gas} \quad (3.8)$$

or for mass, m, of the gas

$$W = p_1 V_1 \ln\left(\frac{p_2}{p_1}\right) \quad (3.9)$$

Using equation (2.5)

$$p_1 v_1 = RT$$

Hence, substituting in equation (3.8)

$$W = RT \ln\left(\frac{p_2}{p_1}\right) \text{ per unit mass of gas} \quad (3.10)$$

or for mass, m, of the gas

$$W = mRT \ln\left(\frac{p_2}{p_1}\right) \quad (3.11)$$

There are clearly a large number of equations for the work done, and no attempt should be made to memorize these since they can all be derived very simply from first principles.

For a perfect gas from Joule's law, equation (2.14), we have

$$U_2 - U_1 = mc_v(T_2 - T_1)$$

Hence for an isothermal process for a perfect gas, since $T_2 = T_1$, then

$$U_2 - U_1 = 0$$

i.e. the internal energy remains constant in an isothermal process for a perfect gas.

From the non-flow energy equation (1.4) for unit mass

$$Q + W = u_2 - u_1$$

Therefore, since $u_2 = u_1$, then

$$Q + W = 0 \quad (3.12)$$

for an isothermal process for a perfect gas.

Note that the heat flow plus the work input is zero in an isothermal process *for a perfect gas only*. From Example 3.2 for steam it is seen that, although the process is isothermal, the change in internal energy is 217.5 kJ/kg, and therefore the heat supplied plus the work done is not zero.

Example 3.3 1 kg of nitrogen (molar mass 28 kg/kmol) is compressed reversibly and isothermally from 1.01 bar, 20 °C to 4.2 bar. Calculate the work done and the heat flow during the process. Assume nitrogen to be a perfect gas.

Solution From equation (2.9), for nitrogen,

$$R = \frac{\tilde{R}}{\tilde{m}} = \frac{8.3145}{28} = 0.297 \text{ kJ/kg K}$$

The process is shown on a p–v diagram in Fig. 3.8.

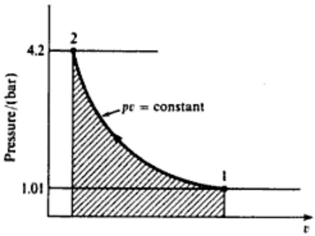


Fig. 3.8 Isothermal process on a p–v diagram for Example 3.3

From equation (3.10)

$$W = RT \ln\left(\frac{p_2}{p_1}\right) = 0.297 \times 293 \times \ln\left(\frac{4.2}{1.01}\right) = 124 \text{ kJ/kg}$$

where $T = 20 + 273 = 293$ K.

i.e. Work input = 124 kJ/kg

From equation (3.12), for an isothermal process for a perfect gas,

$$Q + W = 0$$

therefore

$$Q = -124 \text{ kJ/kg}$$

i.e. Heat rejected = 124 kJ/kg

3.2 Reversible adiabatic non-flow processes

An *adiabatic* process is one in which no heat is transferred to or from the fluid during the process. Such a process can be reversible or irreversible. The reversible adiabatic non-flow process will be considered in this section.

From the non-flow equation (1.4),

$$Q + W = u_2 - u_1$$

and for an adiabatic process

$$Q = 0$$

Therefore we have

$$W = u_2 - u_1 \quad \text{for any adiabatic non-flow process} \tag{3.13}$$

Equation (3.13) is true for an adiabatic non-flow process whether or not the process is reversible. In an adiabatic compression process all the work done on the fluid goes to increasing the internal energy of the fluid. Similarly in an adiabatic expansion process, the work done by the fluid is at the expense of a reduction in the internal energy of the fluid. For an adiabatic process to take place, perfect thermal insulation for the system must be available.

For a vapour undergoing a reversible adiabatic process the work done can be found from equation (3.13) by evaluating u_1 and u_2 from tables. In order to fix state 2, use must be made of the fact that the process is reversible and adiabatic. When the property entropy, s, is introduced in Chapter 4 it will be shown that a reversible adiabatic process takes place at constant entropy, and this fact can be used to fix state 2.

For a perfect gas, a law relating p and v may be obtained for a reversible adiabatic process, by considering the non-flow energy equation in differential form. From equation (1.4) for unit mass

$$dQ + dW = du$$

Also for a reversible process $dW = -p\,dv$, hence for a reversible adiabatic process

$$dQ = du + p\,dv = 0 \tag{3.14}$$

Since $\quad h = u + pv$

then $\quad dh = du + p\,dv + v\,dp$

i.e. $\quad du + p\,dv = dh - v\,dp$

and hence, using equation (3.14),

$$dh - v\,dp = 0$$

i.e.

$$dh = v\,dp \tag{3.15}$$

Also, using equations (2.5) and (3.14), we have

$$du + \frac{RT\,dv}{v} = 0$$

From equation (2.14)

$$u = c_v T \quad \text{or} \quad du = c_v\,dT$$

therefore

$$c_v \, dT + \frac{RT \, dv}{v} = 0$$

Dividing through by T to give a form that can be integrated, i.e.

$$c_v \frac{dT}{T} + \frac{R \, dv}{v} = 0$$

Integrating

$$c_v \ln T + R \ln v = \text{constant}$$

Using equation (2.5) we have $T = (pv)/R$, therefore substituting

$$c_v \ln\left(\frac{pv}{R}\right) + R \ln v = \text{constant}$$

Dividing through by c_v

$$\ln\left(\frac{pv}{R}\right) + \frac{R}{c_v} \ln v = \text{constant}$$

Also, from equation (2.21),

$$c_v = \frac{R}{(\gamma - 1)} \quad \text{or} \quad \frac{R}{c_v} = \gamma - 1$$

Hence substituting

$$\ln\left(\frac{pv}{R}\right) + (\gamma - 1) \ln v = \text{constant}$$

or
$$\ln\left(\frac{pv}{R}\right) + \ln(v^{\gamma-1}) = \text{constant}$$

therefore

$$\ln\left(\frac{pvv^{\gamma-1}}{R}\right) = \text{constant}$$

i.e.
$$\ln\left(\frac{pv^{\gamma}}{R}\right) = \text{constant}$$

therefore

$$\frac{pv^{\gamma}}{R} = e^{(\text{constant})} = \text{constant}$$

or
$$pv^{\gamma} = \text{constant} \tag{3.16}$$

We therefore have a simple relationship between p and v for any perfect gas undergoing a reversible adiabatic process, each perfect gas having its own value of γ.

Using equation (2.5), $pv = RT$, relationships between T and v, and T and p, may be derived,

i.e. $$pv = RT$$

therefore

$$p = \frac{RT}{v}$$

Substituting in equation (3.16)

$$\frac{RT}{v}v^{\gamma} = \text{constant}$$

i.e. $$Tv^{\gamma-1} = \text{constant} \qquad (3.17)$$

Also, $v = (RT)/p$; hence substituting in equation (3.16)

$$p\left(\frac{RT}{p}\right)^{\gamma} = \text{constant}$$

therefore

$$\frac{T^{\gamma}}{p^{\gamma-1}} = \text{constant}$$

or $$\frac{T}{p^{(\gamma-1)/\gamma}} = \text{constant} \qquad (3.18)$$

Therefore for a reversible adiabatic process for a perfect gas between states 1 and 2 we can write as follows. From equation (3.16)

$$p_1v_1^{\gamma} = p_2v_2^{\gamma} \quad \text{or} \quad \frac{p_1}{p_2} = \left(\frac{v_2}{v_1}\right)^{\gamma} \qquad (3.19)$$

From equation (3.17)

$$T_1v_1^{\gamma-1} = T_2v_2^{\gamma-1} \quad \text{or} \quad \frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{\gamma-1} \qquad (3.20)$$

From equation (3.18)

$$\frac{T_1}{p_1^{(\gamma-1)/\gamma}} = \frac{T_2}{p_2^{(\gamma-1)/\gamma}} \quad \text{or} \quad \frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma} \qquad (3.21)$$

From equation (3.13) the work done in an adiabatic process per unit mass of gas is given by $W = (u_2 - u_1)$. The gain in internal energy of a perfect gas is given by equation (2.16),

i.e. for unit mass $\quad u_2 - u_1 = c_v(T_2 - T_1)$

therefore

$$W = c_v(T_2 - T_1)$$

Also, from equation (2.21),

$$c_v = \frac{R}{(\gamma - 1)}$$

Hence substituting

$$W = \frac{R(T_2 - T_1)}{(\gamma - 1)} \tag{3.22}$$

Using equation (2.5), $pv = RT$,

$$W = \frac{p_2 v_2 - p_1 v_1}{\gamma - 1} \tag{3.23}$$

A reversible adiabatic process for a perfect gas is shown on a p–v diagram in Fig. 3.9. We have

$$-W = \int_{v_1}^{v_2} p \, dv = \text{shaded area}$$

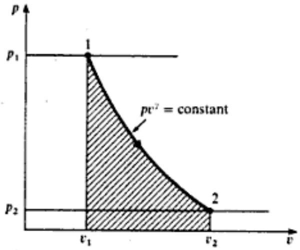


Fig. 3.9 Reversible adiabatic process for a perfect gas on a p–v diagram

Therefore, since pv^γ = constant, c, then

$$W = -\int_{v_1}^{v_2} \frac{c \, dv}{v^\gamma}$$

i.e. $$W = -c \int_{v_1}^{v_2} \frac{dv}{v^\gamma} = -c \left[\frac{v^{-\gamma+1}}{-\gamma+1} \right]_{v_1}^{v_2}$$

$$= -c\left(\frac{v_2^{-\gamma+1} - v_1^{-\gamma+1}}{1-\gamma}\right) = -c\left(\frac{v_1^{-\gamma+1} - v_2^{-\gamma+1}}{\gamma - 1}\right)$$

The constant in this equation can be written as $p_1 v_1^\gamma$ or as $p_2 v_2^\gamma$. Hence

$$W = \frac{p_2 v_2^\gamma v_2^{1-\gamma} - p_1 v_1^\gamma v_1^{1-\gamma}}{\gamma - 1} = \frac{p_2 v_2 - p_1 v_1}{\gamma - 1}$$

This is the same expression obtained before as equation (3.23).

Example 3.4 1 kg of steam at 100 bar and 375 °C expands reversibly in a perfectly thermally insulated cylinder behind a piston until the pressure is 38 bar and the steam is then dry saturated. Calculate the work done.

Solution From superheat tables at 100 bar and 375 °C,

$$h_1 = 3017\ \text{kJ/kg} \quad \text{and} \quad v_1 = 0.02453\ \text{m}^3/\text{kg}$$

Using equation (1.9)

$$u = h - pv$$

therefore

$$u_1 = 3017 - \frac{100 \times 10^5 \times 0.02453}{10^3} = 2771.7\ \text{kJ/kg}$$

Also, $u_2 = u_g$ at 38 bar = 2602 kJ/kg

Since the cylinder is perfectly thermally insulated then no heat flows to or from the steam during the expansion; the process is therefore adiabatic. Using equation (3.13),

$$W = u_2 - u_1 = 2602 - 2771.7$$

therefore

$$W = -169.7\ \text{kJ/kg}$$

i.e. Work done *by* the steam = +169.7 kJ/kg

The process is shown on a p–v diagram in Fig. 3.10, the shaded area representing the work done by the steam.

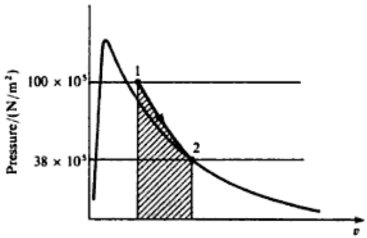


Fig. 3.10 Reversible adiabatic process for steam on a p–v diagram for Example 3.4

Example 3.5 Air at 1.02 bar, 22 °C, initially occupying a cylinder volume of 0.015 m^3, is compressed reversibly and adiabatically by a piston to a pressure of 6.8 bar. Calculate the final temperature, the final volume, and the work done on the mass of air in the cylinder.

Solution From equation (3.21)

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma} \quad \text{or} \quad T_2 = T_1 \times \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$$

i.e.
$$T_2 = 295 \times \left(\frac{6.8}{1.02}\right)^{(1.4-1)/1.4}$$

$$= 295 \times 1.7195 = 507.3 \text{ K}$$

where $T_1 = 22 + 273 = 295$ K; γ for air = 1.4,

i.e. Final temperature = 507.3 − 273 = 234.3 °C

From equation (3.19)

$$\frac{p_1}{p_2} = \left(\frac{V_2}{V_1}\right)^{\gamma} \quad \text{or} \quad \frac{V_1}{V_2} = \left(\frac{p_2}{p_1}\right)^{1/\gamma}$$

therefore

$$\frac{0.015}{V_2} = \left(\frac{6.8}{1.02}\right)^{1/1.4} = 3.877$$

therefore

$$V_2 = \frac{0.015}{3.877} = 0.003\,87 \text{ m}^3$$

i.e. Final volume = 0.003 87 m^3

From equation (3.13), for an adiabatic process

$$W = u_2 - u_1$$

and for a perfect gas, from equation (2.14), $u = c_v T$ per kg of gas, therefore

$$W = c_v(T_2 - T_1) = 0.718(507.3 - 295)$$

$$= 152.4 \text{ kJ/kg}$$

i.e. Work input = 152.4 kJ/kg

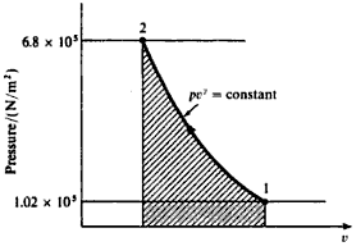
The mass of air can be found using equation (2.6), $pV = mRT$. Therefore

$$m = \frac{p_1 v_1}{RT_1} = \frac{1.02 \times 10^5 \times 0.015}{0.287 \times 10^3 \times 295} = 0.0181 \text{ kg}$$

i.e. Total work done = 0.0181 × 152.4 = 2.76 kJ

The process is shown on a p–v diagram in Fig. 3.11, the shaded area representing the work input per unit mass of air.

Fig. 3.11 Reversible adiabatic process for air on a p–v diagram for Example 3.5



3.3 Polytropic processes

It is found that many processes in practice approximate to a reversible law of the form pv^n = constant, where n is a constant. Both vapours and perfect gases obey this type of law closely in many non-flow processes. Such processes are internally reversible.

From equation (1.2) for any reversible process,

$$W = -\int p\,dv$$

For a process in which pv^n = constant, we have $p = c/v^n$, where c is a constant. Therefore

$$W = -c\int_{v_1}^{v_2} \frac{dv}{v^n} = -c\left[\frac{v^{-n+1}}{-n+1}\right] = -c\left(\frac{v_2^{-n+1} - v_1^{-n+1}}{-n+1}\right)$$

i.e. $$W = c\left(\frac{v_2^{1-n} - v_1^{1-n}}{n-1}\right) = \frac{p_2 v_2^n v_2^{1-n} - p_1 v_1^n v_1^{1-n}}{n-1}$$

since the constant, c, can be written as $p_1 v_1^n$ or as $p_2 v_2^n$,

i.e. $$\text{Work input} = \frac{p_2 v_2 - p_1 v_1}{n-1} \tag{3.24}$$

Equation (3.24) is true for any working substance undergoing a reversible polytropic process. It follows also that for any polytropic process we can write

$$\frac{p_1}{p_2} = \left(\frac{v_2}{v_1}\right)^n \tag{3.25}$$

Example 3.6 At the commencement of compression in the reciprocating compressor of a refrigeration plant the refrigerant is dry saturated at 1 bar. The compression process follows the law $pv^{1.1}$ = constant until the pressure is 10 bar. Using

Table 3.1 Properties of refrigerant for Example 3.6

Saturation values					Superheat values at 10 bar	
p_s	t_s	v_g	h_f	h_g	v	h
(bar)	(°C)	(m³/kg)	(kJ/kg)		(m³/kg)	(kJ/kg)
1	−30	0.160	8.9	174.2		
10	42	0.018	76.3	203.8	0.020	224.0

the properties of refrigerant given in Table 3.1, interpolating where necessary, calculate:

(i) the work done on the refrigerant during the process;
(ii) the heat transferred to or from the cylinder walls during the process.

Solution (i) From Table 3.1, $v_1 = v_{g1} = 0.16\ \mathrm{m^3/kg}$. We then have

$$\frac{v_2}{v_1} = \left(\frac{p_1}{p_2}\right)^{1/1.1} = \left(\frac{1}{10}\right)^{0.909} = 0.1233$$

therefore

$$v_2 = 0.1233 \times 0.16 = 0.01973\ \mathrm{m^3/kg}$$

From equation (3.24)

$$W = \frac{p_2 v_2 - p_1 v_1}{n - 1}$$

$$= \left\{\frac{(10 \times 0.01973) - (1 \times 0.16)}{1.1 - 1}\right\} \times 10^5$$

$$= 37\,300\ \mathrm{N\,m} = 37.3\ \mathrm{kJ}$$

i.e. Work done on the refrigerant = 37.3 kJ

(ii) To find the heat transferred it is first necessary to evaluate the internal energies at the end states. Using equation (1.9), $h = u + pv$, we have,

$$u_1 = u_{g1} = h_{g1} - p_{g1} v_{g1}$$

$$= 174.2 - \left(\frac{1 \times 10^5 \times 0.16}{10^3}\right) = 158.2\ \mathrm{kJ/kg}$$

Interpolating from superheat tables at 10 bar, $v_2 = 0.01973\ \mathrm{m^3/kg}$ we have

$$h_2 = 203.8 + \frac{(0.01973 - 0.018)}{(0.02 - 0.018)} \times (224 - 203.8)$$

$$= 221.3\ \mathrm{kJ/kg}$$

Then using equation (1.9)

$$u_2 = 221.3 - \left(\frac{10 \times 10^5 \times 0.01973}{10^3}\right) = 201.6 \text{ kJ/kg}$$

From equation (1.4)

$$Q + W = (u_2 - u_1)$$

therefore

$$Q = -37.3 + (201.6 - 158.2) = 6.1 \text{ kJ/kg}$$

i.e. the heat transferred from the cylinder walls to the refrigerant during the compression process is 6.1 kJ/kg.

Consider now the polytropic process for a perfect gas. From equation (2.5)

$$pv = RT \quad \text{or} \quad p = \frac{RT}{v}$$

Hence, substituting in the equation pv^n = constant, we have

$$\frac{RT}{v}v^n = \text{constant} \quad \text{or} \quad Tv^{n-1} = \text{constant} \tag{3.26}$$

Also, writing $v = RT/p$, we have

$$p\left(\frac{RT}{p}\right)^n = \text{constant} \quad \text{or} \quad \frac{T}{p^{(n-1)/n}} = \text{constant} \tag{3.27}$$

It can be seen that these equations are similar to the equations (3.17) and (3.18) for a reversible adiabatic process for a perfect gas. In fact the reversible adiabatic process for a perfect gas is a particular case of a polytropic process with the index, n, equal to γ.

Equations (3.26) and (3.27) can be written as

$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{n-1} \tag{3.28}$$

and

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(n-1)/n} \tag{3.29}$$

Note that equations (3.26), (3.27), (3.28) and (3.29) do not apply to a vapour undergoing a polytropic process, since the characteristic equation of state, $pv = RT$, which was used in the derivation of the equations, applies only to a perfect gas.

For a perfect gas expanding polytropically it is sometimes more convenient to express the work input in terms of the temperatures at the end states. From equation (3.24)

$$W = (p_2v_2 - p_1v_1)/(n-1)$$

then, from equation (2.5), $p_1v_1 = RT_1$ and $p_2v_2 = RT_2$. Hence,

$$W = \frac{R(T_2 - T_1)}{n - 1} \tag{3.30}$$

or for mass, m,

$$W = \frac{mR(T_2 - T_1)}{n - 1} \tag{3.31}$$

Using the non-flow energy equation, (1.4), the heat flow during the process can be found,

i.e. $$Q + W = u_2 - u_1 = c_v(T_2 - T_1)$$

i.e. $$Q + \frac{R(T_2 - T_1)}{(n - 1)} = c_v(T_2 - T_1)$$

From equation (2.21)

$$c_v = \frac{R}{(\gamma - 1)}$$

Hence substituting

$$Q = \frac{R}{(\gamma - 1)}(T_2 - T_1) - \frac{R}{(n - 1)}(T_2 - T_1)$$

i.e. $$Q = R(T_2 - T_1)\left(\frac{1}{\gamma - 1} - \frac{1}{n - 1}\right) = \frac{R(T_2 - T_1)(n - 1 - \gamma + 1)}{(\gamma - 1)(n - 1)}$$

therefore

$$Q = \left(\frac{n - \gamma}{\gamma - 1}\right)\frac{R(T_2 - T_1)}{(n - 1)}$$

Now from equation (3.30), $W = R(T_2 - T_1)/(n - 1)$ per unit mass of gas, therefore

$$Q = \left(\frac{n - \gamma}{\gamma - 1}\right)W \tag{3.32}$$

Equation (3.32) is a convenient and concise expression relating the heat supplied and the work input in a polytropic process. In a compression process work is done on the gas, and hence the term W is positive. Therefore it can be seen from equation (3.32) that when the polytropic index n is greater than γ, in a compression process, then the right-hand side of the equation is positive (i.e. heat is supplied during the process). Conversely, when n is less than γ in a compression process, then heat is rejected by the gas. Similarly, the work input in an expansion process is negative, therefore when n is greater than γ, in an expansion process, heat is rejected; and when n is less than γ, in an expansion process, heat must be supplied to the gas during the process. It was shown in section 2.3 that γ for all perfect gases has a value greater than unity.

Example 3.7 1 kg of a perfect gas is compressed from 1.1 bar, 27 °C according to a law $pv^{1.3}$ = constant, until the pressure is 6.6 bar. Calculate the heat flow to or from the cylinder walls:

(i) When the gas is ethane (molar mass 30 kg/kmol), which has $c_p = 2.10$ kJ/kg K.
(ii) When the gas is argon (molar mass 40 kg/kmol), which has $c_p = 0.520$ kJ/kg K.

Solution From equation (3.29), for both ethane and argon,

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(n-1)/n} \quad \text{or} \quad T_2 = T_1\left(\frac{p_2}{p_1}\right)^{(n-1)/n}$$

i.e.
$$T_2 = 300\left(\frac{6.6}{1.1}\right)^{1.3-1/1.3} = 300 \times 6^{0.231} = 300 \times 1.512 = 453.6 \text{ K}$$

where $T_1 = 27 + 273 = 300$ K.

(i) From equation (2.9), $R = \tilde{R}/\tilde{m}$, therefore, for ethane

$$R = \frac{8.3145}{30} = 0.277 \text{ kJ/kg K}$$

Then from equation (2.17), $c_p - c_v = R$, therefore

$$c_v = 2.10 - 0.277 = 1.823 \text{ kJ/kg K}$$

where $c_p = 1.75$ kJ/kg K for ethane. Then from equation (2.20)

$$\gamma = \frac{c_p}{c_v} = \frac{2.10}{1.823} = 1.152$$

From equation (3.30)

$$W = \frac{R(T_2 - T_1)}{n-1} = \frac{0.277 \times (453.6 - 300)}{1.3 - 1} = 141.8 \text{ kJ/kg}$$

Then from equation (3.32)

$$Q = \left(\frac{n-\gamma}{\gamma - 1}\right)W = \left(\frac{1.3 - 1.152}{1.152 - 1}\right) \times 141.8 = 138.1 \text{ kJ/kg}$$

i.e. Heat supplied = 138.1 kJ/kg

(ii) Using the same method for argon we have

$$R = \frac{8.3145}{40} = 0.208 \text{ kJ/kg K}$$

Also $c_v = 0.520 - 0.208 = 0.312$ kJ/kg K

therefore

$$\gamma = \frac{0.520}{0.312} = 1.667$$

Then the work input is given by

$$W = \frac{R(T_1 - T_2)}{n - 1} = \frac{0.208 \times (453.6 - 300)}{1.3 - 1} = 106.5 \text{ kJ/kg}$$

Then, $$Q = \left(\frac{n - \gamma}{\gamma - 1}\right)W = \left(\frac{1.3 - 1.667}{1.667 - 1}\right) \times 106.5 = -58.6 \text{ kJ/kg}$$

i.e. Heat rejected = 58.6 kJ/kg

In a polytropic process the index n depends only on the heat and work quantities during the process. The various processes considered in sections 3.1 and 3.2 are special cases of the polytropic process for a perfect gas.

When $n = 0$

$$pv^0 = \text{constant, i.e. } p = \text{constant}$$

When $n = \infty$,

$$pv^\infty = \text{constant} \quad \text{or} \quad p^{1/\infty}v = \text{constant, i.e. } v = \text{constant}$$

When $n = 1$

$$pv = \text{constant, i.e. } T = \text{constant}$$

since pv/T = constant for a perfect gas.

When $n = \gamma$

$$pv^\gamma = \text{constant, i.e. reversible adiabatic}$$

This is illustrated on a p–v diagram in Fig. 3.12. Thus,

state 1 to state A is constant pressure cooling ($n = 0$)

state 1 to state B is isothermal compression ($n = 1$)

state 1 to state C is reversible adiabatic compression ($n = \gamma$)

state 1 to state D is constant volume heating ($n = \infty$)

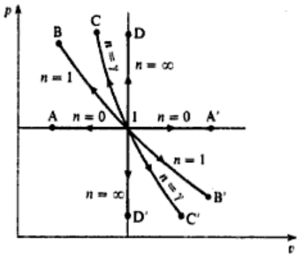


Fig. 3.12 General polytropic processes plotted on a p–v diagram

Similarly, 1 to A′ is constant pressure heating; 1 to B′ is isothermal expansion; 1 to C′ is reversible adiabatic expansion; 1 to D′ is constant volume cooling. Note that, since γ is always greater than unity, then process 1 to C must lie between processes 1 to B and 1 to D; similarly, process 1 to C′ must lie between processes 1 to B′ and 1 to D′.

For a vapour a generalization such as the above is not possible. A vapour may undergo a process according to a law pv = constant. In this case, since the characteristic equation of state, $pv = RT$, does not apply to a vapour, then the process is not isothermal. Tables must be used to find the properties at the end states, making use of the fact that $p_1v_1 = p_2v_2$. Expansion of steam in a reciprocating engine is found to approximate to a hyperbolic expansion (pv = constant); such engines are rarely used nowadays.

3.4 Reversible flow processes

Although flow processes in practice are usually highly irreversible, it is sometimes convenient to assume that a flow process is reversible in order to provide an ideal comparison. An observer travelling with the flowing fluid would appear to see a change in thermodynamic properties as in a non-flow process. For example, in a reversible adiabatic process for a perfect gas, an observer travelling with the gas would appear to see a process pv^γ = constant taking place, but the work input would not be given by $-\int p\,dv$, or by the change in internal energy as given by equation (3.13). Some work is done by virtue of the forces acting between the moving gas and its surroundings. For example, for a reversible adiabatic flow process for a perfect gas, from the flow equation (1.10), for unit mass flow rate

$$\left(h_1 + \frac{C_1^2}{2}\right) + Q + W = \left(h_2 + \frac{C_2^2}{2}\right)$$

Then since $Q = 0$

$$W = (h_2 - h_1) + \left(\frac{C_2^2}{2} - \frac{C_1^2}{2}\right)$$

Also, since the process is assumed to be reversible, then for a perfect gas, pv^γ = constant. This equation can be used to fix the end states. Note that even if the kinetic energy terms are negligibly small the work input in a reversible adiabatic flow process between two states is not equal to the work input in a reversible adiabatic non-flow process between the same states (given by equation (3.13) as $W = u_2 - u_1$).

Example 3.8 A gas turbine receives gases from the combustion chamber at 7 bar and 650 °C, with a velocity of 9 m/s. The gases leave the turbine at 1 bar with a velocity of 45 m/s. Assuming that the expansion is adiabatic and reversible in the ideal case, calculate the power output per unit mass flow rate. For the gases take $\gamma = 1.333$ and $c_p = 1.11$ kJ/kg K.

Solution Using the flow equation for an adiabatic process

$$W = \dot{m}\left\{(h_2 - h_1) + \left(\frac{C_2^2 - C_1^2}{2}\right)\right\}$$

For a perfect gas from equation (2.18), $h = c_p T$, therefore,

$$W = \dot{m}\left\{c_p(T_2 - T_1) + \left(\frac{C_2^2 - C_2^2}{2}\right)\right\}$$

To find T_2 use equation (3.21),

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma - 1)/\gamma}$$

i.e. $$\frac{T_1}{T_2} = \left(\frac{7}{1}\right)^{(1.333 - 1)/1.333} = 1.626$$

therefore

$$T_2 = \frac{T_1}{1.626} = \frac{923}{1.626} = 567.7 \text{ K}$$

where $T_1 = 650 + 273 = 923$ K.

Hence substituting for unit mass flow rate

$$\dot{W} = 1 \times 1.11(567.7 - 923) + \left(\frac{45^2 - 9^2}{2 \times 10^3}\right)$$

therefore

$$\dot{W} = -394.4 + 0.97 = -393.4 \text{ kW}$$

i.e. Power output per kilogram per second = 393.4 kW

Note that in Example 3.8 the kinetic energy change is small compared with the enthalpy change. This is often the case in problems on flow processes, and the change in kinetic energy can sometimes be taken to be negligible.

For a vapour undergoing a reversible adiabatic flow process the end state is fixed by equating the initial and final entropies (see Ch. 4).

3.5 Irreversible processes

The criteria of reversibility are stated in section 1.4. The equations of sections 3.1, 3.2, and 3.3 can only be used when the process obeys the criteria of reversibility to a close approximation. In processes in which a fluid is enclosed in a cylinder behind a piston, friction effects can be assumed to be negligible. However, in order to satisfy criterion (c) in section 1.4 heat must never be transferred to or from the system through a finite temperature difference. Only in an isothermal process is this conceivable, since in all other processes the temperature of the system is continually changing during the process; in order to satisfy criterion (c) the temperature of the cooling or heating medium external to the system would be required to change correspondingly. Ideally a way of achieving reversibility can be imagined, but in practice it cannot even be approached as an approximation. Nevertheless, if we accept inevitable irreversibilities in the surroundings, we can still have processes which are internally reversible. That is, the system undergoes a process which can be reversed, but the surroundings undergo an irreversible change. Most processes occurring in a cylinder behind a piston can be assumed to be internally reversible to a close approximation, and the equations of sections 3.1, 3.2, and 3.3 can be used where applicable. Certain processes cannot be assumed to be internally reversible, and the important cases will now be considered.

Unresisted, or free, expansion

This process was mentioned in section 1.5 in order to show that in an irreversible process the work done is not given by $-\int p\,dv$. Consider two vessels A and B, interconnected by a short pipe with a valve, and perfectly thermally insulated (see Fig. 3.13). Initially let the vessel A be filled with a fluid at a certain pressure, and let B be completely evacuated. When the valve is opened the fluid in A will expand rapidly to fill both vessels A and B. The pressure finally will be lower than the initial pressure in vessel A. This is known as an unresisted expansion or a free expansion. The process is not reversible, since external work would have to be done to restore the fluid to its initial condition. The non-flow energy equation, (1.4), can be applied between the initial and final states,

i.e. $Q + W = u_2 - u_1$

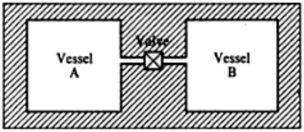


Fig. 3.13 Two perfectly insulated interconnected vessels

Now in this process no work is done on or by the fluid, since the boundary of the system does not move. No heat flows to or from the fluid since the system is well lagged. The process is therefore adiabatic, but irreversible,

i.e. $u_2 - u_1 = 0$ or $u_2 = u_1$

In a free expansion therefore the internal energy initially equals the internal energy finally.

For a perfect gas, we have, from equation (2.14),

$$u = c_v T$$

Therefore for a free expansion of a perfect gas

$$c_v T_1 = c_v T_2$$

i.e. $T_1 = T_2$

That is, for a perfect gas undergoing a free expansion, the initial temperature is equal to the final temperature.

Example 3.9 Air at 20 bar is initially contained in vessel A of Fig. 3.13, the volume of which can be assumed to be 1 m³. The valve is opened and the air expands to fill vessels A and B. Assuming that the vessels are of equal volume, calculate the final pressure of the air.

Solution For a perfect gas for a free expansion, $T_1 = T_2$. Also from equation (2.6), $pV = mRT$, hence $p_1 V_1 = p_2 V_2$.

Now V_2 is the combined volumes of vessels A and B,

i.e. $V_2 = V_A + V_B = 1 + 1 = 2\,\text{m}^3$ and $V_1 = 1\,\text{m}^3$

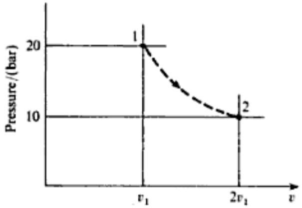
Therefore we have

$$p_2 = p_1 \times \frac{V_1}{V_2} = 20 \times \tfrac{1}{2} = 10\,\text{bar}$$

i.e. Final pressure = 10 bar

The process is shown on a p–v diagram in Fig. 3.14. State 1 is fixed at 20 bar and 1 m³ when the mass of gas is known; state 2 is fixed at 10 bar and 2 m³ for the same mass of gas. The process between these states is irreversible and must be drawn dotted. The points 1 and 2 lie on an isothermal line, but the process between 1 and 2 cannot be called isothermal, since the intermediate temperatures are not the same throughout the process. There is no work done during the process, and the area under the dotted line does not represent work done.

Fig. 3.14 Irreversible process on a p–v diagram for Example 3.9



Throttling

A flow of fluid is said to be throttled when there is some restriction to the flow, when the velocities before and after the restriction are either equal or neglibly small, and when there is a negligible heat loss to the surroundings. The restriction to flow can be a partly open valve, an orifice, or any other sudden reduction in the cross-section of the flow.

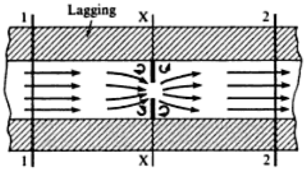
An example of throttling is shown in Fig. 3.15. The fluid, flowing steadily along a well-lagged pipe, passes through an orifice at section X–X. Since the pipe is well lagged it can be assumed that no heat flows to or from the fluid. The flow equation (1.10) can be applied between any two sections of the flow,

i.e. $$\dot{m}\left(h_1 + \frac{C_1^2}{2}\right) + \dot{Q} + \dot{W} = \dot{m}\left(h_2 + \frac{C_2^2}{2}\right)$$

Now since $Q = 0$, and $W = 0$, then

$$h_1 + \frac{C_1^2}{2} = h_2 + \frac{C_2^2}{2}$$

Fig. 3.15 Throttling process



When the velocities C_1 and C_2 are small, or when C_1 is approximately equal to C_2, then the kinetic energy terms may be neglected. (Note that sections 1–1 and 2–2 can be chosen well upstream and well downstream of the disturbance to the flow, so that this latter assumption is justified.) Then $h_1 = h_2$. Therefore for a throttling process, the enthalpy initially is equal to the enthalpy finally.

The process is adiabatic, but is highly irreversible because of the eddying of the fluid round the orifice at X–X. Between sections 1–1 and X–X the enthalpy decreases and the kinetic energy increases as the fluid accelerates through the orifice. Between sections X–X and 2–2 the enthalpy increases as the kinetic energy is destroyed by fluid eddies.

For a perfect gas, from equation (2.18), $h = c_p T$, therefore,

$$c_p T_1 = c_p T_2 \quad \text{or} \quad T_1 = T_2$$

For throttling of a perfect gas, therefore, the temperature initially equals the temperature finally.

The process of throttling can be used to find the dryness fraction of steam. A sample of steam is drawn off the steam main, passed through a mechanical separator, then through a throttle valve, and finally through a condenser; the water separated from the mechanical separator and the water from the condenser are weighed and the dryness fraction calculated as shown in the following example.

Example 3.10 The dryness fraction of wet steam in a main is determined using a separating and throttling calorimeter. The pressure in the main is 5 bar; after throttling, the steam pressure and temperature are 1.013 25 bar and 120 °C; the water collected from the separator is at the rate of 0.5 kg/h, and that from the condenser at the rate of 9 kg/h. Making suitable assumptions, calculate the dryness fraction of the steam in the main.

Solution The assumptions made are as follows: negligible pressure drop of steam in the separator; no change of kinetic energy across the throttle valve; negligible heat loss in the separator and in the throttling process.

The processes are shown on a $p-v$ diagram in Fig. 3.16; process 1–2 represents the separating process, process 2–3 the throttling process, and process 3–4 the condensing process. Process 2–3 is shown dotted since the process is irreversible; no work is done during the process and the area under line 2–3 is *not* equal to work done.

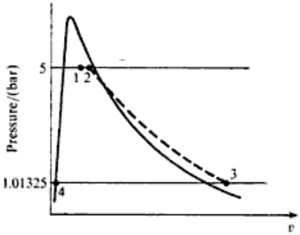


Fig. 3.16 Processes on a $p-v$ diagram for Example 3.10

The enthalpy after throttling is obtained by interpolating from steam tables,

$$h_3 = 2676 + \frac{(120 - 100)}{(150 - 100)} \times (2777 - 2676)$$

$$= 2716.4 \text{ kJ/kg}$$

For an adiabatic throttling process neglecting kinetic energy changes, $h_2 = h_3$, therefore using equation (2.2)

$$h_2 = h_3 = h_{f2} + x_2 h_{fg2}$$

therefore

$$x_2 = \frac{2716.4 - 640}{2109} = 0.985$$

where $h_{f2} = 640$ kJ/kg, and $h_{fg2} = 2109$ kJ/kg, are read from saturation tables at 5 bar.

The mass flow rate of water in the steam at state 2 is therefore given by

$$\dot{m}_{w2} = (1 - x_2) \times (\text{mass flow rate of condensate})$$

$$= (1 - 0.985) \times 9 = 0.135 \text{ kg/h}$$

Therefore the total mass flow rate of water in the steam sample from the main is given by the mass flow rate after separation, $\dot{m}_{w2}$ plus the mass of water separated, given as 0.5 kg/h,

i.e. $\dot{m}_{w1} = 0.135 + 0.5 = 0.635$ kg/h

The mass flow rate of dry vapour in the sample is therefore the total mass flow rate of (0.5 + 9) kg/h minus $\dot{m}_{w2}$, (= 0.635 kg/h)

i.e. Mass flow rate of dry vapour in sample

$$= 0.5 + 9 - 0.635 = 8.865 \text{ kg/h}$$

Then the dryness fraction in the main is the mass flow rate of dry vapour divided by the total mass flow rate,

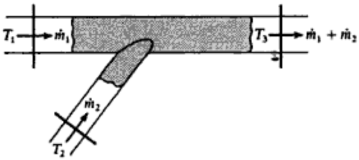
i.e. $$x_1 = \frac{8.865}{(0.5 + 9)} = 0.933$$

Adiabatic mixing

The mixing of two streams of fluid is quite common in engineering practice, and can usually be assumed to occur adiabatically. Consider two streams of a fluid mixing as shown in Fig. 3.17. Let the streams have mass flow rates $\dot{m}_1$ and $\dot{m}_2$ and temperatures T_1 and T_2. Let the resulting mixed stream have a temperature T_3. There is no heat flow to or from the fluid, and no work is done, hence from the flow equation, we have, neglecting changes in kinetic energy,

$$\dot{m}_1 h_1 + \dot{m}_2 h_2 = \dot{m}_3 h_3 \qquad (3.33)$$

Fig. 3.17 Mixing process



For a perfect gas, from equation (2.18), $h = c_p T$, hence,

$$\dot{m}_1 c_{p_1} T_1 + \dot{m}_2 c_{p_2} T_2 = (\dot{m}_1 c_{p_1} + \dot{m}_2 c_{p_2}) T_3$$

Or, assuming that the two streams 1 and 2 are of the same fluid with the same specific heat capacity,

$$\dot{m}_1 T_1 + \dot{m}_2 T_2 = (\dot{m}_1 + \dot{m}_2) T_3 \qquad (3.34)$$

The mixing process is highly irreversible due to the large amount of eddying and churning of the fluid that takes place.

3.6 Nonsteady-flow processes

There are many cases in practice when the rate of mass flow crossing the boundary of a system at inlet is not the same as the rate of mass flow crossing the boundary of the system at outlet. Also, the rate at which work is done on or by the fluid, and the rate at which heat is transferred to or from the system is not necessarily constant with time. In a case of this kind the total energy of the system within the boundary is no longer constant, as it is in a steady-flow process, but varies with time.

Let the total energy of the system within the boundary at any instant be E. During a small time interval let the mass entering the system be δm_1, and let the mass leaving the system be δm_2; let the heat supplied and the work input during the same time be δQ and δW respectively. Consider a similar system to the one shown in Fig. 1.22. Now, as shown in section 1.8 (p. 19), work is done at inlet and outlet in introducing and expelling mass across the system boundaries, i.e. at inlet

$$\text{Energy required} = \delta m_1 p_1 v_1$$

and at outlet

$$\text{Energy required} = \delta m_2 p_2 v_2$$

Also, as before, the energy of unit mass of the flowing fluid is given by $(u_1 + C_1^2/2 + Z_1 g)$ at inlet, and by $(u_2 + C_2^2/2 + Z_2 g)$ at outlet. Hence

$$\text{Energy entering system}$$
$$= \delta Q + \delta W + \delta m_1(u_1 + C_1^2/2 + Z_1 g) + \delta m_1 p_1$$

and

$$\text{Energy leaving system} = \delta m_2(u_2 + C_2^2/2 + Z_2 g) + \delta m_2 p_2 v_2$$

Then, applying the first law,

$$\text{Energy entering} - \text{energy leaving} = \text{increase of energy of the system, } \delta E$$

therefore

$$\delta Q + \delta W + \delta m_1(u_1 + C_1^2/2 + Z_1 g + p_1 v_1)$$
$$- \delta m_2(u_2 + C_2^2/2 + Z_2 g + p_2 v_2) = \delta E$$

During a finite time the total heat transferred is given by $\sum \delta Q = Q$, and the total work done is given by $\sum \delta W = W$.

Let the initial mass within the system boundaries be m', at a height, Z', and the initial internal energy be u'; let the final mass within the boundaries at the end of the time interval be m'', at a height, Z'', and the final internal energy be u''. Therefore

$$\sum \delta E = m''(u'' + Z''g) - m'(u' + Z'g)$$

Therefore we have

$$Q + W + \sum[\delta m_1(u_1 + p_1 v_1 + C_1^2/2 + Z_1 g)]$$
$$= \sum[\delta m_2(u_2 + p_2 v_2 + C_2^2/2 + Z_2 g)]$$
$$+ m''(u'' + Z''g) - m'(u' + Z'g) \qquad (3.35)$$

or

$$Q + W + \sum \delta m_1(h_1 + C_1^2/2 + Z_1 g) = \sum \delta m_2(h_2 + C_2^2/2 + Z_2 g) + (m''u'' - m'u') + (m''Z''g - m'Z'g) \quad (3.36)$$

Also, from continuity of mass,

Mass entering − mass leaving
= increase of mass within system boundary

i.e. $$\sum \delta m_1 - \sum \delta m_2 = m'' - m' \quad (3.37)$$

One of the most commonly occurring problems involving the nonsteady-flow equation is the filling of a bottle or reservoir from a source which is large in comparison with the bottle or reservoir. Figure 3.18 shows a typical example. It is assumed that the condition of the fluid in the pipeline is unchanged during the filling process. In this case there is no work done on the system boundary; also, no mass leaves the system during the process, hence $\delta m_2 = 0$.

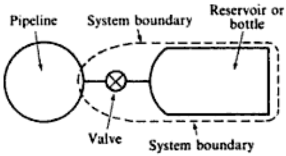


Fig. 3.18 Filling a bottle or reservoir from a pipeline

Applying equation (3.36), making the additional assumption that changes in potential energy are zero, and that the kinetic energy, $C_1^2/2$, is small compared with the enthalpy, h_1, we have

$$Q + \sum(\delta m_1 h_1) = m''u'' - m'u'$$

Or, since, h_1 is constant during the process,

$$Q + h_1 \sum(\delta m_1) = m''u'' - m'u'$$

In this case equation (3.37) becomes

$$\sum \delta m_1 = m'' - m'$$

Hence substituting

$$Q + h_1(m'' - m') = m''u'' - m'u' \quad (3.38)$$

It is often possible to assume that the process is adiabatic, and in that case we have

$$h_1(m'' - m') = m''u'' - m'u'$$

Or in words:

Enthalpy of mass which enters the bottle
= increase of internal energy of the system

Example 3.11 A rigid vessel of volume 10 m³ containing steam at 2.1 bar and dryness fraction 0.9 is connected to a pipeline, and steam is allowed to flow from the pipeline into the vessel until the pressure and temperature in the vessel are 6 bar and 200 °C respectively. The steam in the pipeline is at 10 bar and 250 °C throughout the process. Calculate the heat transfer to or from the vessel during the process.

Solution Using the notation previously introduced we have

$$u' = u_f'(1 - 0.9) + (u_g' \times 0.9) = 511 \times 0.1 + 2531 \times 0.9$$

i.e. $u' = 2329\ \text{kJ/kg}$

Also, $m' = V/v' = 10/0.9v_g = 10/(0.9 \times 0.8461) = 13.13\ \text{kg}$

The steam is superheated finally at 6 bar and 200 °C, therefore

$$u'' = 2640\ \text{kJ/kg}$$

and $v'' = 0.3522\ \text{m}^3/\text{kg}$

i.e. $m'' = V/v'' = 10/0.3522 = 28.4\ \text{kg}$

The steam in the pipeline is superheated at 10 bar and 250 °C, hence

$$h_1 = 2944\ \text{kJ/kg}$$

Then using equation (3.38)

$$Q + 2944(28.4 - 13.13) = (28.4 \times 2640) - (13.13 \times 2329)$$

therefore

$$Q = 74\,980 - 30\,590 - 44\,940 = -550\ \text{kJ}$$

i.e. Heat rejected from vessel = 550 kJ

Another commonly occurring example of the nonsteady-flow process is the case in which a vessel is opened to a large space and fluid is allowed to escape (Fig. 3.19). There is no work done and in this case $\delta m_1 = 0$ since no mass enters the system. Neglecting changes in potential energy and applying equation (3.36):

$$Q = \sum[\delta m_2(h_2 + C_2^2/2)] + (m''u'' - m'u')$$

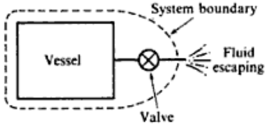


Fig. 3.19 Fluid escaping from a vessel

The difficulty arising in this analysis is that the state 2 of the mass leaving the vessel is continually changing, and hence it is impossible to evaluate the term $\sum[\delta m_2(h_2 + C_2^2/2)]$. An approximation can be made in order to find the mass of fluid which leaves the vessel as the pressure drops to a given value. It can be assumed that the fluid remaining in the vessel undergoes a reversible adiabatic expansion. This is a good approximation if the vessel is well lagged, or if the duration of the process is short. Using this assumption the end state of the fluid in the vessel can be found, and hence the mass remaining in the vessel, m'', can be calculated.

Example 3.12 An air receiver of volume 6 m³ contains air at 15 bar and 40.5 °C. A valve is opened and some air is allowed to blow out to atmosphere. The pressure of the air in the receiver drops rapidly to 12 bar when the valve is then closed. Calculate the mass of air which has left the receiver.

Solution Initially

$$m' = p'V/RT' = \frac{15 \times 10^5 \times 6}{0.287 \times 10^3 \times 313.5} = 100 \text{ kg}$$

Assuming that the mass in the receiver undergoes a reversible adiabatic process, then using equation (3.21)

$$\frac{T'}{T''} = \left(\frac{p'}{p''}\right)^{\gamma-1/\gamma} = \left(\frac{15}{12}\right)^{0.4/1.4} = 1.25^{0.286} = 1.066$$

therefore

$$T'' = 313.5/1.066 = 294.1 \text{ K}$$

Hence $$m'' = p''V/RT'' = \frac{12 \times 10^5 \times 6}{0.287 \times 10^3 \times 294.1} = 85.3 \text{ kg}$$

Therefore

Mass of air which left receiver = 100 − 85.3 = 14.7 kg

In the case of a vapour undergoing a reversible adiabatic expansion no equation such as (3.21), as used above, holds true. It is necessary to make use of the property entropy, s, which can be shown to remain constant during a reversible adiabatic process, i.e. $s' = s''$. Then using tables the value of v'' can be calculated and hence m'' found (see Problem 4.22).

Example 3.13 At the beginning of the induction stroke of a petrol engine of compression ratio 8/1, the clearance volume is occupied by residual gas at a temperature of 840 °C and pressure 1.034 bar. The volume of mixture induced during the stroke, measured at atmospheric conditions of 1.013 bar and 15 °C, is 0.75 of the cylinder swept volume. The mean pressure and temperature in the induction manifold during induction is 0.965 bar and 27 °C respectively, and the mean pressure in the cylinder during the induction stroke is 0.828 bar. Calculate the temperature and pressure of the mixture at the end of the induction stroke assuming the process to be adiabatic. For the induced mixture and final mixture take $c_v = 0.718$ kJ/kg K and $R = 0.287$ kJ/kg K; for the residual gas take $c_v = 0.840$ kJ/kg K and $R = 0.296$ kJ/kg K.

Solution Let swept volume be V_s and clearance volume be V_c. Then

$$\text{Compression ratio} = \frac{V_s + V_c}{V_c} = 8 \text{ (see p. 135)}$$

i.e. $V_s = 7V_c$

Initially the residual gas occupies the volume, $V_c = V_s/7$, therefore

$$m' = \frac{p'V_c}{RT'} = \frac{1.034 \times 10^5 \times V_s}{0.296 \times 1113 \times 7 \times 10^3} = 0.0448V_s \text{ kg}$$

where $T' = 840 + 273 = 1113$ K.

Also using equation (3.37)

$$m'' - m' = \sum \delta m_1 - \sum \delta m_2$$

and noting that in this example $\sum \delta m_2 = 0$, we have

$$m'' - m' = m_1 = \frac{1.013 \times 10^5 \times 0.75V_s}{0.287 \times 288 \times 10^3} = 0.9192V_s \text{ kg}$$

therefore

$$m'' = 0.9192V_s + 0.0448V_s = 0.964V_s \text{ kg}$$

Changes in kinetic and potential energy can be neglected, and the process is adiabatic (i.e. $Q = 0$), hence applying equation (3.36) we have

$$m_1 h_1 + W = m''u'' - m'u'$$

Also, the temperature of the mixture in the induction manifold is constant throughout the stroke, i.e. $h_1 = c_p T_1 =$ constant. Therefore

$$m_1 c_p T_1 + W = m'' c_v T'' - m' c_v T' \qquad [1]$$

The work input is given by

$$-W = (\text{mean pressure in cylinder during induction} \times \text{swept volume})$$
$$= 0.828 \times 10^5 \times V_s = 82\,800V_s \text{ N m} = 82.8V_s \text{ kJ}$$

therefore

$$W = -82.8V_s \text{ kJ}$$

For the mixture induced, $c_p = c_v + R = 0.718 + 0.287 = 1.005$ kJ/kg K. Then substituting values in equation [1]

$$(0.9192 \times V_s \times 1.005 \times 300) - 82.8V_s$$
$$= (0.964V_s \times 0.718 \times T'') - (0.0448V_s \times 0.84 \times 1113)$$

therefore

$$T'' = 341.3 \text{ K} = 68.3\,^\circ\text{C}$$

i.e. Final temperature $= 68.3\,^\circ$C

Then

$$p'' = \frac{m''RT''}{(V_s + V_c)} = \frac{0.964V_s \times 0.287 \times 341.3 \times 10^3}{8V_s/7} = 82\,623 \text{ N/m}^2$$

i.e. Final pressure = 0.826 bar

Problems

3.1 1 kg of air enclosed in a rigid container is initially at 4.8 bar and 150 °C. The container is heated until the temperature is 200 °C. Calculate the pressure of the air finally and the heat supplied during the process.

(5.37 bar; 35.9 kJ/kg)

3.2 A rigid vessel of volume 1 m^3 contains steam at 20 bar and 400 °C. The vessel is cooled until the steam is just dry saturated. Calculate the mass of steam in the vessel, the final pressure of the steam, and the heat rejected during the process.

(6.62 kg; 13.01 bar; 2355 kJ)

3.3 Oxygen (molar mass 32 kg/kmol) expands reversibly in a cylinder behind a piston at a constant pressure of 3 bar. The volume initially is 0.01 m^3 and finally is 0.03 m^3; the initial temperature is 17 °C. Calculate the work input and the heat supplied during the expansion. Assume oxygen to be a perfect gas and take $c_p = 0.917$ kJ/kg K.

(−6 kJ; 21.18 kJ)

3.4 Steam at 7 bar, dryness fraction 0.9, expands reversibly at constant pressure until the temperature is 200 °C. Calculate the work input and heat supplied per unit mass of steam during the process.

(−38.2 kJ/kg; 288.7 kJ/kg)

3.5 0.05 m^3 of a perfect gas at 6.3 bar undergoes a reversible isothermal process to a pressure of 1.05 bar. Calculate the heat supplied.

(56.4 kJ)

3.6 Dry saturated steam at 7 bar expands reversibly in a cylinder behind a piston until the pressure is 0.1 bar. If heat is supplied continuously during the process in order to keep the temperature constant, calculate the change of internal energy per unit mass of steam.

(37.2 kJ/kg)

3.7 1 kg of air is compressed isothermally and reversibly from 1 bar and 30 °C to 5 bar. Calculate the work input and the heat supplied.

(140 kJ/kg; −140 kJ/kg)

3.8 1 kg of air at 1 bar, 15 °C is compressed reversibly and adiabatically to a pressure of 4 bar. Calculate the final temperature and the work input.

(155 °C; 100.5 kJ/kg)

3.9 Nitrogen (molar mass 28 kg/kmol) expands reversibly in a perfectly thermally insulated cylinder from 3.5 bar, 200 °C to a volume of 0.09 m^3. If the initial volume occupied was 0.03 m^3, calculate the work input. Assume nitrogen to be a perfect gas and take $c_v = 0.741$ kJ/kg K.

(−9.31 kJ)

3.10 A certain perfect gas is compressed reversibly from 1 bar, 17 °C to a pressure of 5 bar in a perfectly thermally insulated cylinder, the final temperature being 77 °C. The work done on the gas during the compression is 45 kJ/kg. Calculate γ, c_v, R, and the molar mass of the gas.

(1.132; 0.75 kJ/kg K; 0.099 kJ/kg K; 84 kg/kmol)

3.11 1 kg of air at 1.02 bar, 20 °C is compressed reversibly according to a law $pv^{1.3}$ = constant, to a pressure of 5.5 bar. Calculate the work done on the air and the heat supplied during the compression.

(133.46 kJ/kg; −33.3 kJ/kg)

3.12 Oxygen (molar mass 32 kg/kmol) is compressed reversibly and polytropically in a cylinder from 1.05 bar, 15 °C to 4.2 bar in such a way that one-third of the work input is rejected as heat to the cylinder walls. Calculate the final temperature of the oxygen. Assume oxygen to be a perfect gas and take c_v = 0.649 kJ/kg K.

(113 °C)

3.13 A mass of 0.05 kg of carbon dioxide (molar mass 44 kg/kmol), occupying a volume of 0.03 m^3 at 1.025 bar, is compressed reversibly until the pressure is 6.15 bar. Calculate the final temperature, the work done on the CO_2, and the heat supplied:

(i) when the process is according to a law $pv^{1.4}$ = constant;
(ii) when the process is isothermal;
(iii) when the process takes place in a perfectly thermally insulated cylinder.

Assume carbon dioxide to be a perfect gas, and take $\gamma = 1.3$.

(270 °C; 5.135 kJ; 1.712 kJ; 52.5 °C; 5.51 kJ; −5.51 kJ; 219 °C; 5.25 kJ; 0 kJ)

3.14 A refrigerant is compressed reversibly in a cylinder according to a polytropic law from 2.62 bar, dry saturated, to 8.20 bar when the temperature is then 40 °C. Using the refrigerant properties given as Table 3.2, calculate:

(i) the polytropic index;
(ii) the work input during the compression process;
(iii) the heat transferred to or from the cylinder walls during the process.

(1.073; 21.93 kJ/kg; 6.16 kJ/kg)

Table 3.2 Properties of refrigerant for Problem 3.14

Saturation values			Superheat values at 8.2 bar, 40 °C	
p_g	v_g	h_g	v	h
(bar)	(m^3/kg)	(kJ/kg)	(m^3/kg)	(kJ/kg)
2.62	0.0757	292.9	0.02615	322.6

3.15 A refrigerant is dry saturated at 2 bar and is compressed reversibly in a cylinder according to a law pv = constant to a pressure of 10 bar. Using the properties of refrigerant given as Table 3.3, calculate:

(i) the final specific volume and temperature of the refrigerant:
(ii) the final specific volume and temperature when the working substance is air, compressed between the same pressures and from the same initial temperature.

(0.024 m^3/kg, 24 °C; 0.071 m^3/kg, −25 °C)

Table 3.3 Properties of refrigerant for Problem 3.15

t_s (°C)	p_s (bar)	v_g (m³/kg)
−25	2	0.120
24	10	0.024

3.16 A refrigerant leaves a condenser as a saturated liquid at a temperature of 25 °C, and is throttled to a pressure of 1.83 bar where it enters the evaporator. Using the properties of refrigerant given as Table 3.4, calculate the dryness fraction of the refrigerant vapour entering the evaporator.

(0.236)

Table 3.4 Properties of refrigerant for Problem 3.16

t_g (°C)	p_s (bar)	h_f (kJ/kg)	h_g
25	6.52	59.7	197.7
−15	1.83	22.3	181.0

3.17 The pressure in a steam main is 12 bar. A sample of steam is drawn off and passed through a throttling calorimeter, the pressure and temperature at exit from the calorimeter being 1 bar and 140 °C respectively. Calculate the dryness fraction of the steam in the main, stating any assumptions made in the throttling process.

(0 .966)

3.18 Air at 6.9 bar, 260 °C is throttled to 5.5 bar before expanding through a nozzle to a pressure of 1.1 bar. Assuming that the air flows reversibly in steady flow through the nozzle, and that no heat is rejected, calculate the velocity of the air at exit from the nozzle when the inlet velocity is 100 m/s.

(636 m/s)

3.19 Air at 40 °C enters a mixing chamber at a rate of 225 kg/s where it mixes with air at 15 °C entering at a rate of 540 kg/s. Calculate the temperature of the air leaving the chamber, assuming steady-flow conditions. Assume that the heat loss is negligible.

(22.4 °C)

3.20 Steam from a superheater at 7 bar, 300 °C is mixed in steady adiabatic flow with wet steam at 7 bar, dryness fraction 0.9. Calculate the mass of wet steam required per kilogram of superheated steam to produce steam at 7 bar, dry saturated.

(1.43 kg)

3.21 A rigid cylinder contains helium (molar mass 4 kg/kmol) at a pressure of 5 bar and a temperature of 15 °C. The cylinder is now connected to a large source of helium at 10 bar and 15 °C, and the valve connecting the cylinder is closed when the cylinder pressure has risen to 8 bar. Calculate the final temperature of the helium in the cylinder assuming that the heat transfer during the process is negligibly small. Take c_v for helium as 3.12 kJ/kg K.

(65.8 °C)

3.22 A well-lagged vessel of volume 1 m^3, containing 1.25 kg of steam at a pressure of 2.2 bar, is connected via a valve to a large source of steam at 20 bar. The valve is opened and the pressure in the vessel is allowed to rise until the steam in the vessel is just dry saturated at 4 bar and the valve is then closed. Calculate the dryness fraction of the steam supplied.

(0.904)

3.23 An air receiver contains 10 kg of air at 7 bar. A blow-off valve is opened in error and closed again within seconds, but the pressure is observed to drop to 6 bar. Calculate the mass of air which has escaped from the receiver, stating clearly any assumptions made.

Calculate also the pressure of the air in the receiver some time after the valve has been closed such that the air temperature has attained its original value.

(1.04 kg; 6.27 bar)

3.24 A vertical cylinder of cross-sectional area 6450 mm^2 is open to the atmosphere at one end and connected to a large storage vessel at the other end by means of a pipeline and valve. A frictionless piston, of weight 100 N, is fitted into the cylinder and the initial cylinder volume is negligible. The valve is then opened and air is slowly admitted from the large storage vessel into the cylinder until the piston has moved very slowly a distance of 0.6 m, when the valve is shut. If the temperature of the air in the cylinder is 30 °C at the end of the operation and the temperature of the air in the large storage vessel is constant at 90 °C, calculate:

(i) the pressure of the air in the cylinder during the process;
(ii) the work done on the air during the process;
(iii) the work done on the piston;
(iv) the heat supplied to the air in the cylinder during the process.

Take the atmospheric pressure as 1.013 bar.

(1.168 bar; −452 N m; 60 N m; −0.31 kJ)

4

The Second Law

In Chapter 1 it is stated that, according to the First Law of Thermodynamics, when a system undergoes a complete cycle the net heat supplied plus the net work input is zero. This is based on the conservation of energy principle which follows from observation of natural events. The Second Law of Thermodynamics, which is also a natural law, indicates that in any complete cycle the *gross* heat supplied plus the net work input must be greater than zero. Thus for any cycle in which there is a net work output (i.e. W –ve), heat must always be rejected. For any cycle in which heat is supplied at a low temperature and rejected at a higher temperature there must always be a positive work input.

To enable the second law to be discussed more fully the heat engine must be defined and discussed.

4.1 The heat engine

A heat engine is a system which operates continuously and across whose boundaries flow only heat and work.

A diagrammatic representation of a heat engine is given in Fig. 4.1; a forward heat engine is shown in Fig. 4.1(a) and a reversed heat engine in Fig. 4.1(b). (Note: the term 'reservoir' is taken to mean an energy source at a uniform temperature.) In both cases the first law applies as given by equation (1.3), $\sum Q + \sum W = 0$, or referring to Fig. 4.1,

$$Q_1 + Q_2 + W = 0$$

As shown in Fig. 4.1, for a forward heat engine cycle such as that used for power production, Q_1 is positive and W and Q_2 are negative; for a reversed cycle such as that used for a refrigerator or heat pump, Q_1 is negative and W and Q_2 are positive.

An example of a forward heat engine is shown in Fig. 4.2; by the first law the heat supplied of 100 units equates to the work output of 30 units plus the heat rejected of 70 units. It can be demonstrated that it is impossible to construct a forward heat engine in which 100 units of heat are supplied and 100 units of work output are produced; some heat must always be rejected. One statement

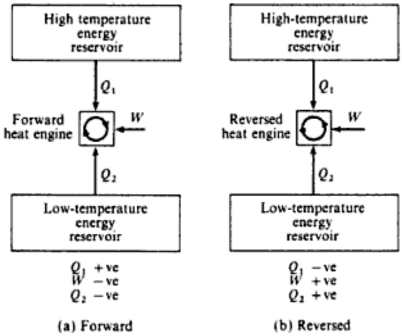


Fig. 4.1 Forward and reversed heat engines

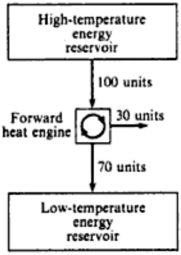


Fig. 4.2 Example of a forward heat engine

of the Second Law of Thermodynamics is therefore as follows:

> *It is impossible for a heat engine to produce a net work output in a complete cycle if it exchanges heat only with a single energy reservoir.*

Using the chosen sign convention for heat and work and referring to Fig. 4.1, we can write this statement of the second law in symbols as follows:

$$Q_1 > -W \tag{4.1}$$

The cycle efficiency of a forward heat engine can then be defined as the ratio of the net work output to the gross heat supplied,

i.e. $$\text{Cycle efficiency, } \eta = \frac{-W}{Q_1} \tag{4.2}$$

The second law implies that the cycle efficiency must always be less than unity. For the heat engine shown in Fig. 4.2 the cycle efficiency is $\eta = 30/100 = 0.3$ or 30%.

An example of a reversed heat engine is shown in Fig. 4.3; by the first law the 70 units of heat supplied from the low-temperature energy reservoir plus the work input of 30 units is equal to the 100 units of heat rejected to the high-temperature reservoir. It can be demonstrated that it is impossible to transfer 70 units of heat from the low-temperature reservoir to the high-temperature reservoir without a work input. An alternative statement of the second law is therefore as follows:

> *It is impossible to construct a device that operating in a cycle will produce no effect other than the transfer of heat from a cooler to a hotter body.*

Referring to Fig. 4.1(b) this statement of the second law can be expressed as

$$W > 0 \tag{4.3}$$

It is interesting to note that in the case of a forward heat engine the second

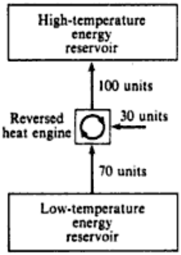


Fig. 4.3 Example of a reversed heat engine

law implies that there must always be some heat rejected to the low-temperature reservoir, but in the case of the reversed heat engine (Fig. 4.1(b)), there is no reason why Q_2 should not be zero. This means that it is possible to convert mechanical energy into heat energy (e.g. on braking a car the kinetic energy is converted into heat at the wheels). On the other hand it is impossible to convert heat energy continuously and completely into mechanical work.

The effectiveness of a reversed heat engine is defined in terms of a coefficient of performance, COP. When the reversed engine is used mainly as a refrigerator then, referring to Fig. 5.1(b), the coefficient of performance is defined as

$$\mathrm{COP}_{\mathrm{ref}} = \frac{Q_2}{W} \tag{4.4}$$

When the reversed heat engine is used as a heat pump the heat transferred to the high-temperature reservoir is the useful energy, and referring to Fig. 4.1(b) we have

$$\mathrm{COP}_{\mathrm{hp}} = \frac{-Q_1}{W} \tag{4.5}$$

(Note: the coefficient of performance of both a refrigerator and a heat pump is always greater than unity; in the example given in Fig. 4.3, $\mathrm{COP}_{\mathrm{ref}} = 70/30 = 2.333$, and $\mathrm{COP}_{\mathrm{hp}} = 100/30 = 3.333$.) Refrigeration and heat pumps are considered in more detail in Chapter 14.

4.2 Entropy

In section 1.7, an important property, internal energy, was found to arise as a consequence of the First Law of Thermodynamics. Another important property, *entropy*, follows from the second law.

Consider a reversible adiabatic process for any system on a p–v diagram. This is represented by line AB on Fig. 4.4. Let us suppose that it is possible for the system to undergo a reversible isothermal process at temperature T_1 from B to C and then be restored to its original state by a second reversible adiabatic process from C to A. Now by definition an adiabatic process is one

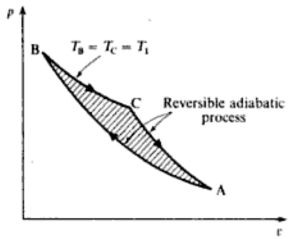


Fig. 4.4 Hypothetical (impossible) cycle on a p–v diagram

in which no heat flows to or from the system. Hence the only heat transferred is from B to C during the isothermal process. The work done *by* the system is given by the enclosed area (see section 1.6). We therefore have a system undergoing a cycle and developing a net work output while drawing heat from a reservoir at one fixed temperature. This is impossible because it violates the second law, as stated in section 4.1. Therefore the original supposition is wrong, and it is not possible to have two reversible adiabatic processes passing through the same state A.

Now one of the characteristics of a property of a system is that there is one unique line which represents a value of the property on a diagram of properties. (For example, the line BC on Fig. 4.4 represents the isothermal at T_1.) Hence there must be a property represented by a reversible adiabatic process. This property is called entropy, *s*.

It follows that there is no change of entropy in a reversible adiabatic process. Each reversible adiabatic process represents a unique value of entropy. On a p–v diagram a series of reversible adiabatic processes appear as shown in Fig. 4.5(a), each line representing one value of entropy. This is similar to Fig. 4.5(b) in which a series of isothermals is drawn, each representing one value of temperature.

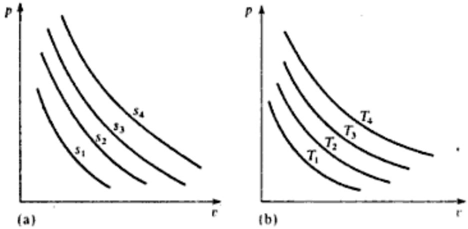


Fig. 4.5 A series of constant entropy and constant temperature lines on a p–v diagram

In order to be able to define entropy in terms of the other thermodynamic properties a rigorous approach is necessary; a much simplified approach has been adopted in this book. For a more rigorous approach ref. 4.1 should be consulted.

In section 3.2 a reversible adiabatic process for a perfect gas was shown to follow a law pv^γ = constant. Now the law pv^γ = constant is a unique line on a p–v diagram, so that the proof given in section 3.2 for a perfect gas is a similar proof to that given above (i.e. the proof that a reversible adiabatic process occupies a unique line on a diagram of properties). The proof given above depends on the second law and has been used to introduce entropy as a property. It follows therefore that the proof of pv^γ = constant in section 3.2 must imply the fact that the entropy does not change during a reversible adiabatic process. Referring to the proof in section 3.2, starting with the non-flow energy equation for a reversible process

$$dQ = du + p\,dv$$

and for a perfect gas

$$dQ = c_v\,dT + RT\frac{dv}{v}$$

This equation can be integrated after dividing through by T,

i.e. $$\frac{dQ}{T} = \frac{c_v\,dT}{T} + \frac{R\,dv}{v}$$

Also for an adiabatic process, $dQ = 0$,

i.e. $$\frac{dQ}{T} = \frac{c_v\,dT}{T} + \frac{R\,dv}{v} = 0 \qquad (4.6)$$

Now apart from mathematical manipulation and the introduction of the relationship between R, c_p, c_v, and γ, there are no other major steps in the proof. This must mean that dividing through by T is the one step which implies the restriction of the second law, and the important fact that the change of entropy is zero. We can say, therefore, $dQ/T = 0$ for a reversible adiabatic process. For any other reversible process $dQ/T \neq 0$.

This result can be shown to apply to all working substances,

i.e. $$ds = \frac{dQ}{T} \quad \text{for all working substances} \qquad (4.7)$$

where s is entropy.

The argument in this section does not constitute a proof of $ds = dQ/T$. For such a proof the reader is recommended to ref. 4.1.

Note that since equation (4.6) is for a reversible process, then dQ in equation (4.7) is the heat added reversibly.

The change of entropy is more important than its absolute value, and the zero of entropy can be chosen quite arbitrarily.

Integrating equation (4.7) gives

$$s_2 - s_1 = \int_1^2 \frac{dQ}{T} \qquad (4.8)$$

Considering unit mass of fluid, the units of entropy are given by kilojoules per kilogram divided by K. That is, the units of specific entropy, s, are kJ/kg K. The symbol S will be used for the entropy of mass, m, of a fluid,

i.e. $$S = ms$$

Rewriting equation (4.7) we have

$$dQ = T\,ds$$

or for any reversible process

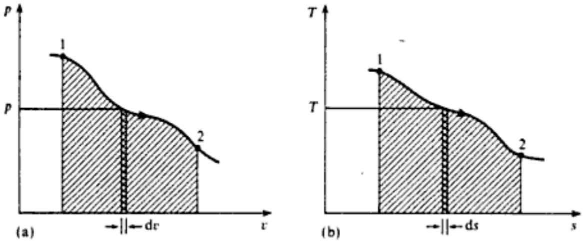
$$Q = \int_1^2 T\,ds \qquad (4.9)$$

This equation is analogous to equation (1.2),

$$W = -\int_1^2 p\,dv \quad \text{for any reversible process}$$

Thus, as there is a diagram on which areas represent work output in a reversible process, there is also a diagram on which areas represent heat supplied in a reversible process. These diagrams are the p–v and the T–s diagrams respectively, as shown in Figs 4.6(a) and 4.6(b). For a reversible process 1–2 in Fig. 4.6(a), the shaded area $\int_1^2 p\,dv$ represents work output, $-W$; for a reversible process 1–2 in Fig. 4.6(b), the shaded area $\int_1^2 T\,ds$ represents heat supplied, Q. Therefore one great use of the property entropy is that it enables a diagram to be drawn on which areas represent heat flow in a reversible process. In the section 4.3 the T–s diagram will be considered for a vapour and for a perfect gas.

Fig. 4.6 Area under a reversible process on a p–v and on a T–s diagram



4.3 The *T–s* diagram

For a vapour

The T–s diagram for steam only will be considered here; the diagram for a refrigerant is exactly similar with the important exception of the zeros of entropy and enthalpy which vary according to the source of the tabular information (see Ch. 14). The T–s diagram for steam is shown in Fig. 4.7. Three lines of constant pressure (p_1, p_2, and p_3) are shown (i.e. lines ABCD, EFGH, and JKLM). The pressure lines in the liquid region are practically coincident with the saturated liquid line (i.e. portions AB, EF, and JK), and the difference is usually neglected. The pressure remains constant with temperature when the latent heat is added, hence the pressure lines are horizontal in the wet region (i.e. portions BC, FG, and KL). The pressure lines curve upwards in the superheat region as shown (i.e. portions CD, GH, and LM). Thus the temperature rises as heating continues at constant pressure. One constant volume line (shown as a broken line) is drawn in Fig. 4.7. Lines of constant volume are concave down in the wet region and slope up more steeply than pressure lines in the superheat region.

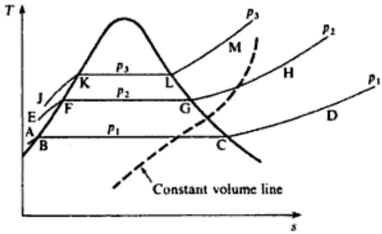


Fig. 4.7 T–s diagram for a vapour

In steam tables the entropy of the saturated liquid and the dry saturated vapour are represented by s_f and s_g respectively. The difference, $s_g - s_f = s_{fg}$, is also tabulated. The entropy of wet steam is given by the entropy of the water in the mixture plus the entropy of the dry steam in the mixture. For wet steam with dryness fraction, x, we have

$$s = (1 - x)s_f + xs_g \tag{4.10}$$

or $$s = s_f + x(s_g - s_f)$$

i.e. $$s = s_f + xs_{fg} \tag{4.11}$$

Then the dryness fraction is given by

$$x = \frac{s - s_f}{s_{fg}} \tag{4.12}$$

It can be seen from equation (4.12) that the dryness fraction is proportional to the distance of the state point from the liquid line on a T–s diagram. For example, for state 1 on Fig. 4.8 the dryness fraction

$$x_1 = \frac{\text{distance F1}}{\text{distance FG}} = \frac{s_1 - s_{f1}}{s_{fg1}}$$

The area under the line FG on Fig. 4.8 represents the specific enthalpy of vaporization h_{fg}. The area under line F1 is given by $x_1 h_{fg}$.

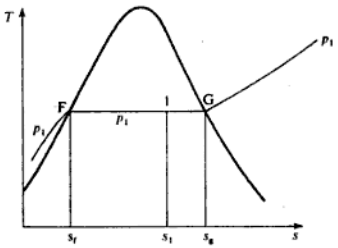


Fig. 4.8 Dryness fraction from areas on a T–s diagram

Example 4.1 1 kg of steam at 7 bar, entropy 6.5 kJ/kg K, is heated reversibly at constant pressure until the temperature is 250 °C. Calculate the heat supplied, and show on a *T–s* diagram the area which represents the heat flow.

Solution At 7 bar, $s_g = 6.709$ kJ/kg K, hence the steam is wet, since the actual entropy, s, is less than s_g.

From equation (4.12)

$$x_1 = \frac{s_1 - s_{f1}}{s_{fg1}} = \frac{6.5 - 1.992}{4.717} = 0.955$$

Then from equation (2.2)

$$h_1 = h_{f1} + x_1 h_{fg1} = 697 + (0.955 \times 2067)$$

i.e. $$h_1 = 697 + 1975 = 2672 \text{ kJ/kg}$$

At state 2 the steam is at 250 °C at 7 bar, and is therefore superheated. From superheat tables, $h_2 = 2955$ kJ/kg.

At constant pressure from equation (3.3)

$$Q = h_2 - h_1 = 2955 - 2672 = 283 \text{ kJ/kg}$$

i.e. Heat supplied = 283 kJ/kg

The *T–s* diagram showing the process is given in Fig. 4.9, the shaded area representing the heat flow.

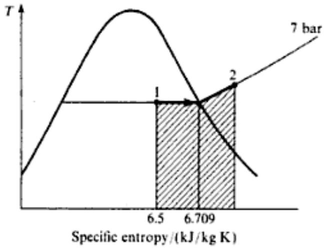


Fig. 4.9 *T–s* diagram for Example 4.1

Example 4.2 A rigid cylinder of volume 0.025 m³ contains steam at 80 bar and 350 °C. The cylinder is cooled until the pressure is 50 bar. Calculate the state of the steam after cooling and the amount of heat rejected by the steam. Sketch the process on a *T–s* diagram indicating the area which represents the heat flow.

Solution Steam at 80 bar and 350 °C is superheated, and the specific volume from tables is 0.02994 m³/kg. Hence the mass of steam in the cylinder is given by

$$m = \frac{0.025}{0.02994} = 0.835 \text{ kg}$$

For superheated steam above 80 bar the internal energy is found from equation (3.7),

$$u_1 = h_1 - p_1 v_1 = 2990 - \frac{80 \times 10^5 \times 0.02994}{10^3} = 2990 - 239.5$$

i.e. $u_1 = 2750.5$ kJ/kg

At state 2, $p_2 = 50$ bar and $v_2 = 0.029\,94$ m^3/kg, therefore the steam is wet, and the dryness fraction is given by equation (2.1)

$$x_2 = \frac{v_2}{v_{g_2}} = \frac{0.029\,94}{0.039\,44} = 0.758$$

From equation (2.3)

$$u_2 = (1 - x_2)u_{f_2} + x_2 u_{g_2} = (0.242 \times 1149) + (0.758 \times 2597)$$

i.e. $u_2 = 278 + 1969 = 2247$ kJ/kg

At constant volume from equation (3.2),

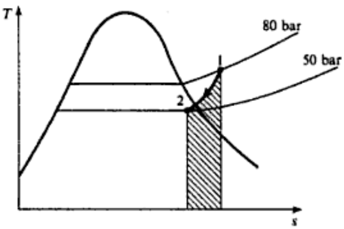
$$Q = U_2 - U_1 = m(u_2 - u_1) = 0.835(2247 - 2750.5)$$

i.e. $Q = -0.835 \times 503.5 = -420$ kJ

i.e. Heat rejected = 420 kJ

Figure 4.10 shows the process drawn on a T–s diagram, the shaded area representing the heat rejected by the steam.

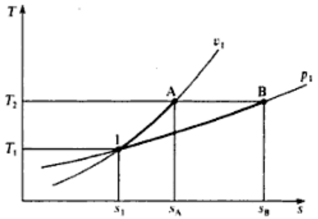
Fig. 4.10 T–s diagram for Example 4.2



For a perfect gas

It is useful to plot lines of constant pressure and constant volume on a T–s diagram for a perfect gas. Since changes of entropy are of more direct application than the absolute value, the zero of entropy can be chosen at any arbitrary reference temperature and pressure. In Fig. 4.11 the pressure line p_1 and the volume line v_1 have been drawn passing through the state point 1. Note that a line of constant pressure slopes less steeply than a line of constant volume.

Fig. 4.11 Entropy changes at constant pressure and at constant volume for a perfect gas on a T–s diagram



This can be proved easily by reference to Fig. 4.11. Let points A and B be at T_2 and v_1, and T_2 and p_1 respectively as shown. Now between 1 and A from equation (4.8) we have

$$s_A - s_1 = \int_1^A \frac{dQ}{T}$$

Also at a constant volume for 1 kg of gas from equation (2.11), $dQ = c_v\,dT$. Therefore

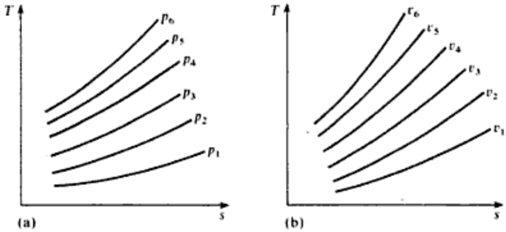
$$s_A - s_1 = \int_1^A \frac{c_v\,dT}{T} = c_v \ln\left(\frac{T_A}{T_1}\right) = c_v \ln\left(\frac{T_2}{T_1}\right)$$

Similarly, at constant pressure for 1 kg of gas, $dQ = c_p\,dT$. Hence,

$$s_B - s_1 = \int_1^B \frac{c_p\,dT}{T} = c_p \ln\left(\frac{T_B}{T_1}\right) = c_p \ln\left(\frac{T_2}{T_1}\right)$$

Now since c_p is greater than c_v for any perfect gas, then $s_B - s_1$ is greater than $s_A - s_1$. Point A must therefore lie to the left of point B on the diagram, and hence a line of constant pressure slopes less steeply than a line of constant volume. Figure 4.12(a) shows a series of constant pressure lines on a T–s diagram, and Fig. 4.12(b) shows a series of constant volume lines on a T–s diagram. Note that in Fig. 4.12(a), $p_6 > p_5 > p_4 > p_3$, etc. and in Fig. 4.12(b), $v_1 > v_2 > v_3$, etc. As the pressure rises the temperature rises and the volume decreases; conversely as the pressure and temperature fall the volume increases.

Fig. 4.12 Constant pressure and constant volume lines plotted on a T–s diagram for a perfect gas



Example 4.3 Air at 15 °C and 1.05 bar occupies 0.02 m^3. The air is heated at constant volume until the pressure is 4.2 bar, and then cooled at constant pressure back to the original temperature. Calculate the net heat flow to or from the air and the net entropy change. Sketch the process on a T–s diagram.

Solution The processes are shown on a T–s diagram in Fig. 4.13. From equation (2.6), for a perfect gas,

$$m = \frac{pV}{RT} = \frac{1.05 \times 10^5 \times 0.02}{0.287 \times 10^3 \times 288} = 0.0254 \text{ kg}$$

where $T_1 = 15 + 273 = 288$ K.

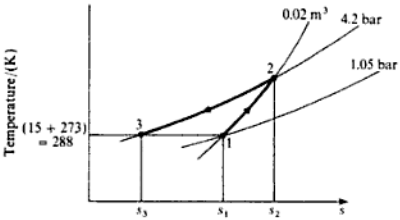


Fig. 4.13 Processes on a T–s diagram for Example 4.3

For a perfect gas at constant volume, $p_1/T_1 = p_2/T_2$, hence

$$T_2 = \frac{4.2 \times 288}{1.05} = 1152 \text{ K}$$

From equation (2.13), at constant volume

$$Q = mc_v(T_2 - T_1) = 0.0254 \times 0.718(1152 - 288)$$

i.e. $Q_{1\text{-}2} = 15.75$ kJ

From equation (2.12), at constant pressure

$$Q = mc_p(T_3 - T_2) = 0.0254 \times 1.005(288 - 1152)$$

i.e. $Q_{2\text{-}3} = -22.05$ kJ

therefore

$$\text{Net heat flow} = Q_{1\text{-}2} + Q_{2\text{-}3} = 15.75 - 22.05 = -6.3 \text{ kJ}$$

i.e. Heat rejected = 6.3 kJ

Referring to Fig. 4.13

$$\text{Net decrease in entropy} = s_1 - s_3 = (s_2 - s_3) - (s_2 - s_1)$$

At constant pressure, $dQ = mc_p\, dT$, hence, using equation (4.8),

$$m(s_2 - s_3) = \int_{288}^{1152} \frac{mc_p\, dT}{T} = 0.0254 \times 1.005 \times \ln\left(\frac{1152}{288}\right)$$

$$= 0.0354 \text{ kJ/K}$$

At constant volume, $dQ = mc_v\,dT$, hence, using equation (4.8)

$$m(s_2 - s_1) = \int_{288}^{1152} \frac{mc_v\,dT}{T} = 0.0254 \times 0.718 \times \ln\left(\frac{1152}{288}\right)$$

$$= 0.0253 \text{ kJ/kg}$$

Therefore,

$$m(s_1 - s_3) = 0.0354 - 0.0253 = 0.0101 \text{ kJ/K}$$

i.e. Decrease in entropy of air = 0.0101 kJ/K

Note that since entropy is a property, the decrease in entropy in Example 4.3, given by $s_1 - s_3$, is independent of the processes undergone between states 1 and 3. The change $s_1 - s_3$ can also be found by imagining a reversible isothermal process taking place between 1 and 3. The isothermal process on the T–s diagram will be considered in section 4.4.

4.4 Reversible processes on the *T–s* diagram

The various reversible processes dealt with in Chapter 3 will now be considered in relation to the T–s diagram. The constant volume and constant pressure processes have been represented on the T–s diagram in section 4.3, and will therefore not be discussed again in this section.

Reversible isothermal process

A reversible isothermal process will appear as a horizontal line on a T–s diagram, and the area under the line must represent the heat flow during the process. For example, Fig. 4.14 shows a reversible isothermal expansion of wet steam into the superheat region. The shaded area represents the heat supplied during the process,

i.e. Heat supplied = $T(s_2 - s_1)$

Note that the absolute temperature must be used.

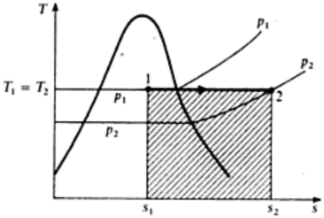


Fig. 4.14 Reversible isothermal process for steam on a T–s diagram

Example 4.4 Dry saturated steam at 100 bar expands isothermally and reversibly to a pressure of 10 bar. Calculate the heat supplied and the work done per kilogram of steam during the process.

Solution The process is shown in Fig. 4.15, the shaded area representing the heat supplied.

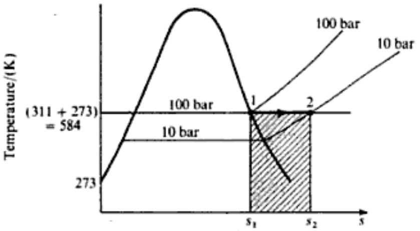


Fig. 4.15 Process on a T–s diagram for Example 4.4

From tables at 100 bar, dry saturated

$$s_1 = s_g = 5.615 \text{ kJ/kg K} \quad \text{and} \quad t_1 = 311\,°\text{C}$$

At 10 bar and 311 °C the steam is superheated, hence interpolating

$$s_2 = 7.124 + \left(\frac{311 - 300}{350 - 300}\right)(7.301 - 7.124)$$

i.e. $s_2 = 7.124 + 0.039 = 7.163 \text{ kJ/kg K}$

Then we have

$$\text{Heat supplied} = \text{shaded area} = T(s_2 - s_1)$$

$$= 584(7.163 - 5.615) = 584 \times 1.548$$

where $T = 311 + 273 = 584$ K.

i.e. Heat supplied = 904 kJ/kg

To find the work done it is necessary to apply the non-flow energy equation,

i.e. $Q + W = u_2 - u_1 \quad \text{or} \quad W = (u_2 - u_1) - Q$

From tables, at 100 bar, dry saturated,

$$u_1 = u_g = 2545 \text{ kJ/kg}$$

At 10 bar and 311 °C, interpolating,

$$u_2 = 2794 + \left(\frac{311 - 300}{350 - 300}\right)(2875 - 2794) = 2794 + 17.8$$

i.e. $u_2 = 2811.8 \text{ kJ/kg}$

Then

$$W = (u_2 - u_1) - Q$$
$$= (2811.8 - 2545) - 904 = 266.8 - 904 = -637.2 \text{ kJ/kg}$$

i.e. Work done *by* the steam = 637.2 kJ/kg

A reversible isothermal process for a perfect gas is shown on a *T–s* diagram in Fig. 4.16. The shaded area represents the heat supplied during the process,

i.e. $Q = T(s_2 - s_1)$

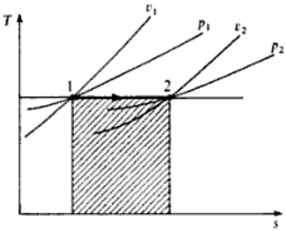


Fig. 4.16 Reversible isothermal process for a perfect gas

For a perfect gas undergoing an isothermal process it is possible to evaluate $s_2 - s_1$. From the non-flow equation (1.6) we have, for a reversible process,

$$dQ = du + p\,dv$$

Also for a perfect gas from Joule's law $du = c_v\,dT$,

i.e. $dQ = c_v\,dT + p\,dv$

For an isothermal process, $dT = 0$, hence

$$dQ = p\,dv$$

Then, since $pv = RT$, we have

$$dQ = RT\frac{dv}{v}$$

Now from equation (4.8)

$$s_2 - s_1 = \int_1^2 \frac{dQ}{T} = \int_{v_1}^{v_2} \frac{RT\,dv}{Tv} = R\int_{v_1}^{v_2} \frac{dv}{v}$$

i.e. $$s_2 - s_1 = R\ln\left(\frac{v_2}{v_1}\right) = R\ln\left(\frac{p_1}{p_2}\right) \quad (4.13)$$

Therefore the heat supplied is given by

$$Q = T(s_2 - s_1) = RT\ln\left(\frac{v_2}{v_1}\right) = RT\ln\left(\frac{p_1}{p_2}\right)$$

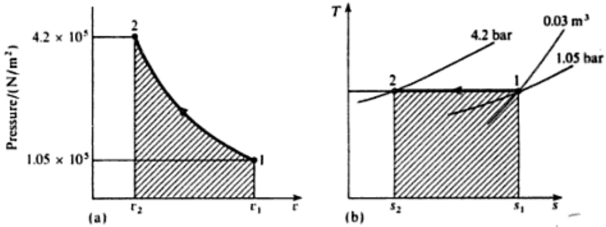
Note that this result is the same as that derived in section 3.1,

i.e. $$Q = -W = RT\ln\left(\frac{p_1}{p_2}\right) = p_1 v_1 \ln\left(\frac{p_1}{p_2}\right)$$

Example 4.5 0.03 m³ of nitrogen (molar mass 28 kg/kmol) contained in a cylinder behind a piston is initially at 1.05 bar and 15 °C. The gas is compressed isothermally and reversibly until the pressure is 4.2 bar. Calculate the change of entropy, the heat flow, and the work done, and sketch the process on a p–v and T–s diagram. Assume nitrogen to act as a perfect gas.

Solution The process is shown on a p–v and a T–s diagram in Figs 4.17(a) and 4.17(b) respectively. The shaded area on Fig. 4.17(a) represents work input, and the shaded area on Fig. 4.17(b) represents heat rejected.

Fig. 4.17 Processes for Example 4.5 on p–v and T–s diagrams



From equation (4.13)

$$s_2 - s_1 = R\ln\left(\frac{p_1}{p_2}\right) = \frac{297}{10^3}\ln\left(\frac{1.05}{4.2}\right)$$

i.e. $$s_2 - s_1 = -\frac{297}{10^3}\ln\left(\frac{4.2}{1.05}\right) = -0.4117\ \text{kJ/kg K}$$

From equation (2.9)

$$R = \frac{\tilde{R}}{\tilde{m}} = \frac{8314.5}{28} = 297\ \text{N m/kg K}$$

Then, since $pV = mRT$, we have

$$m = \frac{pV}{RT} = \frac{1.05 \times 10^5 \times 0.03}{297 \times 288} = 0.0368\ \text{kg}$$

where $T = 15 + 273 = 288$ K.

Then $$S_1 - S_2 = m(s_1 - s_2)$$

$$= 0.0368 \times 0.4117 = 0.01516\ \text{kJ/K}$$

$$\text{Heat rejected} = m\,(\text{shaded area on Fig. 4.17(b)}) = mT(s_1 - s_2)$$

$$= 0.01516 \times 288 = 4.37\ \text{kJ}$$

i.e. $Q = -4.37$ kJ

Then for an isothermal process for a perfect gas, from equation (3.12),

$$Q + W = 0$$

$$-4.37 + W = 0$$

i.e. Work input, $W = 4.37$ kJ

Reversible adiabatic process (or isentropic process)

For a reversible adiabatic process the entropy remains constant, and hence the process is called an *isentropic process.* Note that for a process to be isentropic it need not be either adiabatic or reversible, but the process will always appear as a vertical line on a *T–s* diagram. Cases in which an isentropic process is not both adiabatic and reversible occur infrequently and will be ignored throughout this book.

An isentropic process for superheated steam expanding into the wet region is shown in Fig. 4.18. When the reversible adiabatic process was considered in section 3.1, it was stated that no simple method was available for fixing the end states. Now, using the fact that the entropy remains constant, the end states can be found easily from tables. This is illustrated in the following example.

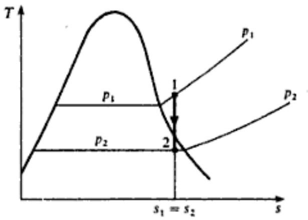


Fig. 4.18 Isentropic process for steam on a *T–s* diagram

Example 4.6 Steam at 100 bar, 375 °C expands isentropically in a cylinder behind a piston to a pressure of 10 bar. Calculate the work done per kilogram of steam.

Solution From superheat tables, at 100 bar, 375 °C, we have

$$s_1 = s_2 = 6.091\ \text{kJ/kg K}$$

At 10 bar and $s_2 = 6.091$, the steam is wet, since s_2 is less than s_{g_2}. Then from equation (4.12)

$$x_2 = \frac{s_2 - s_{f_2}}{s_{fg_2}} = \frac{6.091 - 2.138}{4.448} = 0.889$$

Then from equation (2.3)

$$u_1 = (1 - x_2)u_{f_2} + x_2 u_{g_2} = (0.111 \times 762) + (0.889 \times 2584)$$

i.e. $$u_2 = 84.6 + 2297 = 2381.6 \text{ kJ/kg}$$

At 100 bar, 375 °C, we have from tables, $h_1 = 3017$ kJ/kg and $v_1 = 0.024\,53$ m^3/kg. Then using equation (1.9)

$$u_1 = h_1 - p_1 v_1 = 3017 - \frac{100 \times 10^5 \times 0.024\,53}{10^3} = 3017 - 245.3$$

i.e. $$u_1 = 2771.7 \text{ kJ/kg}$$

For an adiabatic process from equation (3.13),

$$W = u_2 - u_1$$

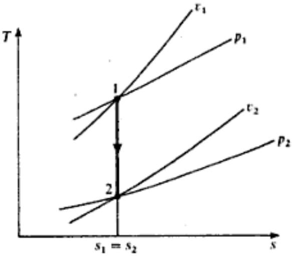
therefore,

$$W = 2381.6 - 2771.7$$
$$= -390.1 \text{ kJ/kg}$$

i.e. Work done *by* the steam = 390.1 kJ/kg

For a perfect gas an isentropic process on a T–s diagram is shown in Fig. 4.19. It is shown in section 3.1 that for a reversible adiabatic process for a perfect gas the process follows a law pv^γ = constant. Since a reversible adiabatic process occurs at constant entropy and is known as an isentropic process, the index γ is known as the *isentropic index* of the gas.

Fig. 4.19 Isentropic process for a perfect gas on a T–s diagram



Polytropic process

To find the change of entropy in a polytropic process for a vapour when the end states have been fixed using $p_1 v_1^n = p_2 v_2^n$, the entropy values at the end states can be read straight from tables.

Example 4.7 In a reciprocating compressor of a refrigeration plant the refrigerant is dry saturated at 2.01 bar at the beginning of compression and is compressed reversibly according to a polytropic law $pv^{1.1}$ = constant to a pressure of 10 bar. Calculate the change of specific entropy during the process using the table of properties of refrigerant given in Table 4.1, interpolating where necessary.

Table 4.1 Properties of refrigerant for Example 4.7

Saturation values			Superheated values at 10 bar	
p_g	v_g	s_g	v	s
(bar)	(m³/kg)	(kJ/kg K)	(m³/kg)	(kJ/kg K)
2.01	0.0978	1.7189	0.0222	1.7564
10	0.0202	1.7033	0.0233	1.7847

Solution From Table 4.1,

$$s_1 = s_{g_1} = 1.7189 \text{ kJ/kg K}$$

and $$v_1 = v_{g_1} = 0.0978 \text{ m}^3\text{/kg}$$

Then,

$$v_2 = v_1\left(\frac{p_1}{p_2}\right)^{1/1.1} = 0.0978\left(\frac{2.01}{10}\right)^{1/1.1}$$

$$= 0.0228 \text{ m}^3\text{/kg}$$

At 10 bar and a specific volume of 0.0228 m³/kg the steam is superheated. The process is shown in Fig. 4.20.

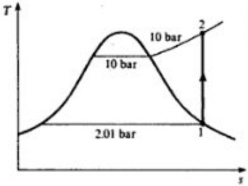


Fig. 4.20 Isentropic compression process for Example 4.7

Interpolating from the superheat tables of Table 4.1,

$$s_2 = 1.7564 + \frac{(0.0228 - 0.0222)}{(0.0233 - 0.0222)} \times (1.7847 - 1.7564)$$

$$= 1.7704 \text{ kJ/kg K}$$

Increase of entropy = 1.7704 − 1.7189 = 0.0515 kJ/kg K

It was shown in section 3.1 that the polytropic process is the general case for a perfect gas. To find the entropy change for a perfect gas in the general case, consider the non-flow energy equation for a reversible process equation (1.6),

$$dQ = du + p\,dv$$

Also for unit mass of a perfect gas from Joule's law $du = c_v\,dT$, and from equation (2.5), $pv = RT$. Therefore

$$dQ = c_v\,RT + \frac{RT\,dv}{v}$$

Then from equation (4.7)

$$ds = \frac{dQ}{T} = \frac{c_v\,dT}{T} + \frac{R\,dv}{v}$$

Hence between any two states 1 and 2

$$s_2 - s_1 = c_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v} = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) \qquad (4.14)$$

This can be illustrated on a T–s diagram as in Fig. 4.21. Since in the process in Fig. 4.21, $T_2 < T_1$, then it is more convenient to write

$$s_2 - s_1 = R \ln\left(\frac{v_2}{v_1}\right) - c_v \ln\left(\frac{T_1}{T_2}\right) \qquad (4.15)$$

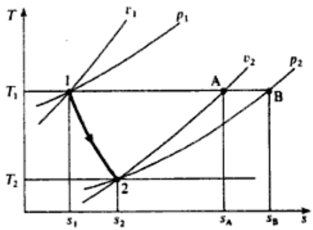


Fig. 4.21 Polytropic process for a perfect gas on a T–s diagram

The first part of the expression for $s_2 - s_1$ in equation (4.15) is the change of entropy in an isothermal process from v_1 to v_2, i.e. from equation (4.13)

$$s_A - s_1 = R \ln\left(\frac{v_2}{v_1}\right) \quad \text{(see Fig. 4.21)}$$

Also the second part of the expression for $s_2 - s_1$ in equation (4.15) is the change of entropy in a constant volume process from T_1 to T_2, i.e. referring to Fig. 4.21,

$$s_A - s_2 = c_v \ln\left(\frac{T_1}{T_2}\right)$$

It can be seen therefore that in calculating the entropy change in a polytropic process from state 1 to state 2 we have in effect replaced the process by two simpler processes: from 1 to A and then from A to 2. It is clear from Fig. 4.21 that

$$s_2 - s_1 = (s_A - s_1) - (s_A - s_2)$$

Any two processes can be chosen to replace a polytropic process in order to find the entropy change. For example, going from 1 to B and then from B to 2 as in Fig. 4.21, we have

$$s_2 - s_1 = (s_B - s_1) - (s_B - s_2)$$

At constant temperature between p_1 and p_2, using equation (4.13),

$$s_B - s_1 = R\ln\left(\frac{p_1}{p_2}\right)$$

and at constant pressure between T_1 and T_2 we have

$$s_B - s_2 = c_p\ln\left(\frac{T_1}{T_2}\right)$$

Hence,

$$s_2 - s_1 = R\ln\left(\frac{p_1}{p_2}\right) - c_p\ln\left(\frac{T_1}{T_2}\right)$$

or

$$s_2 - s_1 = c_p\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{p_1}{p_2}\right) \qquad (4.16)$$

Equation (4.16) can also be derived easily from equation (4.14).

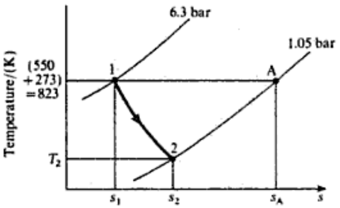
There are obviously a large number of possible equations for the change of entropy in a polytropic process. Each problem can be dealt with by sketching the *T–s* diagram and replacing the process by two other simpler reversible processes, as in Fig. 4.21.

Example 4.8 Calculate the change of entropy of 1 kg of air expanding polytropically in a cylinder behind a piston from 6.3 bar and 550 °C to 1.05 bar. The index of expansion is 1.3.

Solution The process is shown on a *T–s* diagram in Fig. 4.22. From equation 3.29,

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(n-1)/n} = \left(\frac{6.3}{1.05}\right)^{(1.3-1)/1.3} = 1.512$$

Fig. 4.22 Process for Example 4.8 on a *T–s* diagram



therefore

$$T_2 = \frac{823}{1.512} = 544\ \text{K}$$

where $T_1 = 550 + 273 = 823$ K.

Now replace the process 1 to 2 by two processes, 1 to A and A to 2. Then at constant temperature from 1 to A, from equation (4.13)

$$s_A - s_1 = R\ ln\left(\frac{p_1}{p_2}\right) = 0.287\ \ln\left(\frac{6.3}{1.05}\right)$$
$$= 0.514\ \text{kJ/kg K}$$

At constant pressure from A to 2

$$s_A - s_2 = c_p \ln\left(\frac{T_1}{T_2}\right) = 1.005 \ln\left(\frac{823}{544}\right)$$
$$= 0.416$$

Then $\quad s_2 - s_1 = 0.514 - 0.416 = 0.098$ kJ/kg K

i.e. $\quad$ Increase in entropy = 0.098 kJ/kg K

Note that if in Example 4.8 $s_A - s_2$ happened to be greater than $s_A - s_1$, this would mean that s_1 was greater than s_2, and the process should appear as in Fig. 4.23.

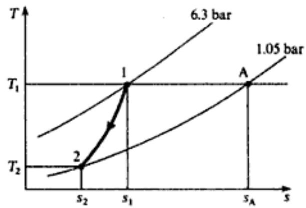


Fig. 4.23 Alternative T–s diagram for Example 4.8

Example 4.9 0.05 kg of carbon dioxide (molar mass 44 kg/kmol) is compressed from 1 bar, 15 °C, until the pressure is 8.3 bar, and the volume is then 0.004 m³. Calculate the change of entropy. Take c_p for carbon dioxide as 0.88 kJ/kg K, and assume carbon dioxide to be a perfect gas.

Solution The two end states are marked on a T–s diagram in Fig. 4.24. The process is not specified in the example and no information about it is necessary. States 1 and 2 are fixed and hence $s_2 - s_1$ is fixed. The process between 1 and 2 could be reversible or irreversible; the change of entropy is the same between the end states given. With reference to Fig. 4.24, to find $s_1 - s_2$ we can first find $s_A - s_2$ and then subtract $s_A - s_1$. First of all it is necessary to find R and then T_2.

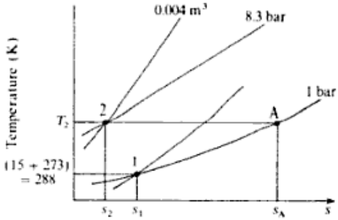


Fig. 4.24 T–s diagram for Example 4.9

From equation (2.9)

$$R = \frac{\tilde{R}}{\tilde{m}} = \frac{8314.5}{44} = 189 \text{ N m/kg K}$$

From equation (2.6), $pV = mRT$, therefore,

$$T_2 = \frac{p_2 V_2}{mR} = \frac{8.3 \times 10^5 \times 0.004}{0.05 \times 189} = 351 \text{ K}$$

Then from equation (4.13)

$$s_A - s_2 = R \ln\left(\frac{p_2}{p_A}\right) = 0.189 \ln\left(\frac{8.3}{1}\right) = 0.4 \text{ kJ/kg K}$$

Also at constant pressure from 1 to A

$$s_A - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) = 0.88 \ln\left(\frac{351}{288}\right) = 0.174 \text{ kJ/kg K}$$

where $T_1 = 15 + 273 = 288$ K. Then

$$s_1 - s_2 = 0.4 - 0.174 = 0.226 \text{ kJ/kg K}$$

Hence for 0.05 kg of carbon dioxide

$$\text{Decrease in entropy} = 0.05 \times 0.226 = 0.0113 \text{ kJ/K}$$

4.5 Entropy and irreversibility

In section 4.4 it is pointed out that, since entropy is a property, the change of entropy depends only on the end states and not on the process between the end states. Therefore, provided an irreversible process gives enough information to fix the end states then the change of entropy can be found. This can best be illustrated by some examples.

Example 4.10 Steam at 7 bar, dryness fraction 0.96, is throttled down to 3.5 bar. Calculate the change of entropy per unit mass of steam.

Solution At 7 bar, dryness fraction 0.96, using equation (4.11) we have

$$s_1 = s_{f_1} + x_1 s_{fg_1} = 1.992 + (0.96 \times 4.717)$$

i.e. $s_1 = 6.522$ kJ/kg K

In section 3.4 it is shown that for a throttling process, $h_1 = h_2$. From equation (2.2)

$$h_2 = h_1 = h_{f_1} + x_1 h_{fg_1} = 697 + (0.96 \times 2067) = 2682 \text{ kJ/kg}$$

At 3.5 bar and $h_2 = 2682$ kJ/kg the steam is still wet, since $h_{g_2} > h_2$. From equation (2.2), $h_2 = h_{f_2} + x_2 h_{fg_2}$, therefore

$$x_2 = \frac{h_2 - h_{f_2}}{h_{fg_2}} = \frac{2682 - 584}{2148} = 0.977$$

Then from equation (4.11)

$$s_2 = s_{f_2} + x_2 s_{fg_2} = 1.727 + (0.977 \times 5.214) = 6.817 \text{ kJ/kg K}$$

Therefore,

$$\text{Increase of entropy} = 6.817 - 6.522 = 0.295 \text{ kJ/kg K}$$

The process is shown on a T–s diagram in Fig. 4.25. Note that the process is shown dotted, and the area under the line does not represent heat flow; a throttling process assumes no heat flow, but there is a change in entropy because the process is irreversible.

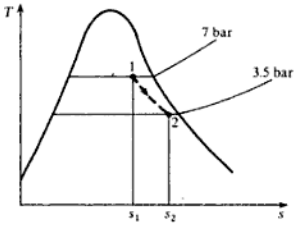


Fig. 4.25 Throttling process for Example 4.10 on a T–s diagram

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Example 4.11 Two vessels of equal volume are connected by a short length of pipe containing a valve; both vessels are well lagged. One vessel contains air and the other is completely evacuated. Calculate the change of entropy per kg of air in the system when the valve is opened and the air is allowed to fill both vessels.

Solution Initially the vessel A contains air and the vessel B is completely evacuated, as in Fig. 4.26; finally the air occupies both vessels A and B. In section 3.4 it was shown that in an unresisted expansion for a perfect gas, the initial and final temperatures are equal. In this case the initial volume is V_A and the final volume

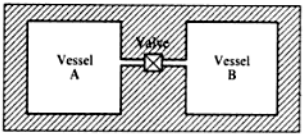


Fig. 4.26 Two well-lagged interconnected vessels for Example 4.11

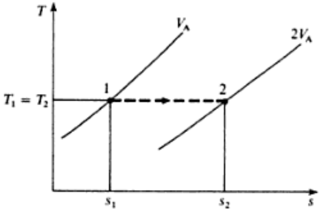


Fig. 4.27 Process on a T–s diagram for Example 4.11

is $V_A + V_B = 2V_A$. The end states can be marked on a T–s diagram as shown in Fig. 4.27. The process 1 to 2 is irreversible and must be drawn dotted. The change of entropy is $s_2 - s_1$, regardless of the path of the process between states 1 and 2. Hence, for the purpose of calculating the change of entropy, imagine the process replaced by a reversible isothermal process between states 1 and 2. Then from equation (4.13)

$$(s_2 - s_1) = R \ln\left(\frac{V_2}{V_1}\right) = 0.287 \ln\left(\frac{2V_A}{V_A}\right)$$

$$= 0.287 \ln 2 = 0.199 \text{ kJ/kg K}$$

i.e. Increase of entropy = 0.199 kJ/kg K

Note that the process is drawn dotted in Fig. 4.27, and the area under the line has no significance; the process is adiabatic and there is a change in entropy since the process is irreversible.

It is important to remember that the equation (4.7), $ds = dQ/T$, is true only for reversible processes. In the same way the equation $dW = -p\,dv$ is true only for reversible processes. In Example 4.11 the volume of the air increased from V_A to $2V_A$, and yet no work was done by the air during the process,

i.e. $dW = 0$ yet $V_2 - V_1 = 2V_A - V_A = V_A$

Similarly, the entropy in Example 4.11 increased by 0.199 kJ/kg K and yet the heat flow was zero, i.e. $ds \neq dQ/T$. No confusion should be caused if the T–s and/or the p–v diagram is drawn for each problem and the state points marked in their correct positions. Then, when a process between two states is reversible, the lines representing the process can be drawn in as full lines, and the area under the line represents heat flow on the T–s diagram and work done on the p–v diagram. When the process between the states is irreversible the line must be drawn dotted, and the area under the line has no significance on either diagram.

It can be shown from the second law that the entropy of a thermally isolated system must either increase or remain the same. For instance, a system undergoing an adiabatic process is thermally isolated from its surroundings since no heat flows to or from the system. We have seen that in a reversible adiabatic process the entropy remains the same. In an irreversible adiabatic process the entropy must always increase, and the gain of entropy is a measure of the irreversibility of the process. The processes in Examples 4.10 and 4.11 illustrate this fact. As another example, consider an irreversible adiabatic expansion in a steam turbine as shown in Fig. 4.28 as process 1 to 2. A reversible adiabatic process between the same pressures is represented by 1 to 2*s* in Fig. 4.28. The increase of entropy, $s_2 - s_1 = s_2 - s_{2s}$, is a measure of the irreversibility of the process. Similarly, in Fig. 4.29, an irreversible adiabatic compression in a rotary compressor is shown as process 1 to 2. A reversible adiabatic process between the same pressures is represented by 1 to 2*s*. As before, the increase of entropy shows the irreversibility of the process.

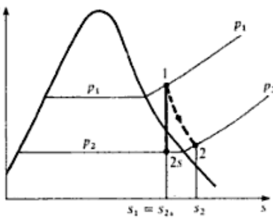


Fig. 4.28 Irreversible adiabatic process for steam on a T–s diagram

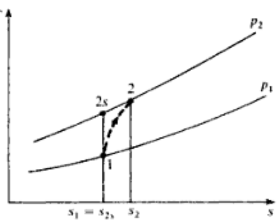


Fig. 4.29 Irreversible adiabatic compression for a perfect gas on a T–s diagram

Example 4.12 In an air turbine the air expands from 6.8 bar and 430 °C to 1.013 bar and 150 °C. The heat loss from the turbine can be assumed to be negligible. Show that the process is irreversible, and calculate the change of entropy per kilogram of air.

Solution Since the heat loss is negligible the process is adiabatic. For a reversible adiabatic process for a perfect gas, using equation (3.21),

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma}$$

i.e.
$$\frac{703}{T_2} = \left(\frac{6.8}{1.013}\right)^{(1.4-1)/1.4}$$

where $T_1 = 430 + 273 = 703$ K,

$$T_2 = \frac{703}{1.723} = 408\text{ K} = 408 - 273 = 135\,°\text{C}$$

But the actual temperature is 150 °C at the pressure of 1.013 bar, hence the process is irreversible. The process is shown as 1 to 2 in Fig. 4.30; the ideal isentropic process 1 to 2s is also shown. It is not possible for process 1 to 2 to be reversible, because in that case the area under line 1–2 would represent heat flow and yet the process is adiabatic.

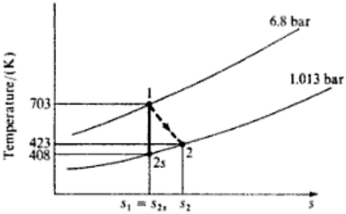


Fig. 4.30 *T–s* diagram for Example 4.12

The change of entropy, $s_2 - s_1$, can be found by considering a reversible constant pressure process between 2s and 2. Then from equation (4.7), $ds = dQ/T$, and at constant pressure for 1 kg of a perfect gas we have $dQ = c_p\,dT$ therefore

$$s_2 - s_{2s} = \int_{2s}^{2} \frac{c_p\,dT}{T} = c_p \ln\left(\frac{T_2}{T_{2s}}\right)$$

$$= 1.005 \ln\left(\frac{423}{408}\right) = 0.0363\text{ kJ/kg K}$$

i.e. Increase of entropy, $s_2 - s_1 = 0.0363$ kJ/kg K

Consider now the case when a system is not thermally isolated from its surroundings. The entropy of such a system can increase, decrease, or remain the same, depending on the heat crossing the boundary. However, if the boundary is extended to include the source or sink of heat with which the system is in communication, then the entropy of this new system must either increase or remain the same. To illustrate this, consider a hot reservoir at T_1 and a cold

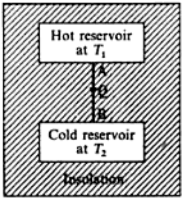


Fig. 4.31 Two thermally-insulated interconnected reservoirs of energy

reservoir at T_2, and assume that the two reservoirs are thermally insulated from the surroundings as in Fig. 4.31. Let the heat flow from the hot to the cold reservoir be Q. There is a continuous temperature gradient from T_1 to T_2 between points A and B, and it can be assumed that heat is transferred reversible from the hot reservoir to point A, and from point B to the cold reservoir. It will be assumed that the reservoirs are such that the temperature of each remains constant. Then we have

$$\text{Heat supplied to cold reservoir} = +Q$$

Hence from equation (4.8)

$$\text{Increase of entropy of cold reservoir} = +\frac{Q}{T_2}$$

Also,

$$\text{Heat supplied to hot reservoir} = -Q$$

therefore

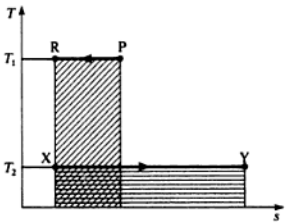
$$\text{Increase of entropy of hot reservoir} = -\frac{Q}{T_1}$$

i.e. $$\text{Net increase of entropy of system, } \Delta s = \left(\frac{Q}{T_2} - \frac{Q}{T_1}\right)$$

Since $T_1 > T_2$ it can be seen that Δs is positive, and hence the entropy of the system must increase. In the limit, when the difference in temperature is infinitely small, then $\Delta s = 0$. This confirms the principle that the entropy of an isolated system must either increase or remain the same. In section 1.4, criterion (c) for reversibility was stated as follows: the difference in temperature between a system and its surroundings must be infinitely small during a reversible process.

In the above example, when $T_1 > T_2$, then the heat flow between the reservoirs is irreversible by the above criterion. Thus the entropy of the system increases when the heat flow process is irreversible, but remains the same when the process is reversible. The increase of entropy is a measure of the irreversibility. The processes occurring in the above example can be drawn on a T–s diagram as in Fig. 4.32. The two processes have been superimposed on the same diagram. Process P–R represents the transfer of Q units of heat from the hot reservoir,

Fig. 4.32 Processes for the hot and cold reservoirs on a T–s diagram



and the area under P–R is equal to Q. Process X–Y represents the transfer of Q units of heat to the cold reservoir, and the area under X–Y is equal to Q. The area under P–R is equal to the area under X–Y, and hence it can be seen from the diagram that the entropy of the cold reservoir must always increase more than the entropy of the hot reservoir decreases. Thus the entropy of the combined system must increase. Note that, since in this example both processes P–R and X–Y are reversible, then the irreversibility occurs between A and B on Fig. 4.31. That is, the irreversibility is caused by the heat transfer process between A and B. Whenever heat is transferred through a finite temperature difference the process is irreversible and there is an increase of entropy of the system and its surroundings.

In certain processes the irreversibility may occur in the surroundings, then the process is internally reversible, and areas on the p–v and T–s diagrams relate closely to the work and heat respectively as before. Internal reversibility was mentioned earlier in section 1.5. In most problems when a process is assumed to be reversible it is internal reversibility which is implied. Conversely, most processes in practice which are said to be irreversible are internally irreversible due to eddying and churning of the working fluid, as in Example 4.13.

Referring to Fig. 4.31, if a heat engine were interposed between the hot and cold reservoirs, some work could be developed. The second law states that heat can never flow unaided from a cold reservoir to a hot reservoir, therefore in order to develop work from the quantity of energy, Q, after it has been transferred to the cold reservoir, it would be necessary to have a third reservoir at lower temperature than the cold reservoir. It is clear that when a quantity of heat is transferred through a finite temperature difference, its usefulness becomes less, and in the limit when the heat has been transferred to the lowest existing temperature reservoir then no more work can be developed. Irreversibility therefore has a degrading effect on the energy available, and entropy can be considered as a measure not only of irreversibility but also of the degradation of energy. Note that, by the principle of conservation of energy, no energy can be destroyed; by the Second Law of Thermodynamics, energy can only become less useful and never more useful. Systems tend naturally to states of lower grade energy; any system moving to a state of higher-grade energy without an external supply of energy would be violating the second law. The second law can be seen to imply a direction or a gradient of usefulness of energy. Work is more useful than heat; the higher the temperature of a reservoir of energy the more useful is the amount of energy available. Applying this latter conclusion to a heat engine it can be deduced that, for a given cold reservoir (e.g. the atmosphere), then the higher the temperature of the hot reservoir, the higher will be the thermal efficiency of the heat engine. This will be discussed more fully in Chapter 5.

4.6 Exergy

The theoretical maximum amount of work that can be obtained from a system at any state p_1 and T_1 when operating with a reservoir at the constant pressure and temperature p_0 and T_0 is called the *exergy* or *availability*.

Non-flow systems

Consider a system consisting of a fluid in a cylinder behind a piston, the fluid expanding reversibly from initial conditions of p_1 and T_1 to final atmospheric conditions of p_0 and T_0. Imagine also that the system works in conjunction with a reversible heat engine which receives heat reversibly from the fluid in the cylinder such that the working substance of the heat engine follows the cycle 01A0 as shown in Figs 4.33(a) and 4.33(b), where $s_1 = s_A$ and $T_0 = T_A$.

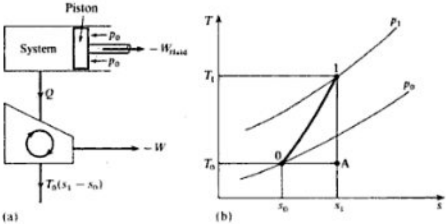


Fig. 4.33 Illustration of the exergy of a system

Note: The only possible way in which this could occur would be if an infinite number of reversible heat engines were arranged in parallel, each operating on a Carnot cycle (see Ch. 5), each one receiving heat at a different constant temperature and each one rejecting heat at T_0. The work done *by* this engine is given by

$$-W = \sum Q$$

therefore

$$-W = Q - T_0(s_1 - s_0)$$

The heat supplied to the engine is equal to the heat rejected by the fluid in the cylinder. Therefore for the fluid in the cylinder undergoing the process 1 to 0, we have

$$-Q + W_{fluid} = u_0 - u_1$$

i.e. $$W_{fluid} = (u_0 - u_1) + Q$$

Therefore the total work output is given by

$$-W_{fluid} - W = -(u_0 - u_1) - Q + Q - T_0(s_1 - s_0)$$
$$= (u_1 - u_0) - T_0(s_1 - s_0)$$

The work done by the fluid on the piston is less than the total work done by the fluid, $-W_{fluid}$, since there is work done on the atmosphere which is at the constant pressure p_0 (see Problem 3.24). That is

Work done by fluid on atmosphere, $-W_{atm} = p_0(v_0 - v_1)$

Note: when a fluid undergoes a complete cycle then the net work done on or by the atmosphere is zero. Hence

$$\begin{aligned}\text{Maximum work available} &= \text{Work done by fluid on piston} \\ &\quad + \text{Work done by engine} \\ &= -W_{\text{fluid}} + W_{\text{atm}} - W \\ &= (u_1 - u_0) - T_0(s_1 - s_0) - p_0(v_0 - v_1) \\ &= (u_1 + p_0 v_1 - T_0 s_1) - (u_0 + p_0 v_0 - T_0 s_0) \\ &= a_1 - a_0\end{aligned}$$

The property $a = u + p_0 v - T_0 s$ is called the *specific non-flow exergy.*

Steady-flow systems

Let fluid flow steadily with a velocity C_1 from a reservoir in which the pressure and temperature remain constant at p_1 and T_1 through an apparatus to atmospheric pressure of p_0. Let the reservoir be at a height Z_1 from the datum, which can be taken at exit from the apparatus, i.e. $Z_0 = 0$. For a maximum work output to be obtained from the apparatus the exit velocity, C_0, must be zero. It can be shown as for non-flow systems above that a reversible heat engine working between the limits would reject $T_0(s_1 - s_0)$ units of heat, where T_0 is the atmospheric temperature.

Therefore we have

$$\text{Specific exergy} = (h_1 + C_1^2/2 + Z_1 g) - h_0 - T_0(s_1 - s_0)$$

In many thermodynamic systems the kinetic and potential energy terms are negligible,

i.e. $$\text{Specific exergy} = (h_1 - T_0 s_1) - (h_0 - T_0 s_0) = b_1 - b_0$$

Effectiveness

Instead of comparing a process to some imaginary ideal process, as is done in the case of isentropic efficiency for instance (see p. 238), it is a better measure of the usefulness of the process to compare the useful output of the process with the loss of exergy of the system. The useful output of a system is given by the increase of exergy of the surroundings,

i.e. $$\text{Effectiveness, } \varepsilon = \frac{\text{increase of exergy of surroundings}}{\text{loss of exergy of the system}} \tag{4.17}$$

For a compression or heating process the effectiveness becomes

$$\varepsilon = \frac{\text{increase of exergy of the system}}{\text{loss of exergy of the surroundings}}$$

Example 4.13 Steam expands adiabatically in a turbine from 20 bar, 400 °C to 4 bar, 250 °C. Calculate:

(i) the isentropic efficiency of the process;
(ii) the loss of exergy of the system assuming an atmospheric temperature of 15 °C;
(iii) the effectiveness of the process.

Neglect changes in kinetic and potential energy.

Solution (i) Initially the steam is superheated at 20 bar and 400 °C, hence from tables,

$$h_1 = 3248 \text{ kJ/kg} \quad \text{and} \quad s_1 = 7.126 \text{ kJ/kg K}$$

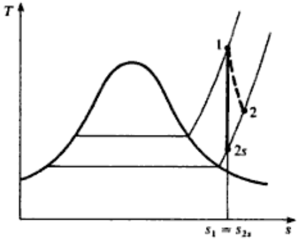
Finally the steam is superheated at 4 bar and 250 °C, hence from tables

$$h_2 = 2965 \text{ kJ/kg} \quad \text{and} \quad s_2 = 7.379 \text{ kJ/kg K}$$

The process is shown as 1 to 2 in Fig. 4.34

$$s_1 = s_{2s} = 7.126 \text{ kJ/kg K}$$

Fig. 4.34 T–s diagram for Example 4.13



Hence interpolating

$$h_{2s} = 2753 + \left(\frac{7.126 - 6.929}{7.172 - 6.929}\right)(2862 - 2753)$$

$$= 2841.4 \text{ kJ/kg}$$

$$\text{Isentropic efficiency} = \frac{\text{actual work output}}{\text{isentropic work}}$$

$$= \frac{h_1 - h_2}{h_1 - h_{2s}} = \frac{3248 - 2965}{3248 - 2841.4} = \frac{283}{406.6} = 69.6\%$$

(ii) $\text{Loss of exergy} = b_1 - b_2 = h_1 - h_2 + T_0(s_2 - s_1)$

$$= 283 + 288(7.379 - 7.126)$$

$$= 355.9 \text{ kJ/kg}$$

(iii) Effectiveness, $\varepsilon = \dfrac{-W}{b_1 - b_2} = \dfrac{h_1 - h_2}{b_1 - b_2}$

i.e.
$$\varepsilon = \frac{283}{355.9} = 79.6\%$$

Note: the effectiveness is greater than the isentropic efficiency; this is because the steam at state 2 has a higher exergy than that at state 2*s* due to the heating effect of the irreversibilities in the expansion process.

Example 4.14 Air at 15 °C is to be heated to 40 °C by mixing it in steady flow with a quantity of air at 90 °C. Assuming that the mixing process is adiabatic and neglecting changes in kinetic and potential energy, calculate the ratio of the mass flow of air initially at 90 °C to that initially at 15 °C. Calculate also the effectiveness of the heating process if the atmospheric temperature is 15 °C.

Solution Let the ratio of mass flows required be y; let the air at 15 °C be stream 1, the air at 90 °C be stream 2, and the mixed airstream at 40 °C be stream 3.

Then $\quad c_pT_1 + yc_pT_2 = (1 + y)c_pT_3$

or $\quad yc_p(T_2 - T_3) = c_p(T_3 - T_1)$

i.e. $\quad y(90 - 40) = 40 - 15$

therefore

$$y = \frac{25}{50} = 0.5$$

Let the system considered be a stream of air of unit mass, heated from 15 to 40 °C.

Increase of exergy of system per unit mass of air initially at 15 °C

$$= b_3 - b_1 = (h_3 - h_1) - T_0(s_3 - s_1)$$
$$= 1.005(40 - 15) - 288(s_3 - s_1)$$
$$s_3 - s_1 = c_p \ln\left(\frac{T_3}{T_1}\right) = 1.005 \ln\left(\frac{313}{288}\right) = 0.0831 \text{ kJ/kg K}$$

therefore

Increase of exergy of system per unit mass of air initially at 15 °C

$$= (1.005 \times 25) - (288 \times 0.0831)$$
$$= 1.195 \text{ kJ/kg}$$

The system, which is the air being heated, is 'surrounded' by the airstream being cooled. Therefore, the loss of exergy of the surroundings is given by $y(b_2 - b_3)$ per unit mass of air initially at 15 °C,
i.e.

Loss of exergy of surroundings per unit mass of air initially at 15 °C

$$= 0.5\{(h_2 - h_3) - T_0(s_2 - s_3)\}$$

$$= 0.5\left(1.005(90 - 40) - 288 \times 1.005 \ln\frac{363}{313}\right)$$

$$= 3.65\ \text{kJ/kg}$$

Therefore

$$\text{Effectiveness} = \frac{1.195}{3.65} = 0.327 \text{ or } 32.7\%$$

The low figure for the effectiveness is an indication of the highly irreversible nature of the mixing process.

Example 4.15 A liquid of specific heat 6.3 kJ/kg K is heated at approximately constant pressure from 15 to 70 °C by passing it through tubes which are immersed in a furnace. The furnace temperature is constant at 1400 °C. Calculate the effectiveness of the heating process when the atmospheric temperature is 10 °C.

Solution Increase of exergy of the liquid is

$$b_2 - b_1 = (h_2 - h_1) - T_0(s_2 - s_1)$$

i.e.

$$b_2 - b_1 = 6.3(70 - 15) - 283 \times 6.3 \ln\left(\frac{343}{288}\right)$$

$$= 34.7\ \text{kJ/kg}$$

Now the heat rejected by the furnace is equal to the heat supplied to the liquid $(h_2 - h_1)$. If this quantity of heat were supplied to a heat engine operating on the Carnot cycle its thermal efficiency would be

$$\left(1 - \frac{T_0}{1400 + 273}\right)$$

For the thermal efficiency of a Carnot cycle see p. 126. Therefore work which could be obtained from a heat engine is given by the product of the thermal efficiency and the heat supplied.

i.e.

$$\text{Possible work of a heat engine} = (h_2 - h_1)\left(1 - \frac{283}{1673}\right)$$

The possible work from a heat engine is a measure of the loss of exergy of the furnace. That is

$$\text{Loss of exergy of surroundings} = 6.3(70 - 15)\left(1 - \frac{283}{1673}\right)$$

$$= 288\ \text{kJ/kg}$$

Then Effectiveness $= \frac{34.7}{288} = 0.121$ or 12.1%

The very low value of effectiveness reflects the irreversibility of the transfer of heat through a large temperature difference. If the furnace temperature were much lower the process would be much more effective, although the heat transferred to the liquid would remain the same.

For further reading on this topic see ref. 4.2.

Problems

4.1 1 kg of steam at 20 bar, dryness fraction 0.9, is heated reversibly at constant pressure to a temperature of 300 °C. Calculate the heat supplied, and the change of entropy, and show the process on a T–s diagram, indicating the area which represents the heat flow.

(415 kJ/kg; 0.8173 kJ/kg K)

4.2 Steam at 0.05 bar, 100 °C is to be condensed completely by a reversible constant pressure process. Calculate the heat rejected per kilogram of steam, and the change of specific entropy. Sketch the process on a T–s diagram and shade in the area which represents the heat flow.

(2550 kJ/kg; 8.292 kJ/kg K)

4.3 0.05 kg of steam at 10 bar, dryness fraction 0.84, is heated reversibly in a rigid vessel until the pressure is 20 bar. Calculate the change of entropy and the heat supplied. Show the area which represents the heat supplied on a T–s diagram.

(0.0704 kJ/kg K; 36.85 kJ)

4.4 A rigid cylinder containing 0.006 m^3 of nitrogen (molar mass 28 kg/kmol) at 1.04 bar, 15 °C, is heated reversibly until the temperature is 90 °C. Calculate the change of entropy and the heat supplied. Sketch the process on a T–s diagram. Take the isentropic index, γ, for nitrogen as 1.4, and assume that nitrogen is a perfect gas.

(0.001 25 kJ/K; 0.407 kJ)

4.5 1 m^3 of air is heated reversibly at constant pressure from 15 to 300 °C, and is then cooled reversibly at constant volume back to the initial temperature. The initial pressure is 1.03 bar. Calculate the net heat flow and the overall change of entropy, and sketch the processes on a T–s diagram.

(101.5 kJ; 0.246 kJ/K)

4.6 1 kg of steam undergoes a reversible isothermal process from 20 bar and 250 °C to a pressure of 30 bar. Calculate the heat flow, stating whether it is supplied or rejected, and sketch the process on a T–s diagram.

(−135 kJ/kg)

4.7 1 kg of air is allowed to expand reversibly in a cylinder behind a piston in such a way that the temperature remains constant at 260 °C while the volume is doubled. The piston is then moved in, and heat is rejected by the air reversibly at constant pressure until the volume is the same as it was initially. Calculate the net heat flow and the overall change of entropy. Sketch the process on a T–s diagram.

(−161.9 kJ/kg; −0.497 kJ/kg K)

4.8 Steam at 5 bar, 25 °C, expands isentropically to a pressure of 0.7 bar. Calculate the final condition of the steam.

(0.967)

4.9 Steam expands reversibly in a cylinder behind a piston from 6 bar dry saturated, to a pressure of 0.65 bar. Assuming that the cylinder is perfectly thermally insulated, calculate the work done during the expansion per kilogram of steam. Sketch the process on a T–s diagram.

(323.8 kJ/kg)

4.10 1 kg of a fluid at 30 bar, 300 °C, expands reversibly and isothermally to a pressure of 0.75 bar. Calculate the heat flow and the work done (i) when the fluid is air, (ii) when the fluid is steam. Sketch each process on a T–s diagram.

(607 kJ/kg; − 607 kJ/kg; 1035 kJ/kg; − 975 kJ/kg)

4.11 1 kg of a fluid at 2.62 bar, −3 °C, is compressed according to a law pv = constant to a pressure of 8.2 bar. Calculate the work input and the heat supplied (i) when the fluid is air, (ii) when the fluid is a refrigerant initially dry saturated with the properties given in Table 4.2. Sketch each process on a T–s diagram.

(88.41 kJ/kg; −88.41 kJ/kg; 22.63 kJ/kg; −6.69 kJ/kg)

Table 4.2 Properties of refrigerant for Problem 4.11

Saturation values				
t_s (°C)	p_s (bar)	v_g (m³/kg)	h_f (kJ/kg)	h_g (kJ/kg)
−3.0	2.62	0.0757	96.07	292.94
32.3	8.20	0.0248	144.29	313.05

4.12 1 kg of air at 1.013 bar, 17 °C, is compressed according to a law $pv^{1.3}$ = constant, until the pressure is 5 bar. Calculate the change of entropy and sketch the process on a T–s diagram, indicating the area which represents the heat flow.

(−0.0885 kJ/kg)

4.13 0.06 m³ of ethane (molar mass 30 kg/kmol), at 6.9 bar and 260 °C, is allowed to expand isentropically in a cylinder behind a piston to a pressure of 1.05 bar and a temperature of 107 °C. Calculate γ, R, c_p, c_v, for ethane, and calculate the work done during the expansion. Assume ethane to be a perfect gas.

The same mass of ethane at 1.05 bar, 107 °C, is compressed to 6.9 bar according to a law $pv^{1.4}$ = constant. Calculate the final temperature of the ethane and the heat flow to or from the cylinder walls during the compression. Calculate also the change of entropy during the compression, and sketch both processes on a p–v and a T–s diagram.

(1.219; 0.277 kJ/kg K; 1.542 kJ/kg K; 1.265 kJ/kg K; 54.2 kJ; 377.7 °C; 43.4 kJ; 0.0862 kJ/K)

4.14 At the start of the compression process in the reciprocating compressor of a refrigeration plant the refrigerant is at 1.5 bar, dry saturated. At the end of the compression process, which is according to a reversible polytropic law $pv^{1.2}$ = constant, the pressure is 6.5 bar. Using the properties of refrigerant given as Table 4.3, interpolating where necessary, calculate:

(i) the change of specific entropy during the process;

(ii) the degree of superheat of the refrigerant after compression.

(0.06 kJ/kg K; 35 K)

Table 4.3 Properties of refrigerant for Problem 4.14

Saturation values				Superheated values at 6.5 bar		
t_g	p_g	v_g	s_g	t	v	s
(°C)	(bar)	(m³/kg)	(kJ/kg K)	(°C)	(m³/kg)	(kJ/kg K)
−20	1.5	0.109	1.12	50	0.030	1.15
25	6.5	0.027	1.11	70	0.034	1.21

4.15 A certain perfect gas for which $\gamma = 1.26$ and the molar mass is 26 kg/kmol, expands reversibly from 727 °C, 0.003 m³ to 2 °C, 0.6 m³, according to a linear law on the T–s diagram. Calculate the work done per kilogram of gas and sketch the process on a T–s diagram.

(− 959.3 kJ/kg)

4.16 1 kg of air at 1.02 bar, 20 °C, undergoes a process in which the pressure is raised to 6.12 bar, and the volume becomes 0.25 m³. Calculate the change of entropy and mark the initial and final states on a T–s diagram.

(0.083 kJ/kg K)

4.17 Steam at 15 bar is throttled to 1 bar and a temperature of 150 °C. Calculate the initial dryness fraction and the change of specific entropy. Sketch the process on a T–s diagram and state the assumptions made in the throttling process.

(0.992; 1.202 kJ/kg K)

4.18 Two vessels, one exactly twice the volume of the other, are connected by a valve and immersed in a constant temperature bath of water. The smaller vessel contains hydrogen (molar mass 2 kg/kmol), and the other is completely evacuated. Calculate the change of entropy per kilogram of gas when the valve is opened and conditions are allowed to settle. Sketch the process on a T–s diagram. Assume hydrogen to be a perfect gas.

(4.567 kJ/kg K)

4.19 A turbine is supplied with steam at 40 bar, 400 °C, which expands through the turbine in steady flow to an exit pressure of 0.2 bar, and a dryness fraction of 0.93. The inlet velocity is negligible, but the steam leaves at high velocity through a duct of 0.14 m² cross-sectional area. If the mass flow is 3 kg/s, and the mechanical efficiency is 90%, calculate the power output of the turbine. Show that the process is irreversible and calculate the change of specific entropy. Heat losses from the turbine are negligible.

(2048 kW; 0.643 kJ/kg K)

4.20 In a centrifugal compressor the air is compressed through a pressure ratio of 4 to 1, and the temperature of the air increases by a factor of 1.65. Show that the process is irreversible and calculate the change of entropy per kilogram of air. Assume that the process is adiabatic. Sketch the process on a T–s diagram.

(0.105 kJ/kg K)

4.21 In a gas turbine unit the gases enter the turbine at 550 °C and 5 bar and leave at 1 bar. The process is approximately adiabatic, but the entropy changes by 0.174 kJ/kg K. Calculate the exit temperature of the gases. Assume the gases to act as a perfect gas, and take $\gamma = 1.333$ and $c_p = 1.11$ kJ/kg K. Sketch the process on a T–s diagram.

(370.9 °C)

4.22 A rigid, well-lagged vessel of 0.3 m^3 capacity contains 0.7614 kg of steam at 6 bar. A valve is opened and the pressure falls to 1.4 bar before the valve is shut again. Calculate the condition of the steam remaining in the vessel, and the mass of steam which has escaped.

(0.989; 0.516 kg)

4.23 A rigid vessel contains 0.5 kg of a perfect gas of specific heat at constant volume 1.1 kJ/kg K. A stirring paddle is inserted into the vessel and 11 kJ of work are done on the paddle by the stirrer motor. Assuming that the vessel is well lagged and that the gas is initially at the temperature of the surroundings which are at 17 °C, calculate the effectiveness of the process.

(3.3%)

4.24 The identical vessel of Problem 4.23 is heated through the same temperature difference by immersing it in a furnace of constant temperature 100 °C. Calculate the effectiveness of the process.

(14.8%)

4.25 Steam enters a turbine at 70 bar, 500 °C and leaves at 2 bar in a dry saturated state. Calculate the isentropic efficiency and the effectiveness of the process. Neglect changes of kinetic and potential energy and assume that the process is adiabatic. The atmospheric temperature is 17 °C.

(84.4%; 88%)

4.26 In an open-type feed heater (see p. 249), steam enters at 15 bar, 200 °C. The feedwater enters the heater at 130 °C and leaves the heater at the saturation temperature corresponding to the pressure in the heater of 15 bar. Calculate the mass of steam entering per unit mass of feed water entering the heater.

Calculate also the loss of exergy of the steam per unit mass and the effectiveness of the heater. Assume that there is no heat loss from the heater and that the atmospheric temperature is 20 °C. State any other assumptions made.

(0.1536 kg; 734.9 kJ/kg; 88.1%)

References

4.1 ROGERS G F C and MAYHEW Y R 1992 *Engineering Thermodynamics, Work and Heat Transfer*, 4th edn Longman

4.2 HAYWOOD R W 1991 *Analysis of Engineering Cycles* Pergamon

5

The Heat Engine Cycle

In this chapter the heat engine cycle is discussed more fully and gas power cycles are considered. It can be shown that there is an ideal theoretical cycle which is the most efficient conceivable; this cycle is called the Carnot cycle. The highest thermal efficiency possible for a heat engine in practice is only about half that of the ideal theoretical Carnot cycle, between the same temperature limits. This is due to irreversibilities in the actual cycle, and to deviations from the ideal cycle, which are made for various practical reasons. The choice of a power plant in practice is a compromise between thermal efficiency and various factors such as the size of the plant for a given power requirement, mechanical complexity, operating cost, and capital cost.

5.1 The Carnot cycle

It can be shown from the Second Law of Thermodynamics that no heat engine can be more efficient than a reversible heat engine working between the same temperature limits (see ref. 5.1). Carnot showed that the most efficient possible cycle is one in which all the heat supplied is supplied at one fixed temperature, and all the heat rejected is rejected at a lower fixed temperature. The cycle therefore consists of two isothermal processes joined by two adiabatic processes. Since all processes are reversible, then the adiabatic processes in the cycle are also isentropic. The cycle is most conveniently represented on a T–s diagram as shown in Fig. 5.1.

Process 1 to 2 is isentropic expansion from T_1 to T_2.
Process 2 to 3 is isothermal heat rejection.
Process 3 to 4 is isentropic compression from T_2 to T_1.
Process 4 to 1 is isothermal heat supply.

The cycle is completely independent of the working substance used.

The cycle efficiency of a heat engine, defined in section 4.1, is given by the net work output divided by the gross heat supplied

i.e. $$\eta = \frac{-\sum W}{Q_1} = \frac{\sum Q}{Q_1} \qquad (5.1)$$

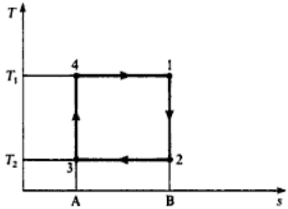


Fig. 5.1 Carnot cycle on a T–s diagram

In the Carnot cycle, with reference to Fig. 5.1, it can be seen that the gross heat supplied, Q_1, is given by the area 41BA4,

i.e. $Q_1 = \text{area 41BA4} = T_1(s_B - s_A)$

Similarly the net heat supplied, $\sum Q$, is given by the area 41234,

i.e. $\sum Q = (T_1 - T_2)(s_B - s_A)$

Hence we have Carnot cycle efficiency

$$\eta_{Carnot} = \frac{(T_1 - T_2)(s_B - s_A)}{T_1(s_B - s_A)}$$

i.e.
$$\eta_{Carnot} = 1 - \frac{T_2}{T_1} \qquad (5.2)$$

If a sink for heat rejection is available at a fixed temperature T_2 (e.g. a large supply of cooling water), then the ratio T_2/T_1 will decrease as the temperature of the source T_1 is increased. From equation (5.2) it can be seen that as T_2/T_1 decreases, then the thermal efficiency increases. Hence for a fixed lower temperature for heat rejection, the upper temperature at which heat is supplied must be made as high as possible. The maximum possible thermal efficiency between any two temperatures is that of the Carnot cycle.

Example 5.1 What is the highest possible theoretical efficiency of a heat engine operating with a hot reservoir of furnace gases at 2000 °C when the cooling water available is at 10 °C?

Solution From equation (5.2)

$$\eta_{Carnot} = 1 - \frac{T_2}{T_1} = 1 - \frac{10 + 273}{2000 + 273} = 1 - \frac{283}{2273}$$

i.e. Highest possible efficiency $= 1 - 0.1246$

$= 0.8754$ or 87.54%

It should be noted that a system in practice operating between similar temperatures (e.g. a steam-generating plant) would have a thermal efficiency of about 30%. The discrepancy is due to losses due to irreversibility in the actual plant, and also because of deviations from the ideal Carnot cycle made for various practical reasons.

It is difficult in practice to devise a system which can receive and reject heat at constant temperature. A wet vapour is the only working substance which can do this conveniently, since for a wet vapour the pressure and temperature remain constant as the specific enthalpy of vaporization is supplied or rejected. A Carnot cycle for a wet vapour is as shown in Fig. 5.2. Although this cycle is the most efficient possible vapour cycle, it is not used in steam plant. The theoretical cycle on which steam cycles are based is known as the Rankine cycle. This will be discussed in detail in Chapter 8, and the reasons for using it in preference to the Carnot cycle will be given.

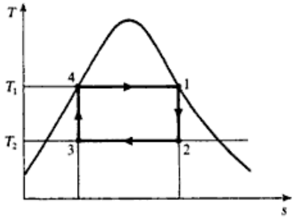


Fig. 5.2 Carnot cycle for a wet vapour on a T–s diagram

5.2 Absolute temperature scale

In the preceding chapters a temperature scale based on the perfect gas thermometer has been assumed. Using the Second Law of Thermodynamics it is possible to establish a temperature scale which is independent of the working substance.

We have, for any heat engine from equation (5.1),

$$\eta = \frac{\sum Q}{Q_1}$$

Also the efficiency of an engine operating on the Carnot cycle depends only on the temperatures of the hot and cold reservoirs. Denoting temperature on an arbitrary scale by X, we have

$$\eta = \phi(X_1, X_2) \tag{5.3}$$

where ϕ is a function, and X_1 and X_2 are the temperatures of the hot and cold reservoirs.

Combining equations (5.1) and (5.3) we have

$$\frac{\sum Q}{Q_1} = \phi(X_1, X_2)$$

There are a large number of possible temperature scales which are all independent of the working substance. Any working scale can be chosen by suitably selecting the value of the function ϕ. The function can be chosen that

$$1 - \frac{\sum Q}{Q_1} = \frac{X_2}{X_1} \tag{5.4}$$

Also from equation (5.2) we have

$$\eta = 1 - \frac{T_2}{T_1}$$

Hence using equation (5.1)

$$\eta = \frac{\sum Q}{Q_1} = 1 - \frac{T_2}{T_1}$$

or

$$1 - \frac{\sum Q}{Q_1} = \frac{T_2}{T_1} \tag{5.5}$$

Comparing equations (5.4) and (5.5) it can be seen that the temperature X is equivalent to the temperature T. Thus by suitably choosing the function ϕ, the ideal temperature scale is made equivalent to the scale based on the perfect gas thermometer.

5.3 The Carnot cycle for a perfect gas

A Carnot cycle for a perfect gas is shown on a T–s diagram in Fig. 5.3. Note that the pressure of the gas changes continuously from p_4 to p_1 during the isothermal heat supply, and from p_2 to p_3 during the isothermal heat rejection. In practice it is much more convenient to heat a gas at approximately constant pressure or at constant volume, hence it is difficult to attempt to operate an actual heat engine on the Carnot cycle using a gas as working substance. Another important reason for not attempting to use the Carnot cycle in practice is illustrated by drawing the cycle on a p–v diagram, as in Fig. 5.4. The net work output of the cycle is given by the area 12341. This is a small quantity compared with the gross work output of the expansion processes of the cycle, given by area 412BA4. The work of the compression processes (i.e. work done on the gas) is given by the area 234AB2. The ratio of the net work output to the gross work output of the system is called the *work ratio*. The Carnot cycle, despite its high thermal efficiency, has a low work ratio.

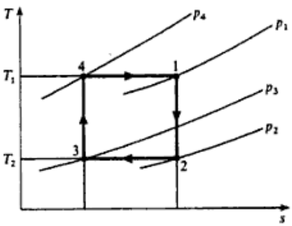
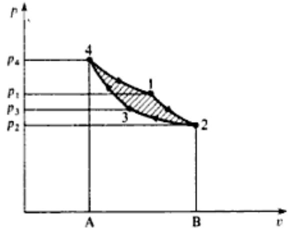


Fig. 5.3 Carnot cycle for a perfect gas on a T–s diagram

Fig. 5.4 Carnot cycle on a p–v diagram



Example 5.2 A hot reservoir at 800 °C and a cold reservoir at 15 °C are available. Calculate the thermal efficiency and the work ratio of a Carnot cycle using air as the working fluid, if the maximum and minimum pressures in the cycle are 210 bar and 1 bar.

Solution The cycle is shown on a T–s and p–v diagram in Figs 5.5(a) and 5.5(b) respectively.

Using equation (5.2),

$$\eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1} = 1 - \frac{15 + 273}{800 + 273} = 1 - 0.268$$

i.e. $\eta_{\text{Carnot}} = 0.732$ or 73.2%

In order to find the work output and the work ratio it is necessary to find the entropy change $(s_1 - s_4)$.

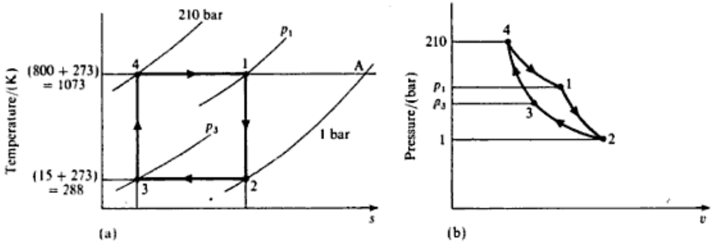
For an isothermal process from 4 to A, using equation (4.12),

$$s_A - s_4 = R \ln\left(\frac{p_4}{p_2}\right) = 0.287 \ln\left(\frac{210}{1}\right) = 1.535 \text{ kJ/kg K}$$

At constant pressure from A to 2, we have

$$s_A - s_2 = c_p \ln\left(\frac{T_1}{T_2}\right) = 1.005 \ln\left(\frac{1073}{288}\right) = 1.321 \text{ kJ/kg K}$$

Fig. 5.5 Carnot cycle for Example 5.2 on p–v and T–s diagrams



therefore

$$s_1 - s_4 = 1.535 - 1.321 = 0.214 \text{ kJ/kg K}$$

Then

$$\text{Net work output} = (T_1 - T_2)(s_1 - s_4) = \text{area } 12341$$
$$= (1073 - 288) \times 0.214 = 168 \text{ kJ/kg}$$

Gross work output is

Work output 4 to 1 + work output 1 to 2

From equation (3.12) for an isothermal process, $Q + W = 0$,

i.e. $$-W_{4\text{-}1} = Q_{4\text{-}1} = \text{area under line 4–1 on Fig. 5.5(a)}$$
$$= (s_1 - s_4) \times T_1 = 0.214 \times 1073$$
$$= 229.6 \text{ kJ/kg}$$

For an isentropic process from 1 to 2, from equation (3.13), $W = (u_2 - u_1)$, therefore for a perfect gas

$$-W_{2\text{-}1} = c_v(T_1 - T_2)$$
$$= 0.718(1073 - 288) = 563.6 \text{ kJ/kg}$$

Therefore

$$\text{Gross work output} = 229.6 + 563.6 = 793.2 \text{ kJ/kg}$$

i.e. $$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{168}{793.2} = 0.212$$

5.4 The constant pressure cycle

In this cycle the heat supply and heat rejection processes occur reversibly at constant pressure. The expansion and compression processes are isentropic. The cycle is shown on a T–s diagram and a p–v diagram in Figs 5.6(a) and 5.6(b). This cycle was at one time used as the ideal basis for a hot-air reciprocating engine, and the cycle was known as the Joule or Brayton cycle. Nowadays the cycle is the ideal for the closed cycle gas turbine unit. A simple line diagram of the plant is shown in Fig. 5.7, with the numbers corresponding to those of Figs 5.6(a) and 5.6(b). The working substance is air which flows in steady flow round the cycle, hence, neglecting velocity changes, and applying the steady-flow energy equation to each part of the cycle, we have

$$\text{Work input to compressor} = (h_2 - h_1) = c_p(T_2 - T_1)$$
$$\text{Work output from turbine} = (h_3 - h_4) = c_p(T_3 - T_4)$$
$$\text{Heat supplied in heater} = (h_3 - h_2) = c_p(T_3 - T_2)$$
$$\text{Heat rejected in cooler} = (h_4 - h_1) = c_p(T_4 - T_1)$$

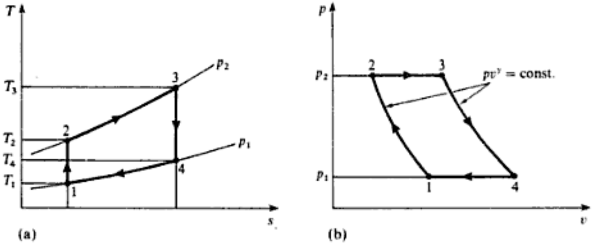


Fig. 5.6 Constant pressure cycle on p–v and T–s diagrams

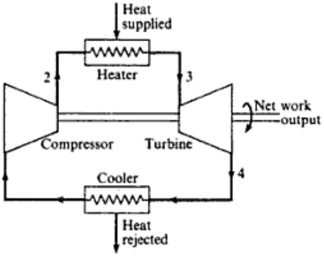


Fig. 5.7 Closed-cycle gas turbine unit

Then from equation (5.1)

$$\eta = \frac{\sum Q}{Q_1} = \frac{c_p(T_3 - T_2) - c_p(T_4 - T_1)}{c_p(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Now since processes 1 to 2 and 3 to 4 are isentropic between the same pressures p_2 and p_1, we have, using equation (3.21),

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma} = \frac{T_3}{T_4} = r_p^{(\gamma-1)/\gamma}$$

where r_p is the pressure ratio, p_2/p_1.

i.e. $\quad T_3 = T_4 r_p^{(\gamma-1)/\gamma}$ and $T_2 = T_1 r_p^{(\gamma-1)/\gamma}$

$$T_3 - T_2 = r_p^{(\gamma-1)/\gamma}(T_4 - T_1)$$

Hence, substituting in the expression for the efficiency

$$\eta = 1 - \frac{T_4 - T_1}{(T_4 - T_1)r_p^{(\gamma-1)/\gamma}} = 1 - \frac{1}{r_p^{(\gamma-1)/\gamma}} \qquad (5.6)$$

Thus for the constant pressure cycle the cycle efficiency depends only on the pressure ratio. In the ideal case the value of γ for air is constant and equal to 1.4. In practice, due to the eddying of the air as it flows through the compressor and turbine which are both rotary machines, the actual cycle efficiency is greatly reduced compared to that given by equation (5.6).

The work ratio of the constant pressure cycle may be found as follows:

$$\text{Work ratio} = \frac{\text{Net work output}}{\text{Gross work output}} = \frac{c_p(T_3 - T_4) - c_p(T_2 - T_1)}{c_p(T_3 - T_4)}$$

$$= 1 - \frac{T_2 - T_1}{T_3 - T_4}$$

Now, as previously,

$$\frac{T_2}{T_1} = r_p^{(\gamma-1)/\gamma} = \frac{T_3}{T_4}$$

therefore

$$T_2 = T_1 r_p^{(\gamma-1)/\gamma} \quad \text{and} \quad T_4 = \frac{T_3}{r_p^{(\gamma-1)/\gamma}}$$

Hence substituting

$$\text{Work ratio} = 1 - \frac{T_1(r_p^{(\gamma-1)/\gamma} - 1)}{T_3[1 - (1/r_p^{(\gamma-1)/\gamma})]}$$

i.e.
$$\text{Work ratio} = 1 - \frac{T_1}{T_3} r_p^{(\gamma-1)/\gamma} \qquad (5.7)$$

It can be seen from equation (5.7) that the work ratio depends not only on the pressure ratio but also on the ratio of the minimum and maximum temperatures. For a given inlet temperature, T_1, the maximum temperature, T_3, must be made as high as possible for a high work ratio.

For an open-cycle gas turbine unit the actual cycle is not such a good approximation to the ideal constant pressure cycle, since fuel is burned with the air, and a fresh charge is continuously induced into the compressor. The ideal cycle provides nevertheless a good basis for comparison, and in many calculations for an ideal open-cycle gas turbine the effects of the mass of fuel and the charge in the working fluid are neglected.

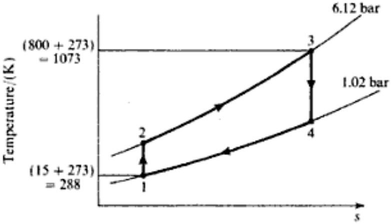
Example 5.3 In a gas turbine unit air is drawn at 1.02 bar and 15 °C, and is compressed to 6.12 bar. Calculate the thermal efficiency and the work ratio of the ideal constant pressure cycle, when the maximum cycle temperature is limited to 800 °C.

Solution The ideal cycle is shown on a T–s diagram in Fig. 5.8. From equation (5.6)

$$\text{Thermal efficiency, } \eta = 1 - \frac{1}{r_p^{(\gamma-1)/\gamma}}$$

i.e.
$$\eta = 1 - \left(\frac{1.02}{6.12}\right)^{(1.4-1)/1.4} = 1 - 0.599$$

Fig. 5.8 T–s diagram for Example 5.3



therefore

$$\text{Thermal efficiency} = 0.401 \text{ or } 40.1\%$$

The net work output of the cycle is given by the work output of the turbine minus the work input in the compressor,

i.e. $\quad$ Net work output $= c_p(T_3 - T_4) - c_p(T_2 - T_1)$

From equation (3.21)

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma} = \frac{T_3}{T_4} = \left(\frac{6.12}{1.02}\right)^{(1.4-1)/1.4} = 1.669$$

therefore

$$T_2 = 1.669 \times T_1 = 1.669 \times 288 = 480.5 \text{ K}$$

where $T_2 = 15 + 273 = 288$ K and

$$T_4 = \frac{T_3}{1.669} = \frac{1073}{1.669} = 642.9 \text{ K}$$

where $T_3 = 800 + 273 = 1073$ K. Therefore

$$\text{Net work output} = 1.005(1073 - 642.9) - 1.005(480.5 - 288)$$
$$= 238.8 \text{ kJ/kg}$$

$$\text{Gross work output} = \text{work output of the turbine} = c_p(T_3 - T_4)$$
$$= 1.005(1073 - 642.9) = 432.3 \text{ kJ/kg}$$

Then $\quad$ $$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{238.8}{432.3} = 0.553$$

5.5 The air standard cycle

Cycles in which the fuel is burned directly in the working fluid are not heat engines in the true meaning of the term since the system is not reduced to its initial state. The working fluid undergoes a chemical change by combustion and the resulting products are exhausted to the atmosphere. In practice such cycles are used frequently and are called internal-combustion cycles. The fuel is burned directly in the working fluid which is normally air. The main advantage of such power units is that high temperatures of the fluid can be attained, since heat is not transferred through metal walls to the fluid. It is seen from equation (5.2), $\eta = 1 - (T_2/T_1)$, that for a given sink for the rejection of heat at T_2, the temperature of the source, T_1, must be as high as possible. This applies to all heat engines. By supplying fuel inside the cylinder as in the internal-combustion engine, higher temperatures for the working fluid can be attained. The maximum temperature of all cycles is limited by the metallurgical limit of the materials used. The fluid in an internal-combustion engine may reach a temperature as high as 3000 K. This is made possible by externally cooling the cylinder by water or air cooling; also, due to the intermittent nature of the cycle, the working fluid reaches its maximum temperature for only an instant during each cycle.

Examples of internal-combustion cycles are the open cycle gas turbine unit, the petrol engine, the diesel engine or oil engine, and the gas engine. The open cycle gas turbine unit, although an internal combustion cycle, is nevertheless in a different category to the other internal-combustion engines; the cycle is a steady-flow cycle in which the working fluid flows from one component to another round the cycle. It will be assumed, therefore, that the gas turbine unit, whether operating on the open or the closed cycle, can be satisfactorily compared with the ideal constant pressure cycle, dealt with in section 5.4. Gas turbine cycles are considered in more detail in Chapter 9.

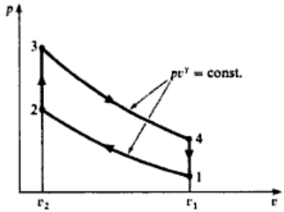
In the petrol engine a mixture of air and petrol is drawn into the cylinder, compressed by the piston, then ignited by an electric spark. The hot gases expand, pushing the piston back, and are then swept out to exhaust, and the cycle recommences with the induction of a fresh charge of petrol and air. In the diesel or oil engine the oil is sprayed under pressure into the compressed air at the end of the compression stroke, and combustion is spontaneous due to the high temperature of the air after compression. In a gas engine a mixture of gas and air is induced into the cylinder, compressed, and then ignited as in the petrol engine, by an electric spark. Reciprocating internal-combustion engines are considered in more detail in Chapter 13. To give a basis of comparison for the actual internal-combustion engine the air standard cycle is defined. In an *air standard cycle* the working substance is assumed to be air throughout, all processes are assumed to be reversible, and the source of heat supply and the sink for heat rejection are assumed to be external to the air. The cycle can be represented on any diagram of properties, and is usually drawn on the p–v diagram, since this allows a more direct comparison to be made with the actual engine machine cycle. It must be stressed that an air standard cycle on a p–v diagram is a true thermodynamic cycle, whereas a record of pressure variations in an engine cylinder against piston displacement is a machine cycle.

5.6 The Otto cycle

The Otto cycle is the ideal air standard cycle for the petrol engine, the gas engine, and the high-speed oil engine. The cycle is shown on a p–v diagram in Fig. 5.9.

Process 1 to 2 is isentropic compression.
Process 2 to 3 is reversible constant volume heating.
Process 3 to 4 is isentropic expansion.
Process 4 to 1 is reversible constant volume cooling.

Fig. 5.9 Otto cycle on a p–v diagram



To give a direct comparison with an actual engine the ratio of the specific volumes, v_1/v_2, is taken to be the same as the compression ratio of the actual engine,

i.e. $$\text{Compression ratio, } r_v = \frac{v_1}{v_2}$$

$$= \frac{\text{swept volume} + \text{clearance volume}}{\text{clearance volume}} \qquad (5.8)$$

The thermal efficiency of the Otto cycle can be found using equation (5.1),

$$\eta = \frac{\sum Q}{Q_1}$$

The heat supplied, Q_1, at constant volume between T_2 and T_3 is given by equation (2.13) per unit mass of air

$$Q_1 = c_v(T_3 - T_2)$$

Similarly the heat rejected per unit mass at constant volume between T_4 and T_1 is given by equation (2.13), $c_v(T_4 - T_1)$.

The processes 1 to 2 and 3 to 4 are isentropic and therefore there is no heat flow during these processes. Therefore

$$\eta = \frac{\sum Q}{Q_1} = \frac{c_v(T_3 - T_2) - c_v(T_4 - T_1)}{c_v(T_3 - T_2)} = 1 - \left(\frac{T_4 - T_1}{T_3 - T_2}\right)$$

Now since processes 1 to 2 and 3 to 4 are isentropic, then using equation (3.20),

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} = \left(\frac{v_4}{v_3}\right)^{\gamma-1} = \frac{T_3}{T_4} = r_v^{\gamma-1}$$

where r_v is the compression ratio from equation (5.8).

Then $T_3 = T_4 r_v^{\gamma-1}$ and $T_2 = T_1 r_v^{\gamma-1}$

Hence substituting

$$\eta = 1 - \frac{T_4 - T_1}{(T_4 - T_1)r_v^{\gamma-1}} = 1 - \frac{1}{r_v^{\gamma-1}} \qquad (5.9)$$

It can be seen from equation (5.9) that the thermal efficiency of the Otto cycle depends only on the compression ratio, r_v.

Example 5.4 Calculate the ideal air standard cycle efficiency based on the Otto cycle for a petrol engine with a cylinder bore of 50 mm, a stroke of 75 mm, and a clearance volume of 21.3 cm³.

Solution

$$\text{Swept volume} = \frac{\pi}{4} \times 50^2 \times 75 = 147\,200\ \text{m}^3 = 147.2\ \text{cm}^3$$

Therefore

$$\text{Total cylinder volume} = 147.2 + 21.3 = 168.5\ \text{cm}^3$$

i.e. $$\text{Compression ratio, } r_v = \frac{168.5}{21.3} = 7.914/1$$

Then using equation (5.9)

$$\eta = 1 - \frac{1}{r_v^{\gamma-1}} = 1 - \frac{1}{7.914^{0.4}} = 1 - 0.437 = 0.563 \text{ or } 56.3\%$$

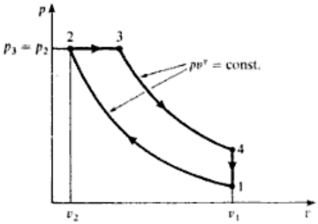
5.7 The diesel cycle

The engines in use today which are called diesel engines are far removed from the original engine invented by Diesel in 1892. Diesel worked on the idea of spontaneous ignition of powdered coal, which was blasted into the cylinder by compressed air. Oil became the accepted fuel used in compression–ignition engines, and the oil was originally blasted into the cylinder in the same way that Diesel had intended to inject the powdered coal. This gave a cycle of operation which has as its ideal counterpart the ideal air standard diesel cycle shown in Fig. 5.10.

As before the compression ratio, r_v, is given by the ratio v_1/v_2.

Process 1 to 2 is isentropic compression.
Process 2 to 3 is reversible constant pressure heating.
Process 3 to 4 is isentropic expansion.
Process 4 to 1 is reversible constant volume cooling.

Fig. 5.10 Diesel cycle on a p–v diagram



From equation (5.1)

$$\eta = \frac{\sum Q}{Q_1}$$

At constant pressure from equation (2.12) per kg of air

$$Q_1 = c_p(T_3 - T_2)$$

Also at constant volume from equation (2.13), per kilogram of air the heat rejected is $c_v(T_4 - T_1)$.

There is no heat flow in processes 1 to 2 and 3 to 4 since these processes are isentropic. Hence by substituting in the expression for thermal efficiency the following equation may be derived:

$$\eta = 1 - \frac{\beta^\gamma - 1}{(\beta - 1)r_v^{\gamma-1}\gamma} \tag{5.10}$$

where $\beta = v_3/v_2$ = cut-off ratio.

Equation (5.10) shows that the thermal efficiency depends not only on the compression ratio but also on the heat supplied between 2 and 3, which fixes the ratio, v_3/v_2. Equation (5.10) is derived by expressing each temperature in terms of T_1 and r_v or β. The derivation is not given here because it is believed that the best method of working out the thermal efficiency is to calculate each temperature individually round the cycle, and then apply equation (5.1), $\eta = \sum Q/Q_1$. This is illustrated in Example 5.5.

Example 5.5 A diesel engine has an inlet temperature and pressure of 15 °C and 1 bar respectively. The compression ratio is 12/1 and the maximum cycle temperature is 1100 °C. Calculate the air standard thermal efficiency based on the diesel cycle.

Solution Referring to Fig. 5.11, $T_1 = 15 + 273 = 288$ K and $T_3 = 1100 + 273 = 1373$ K. From equation (3.20)

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} = r_v^{\gamma-1} = 12^{0.4} = 2.7$$

i.e. $T_2 = 2.7 \times 288 = 778$ K

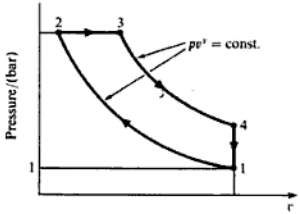


Fig. 5.11 Diesel cycle on a p–v diagram for Example 5.5

At constant pressure from 2 to 3, since $pv = RT$ for a perfect gas, then

$$\frac{T_3}{T_2} = \frac{v_3}{v_2}$$

i.e. $$\frac{v_3}{v_2} = \frac{1373}{778} = 1.765$$

Therefore

$$\frac{v_4}{v_3} = \frac{v_4}{v_2}\frac{v_2}{v_3} = \frac{v_1}{v_2}\frac{v_2}{v_3} = 12 \times \frac{1}{1.765} = 6.8$$

Then using equation (3.20)

$$\frac{T_3}{T_4} = \left(\frac{v_4}{v_3}\right)^{\gamma-1} = 6.8^{0.4} = 2.153$$

i.e. $$T_4 = \frac{1373}{2.153} = 638\text{ K}$$

Then from equation (2.12), per kilogram of air

$$Q_1 = c_p(T_3 - T_2) = 1.005(1373 - 778) = 598\text{ kJ/kg}$$

Also, from equation (2.13), per kilogram of air, the heat rejected is

$$c_v(T_4 - T_1) = 0.718(638 - 288) = 251\text{ kJ/kg}$$

Therefore from equation (5.1)

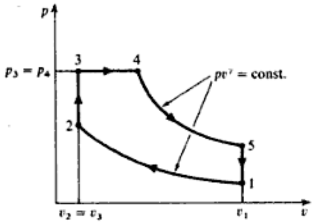
$$\eta = \frac{\sum Q}{Q_1} = \frac{598 - 251}{598} = 0.58 \text{ or } 58\%$$

5.8 The dual-combustion cycle

Modern oil engines, although still called diesel engines, are more closely derived from an engine invented by Ackroyd-Stuart in 1888. All oil engines today use solid injection of the fuel; the fuel is injected by a spring-loaded injector, the fuel pump being operated by a cam driven from the engine crankshaft (see section 13.10). The ideal cycle used as a basis for comparison is called the dual-combustion cycle or the mixed cycle, and is shown on a p–v diagram in Fig. 5.12.

Process 1 to 2 is isentropic compression.
Process 2 to 3 is reversible constant volume heating.
Process 3 to 4 is reversible constant pressure heating.
Process 4 to 5 is isentropic expansion.
Process 5 to 1 is reversible constant volume cooling.

Fig. 5.12 Dual combustion cycle on a p–v diagram



The heat is supplied in two parts, the first part at constant volume and the remainder at constant pressure, hence the name 'dual-combustion'. In order to fix the thermal efficiency completely, three factors are necessary. These are the compression ratio, $r_v = v_1/v_2$, the ratio of pressures, $k = p_3/p_2$, and the ratio of volumes, $\beta = v_4/v_3$.

Then it can be shown that

$$\eta = 1 - \frac{k\beta^\gamma - 1}{[(k-1) + \gamma k(\beta - 1)]r_v^{\gamma-1}} \tag{5.11}$$

Note that when $k = 1$ (i.e. $p_3 = p_2$), then the equation (5.11) reduces to the thermal efficiency of the diesel cycle given by equation (5.10). The efficiency of the dual-combustion cycle depends not only on the compression ratio but also on the relative amounts of heat supplied at constant volume and at constant pressure. Equation (5.11) is much too cumbersome to use, and the best method of calculating thermal efficiency is to evaluate each temperature round the cycle and then use equation (5.1), $\eta = \sum Q/Q_1$. The heat supplied, Q_1, is found by using equations (2.13) and (2.12) for the heat added at constant volume and at constant pressure respectively,

i.e. $Q_1 = c_v(T_3 - T_2) + c_p(T_4 - T_3)$

The heat rejected is given by $c_v(T_5 - T_1)$.

Example 5.6 An oil engine takes in air at 1.01 bar, 20 °C and the maximum cycle pressure is 69 bar. The compressor ratio is 18/1. Calculate the air standard thermal efficiency based on the dual-combustion cycle. Assume that the heat added at constant volume is equal to the heat added at constant pressure.

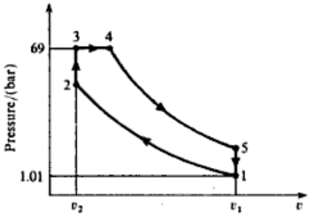


Fig. 5.13 Dual combustion cycle for Example 5.6

Solution The cycle is shown on a p–v diagram in Fig. 5.13. Using equation (3.20),

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} = 18^{0.4} = 3.18$$

i.e. $T_2 = 3.18 \times T_1 = 3.18 \times 293 = 931\ \text{K}$

where $T_1 = 20 + 273 = 293$ K.

From 2 to 3 the process is at constant volume, hence

$$\frac{p_3}{p_2} = \frac{T_3}{T_2} \quad \text{since} \quad \frac{p_3 v_3}{T_3} = \frac{p_2 v_2}{T_2} \quad \text{and} \quad v_3 = v_2$$

i.e. $$T_3 = \frac{p_3}{p_2} \times T_2 = \frac{69 \times 931}{p_2}$$

To find p_2, use equation (3.19),

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^{\gamma} = 18^{1.4} = 57.2$$

i.e. $p_2 = 57.2 \times 1.01 = 57.8\ \text{bar}$

Then substituting

$$T_3 = \frac{69 \times 931}{57.8} = 1112\ \text{K}$$

Now the heat added at constant volume is equal to the heat added at constant pressure in this example, therefore

$$c_v(T_3 - T_2) = c_p(T_4 - T_3)$$

i.e. $0.718(1112 - 931) = 1.005(T_4 - 1112)$

therefore

$$T_4 = \frac{0.718 \times 181}{1.005} + 1112$$

i.e. $T_4 = 1241.4\ \text{K}$

To find T_5 it is necessary to know the value of the volume ratio, v_5/v_4. At constant pressure from 3 to 4

$$\frac{v_4}{v_3} = \frac{T_4}{T_3} = \frac{1241.4}{1112} = 1.116$$

Therefore

$$\frac{v_5}{v_4} = \frac{v_1}{v_4} = \frac{v_1 v_3}{v_2 v_4} = 18 \times \frac{1}{1.116} = 16.14$$

Then using equation (3.20)

$$\frac{T_4}{T_5} = \left(\frac{v_5}{v_4}\right)^{\gamma-1} = 16.14^{0.4} = 3.04$$

i.e. $$T_5 = \frac{1241.4}{3.04} = 408\text{ K}$$

Now the heat supplied, Q_1, is given by

$$Q_1 = c_v(T_3 - T_2) + c_p(T_4 - T_3) \quad \text{or} \quad Q_1 = 2c_v(T_3 - T_2)$$

since in this example the heat added at constant volume is equal to the heat added at constant pressure. Therefore

$$Q_1 = 2 \times 0.718 \times (1112 - 931) = 260\text{ kJ/kg}$$

The heat rejected is given by

$$c_v(T_5 - T_1) = 0.718(408 - 293) = 82.6\text{ kJ/kg}$$

Then from equation (4.3)

$$\eta = \frac{\sum Q}{Q_1} = \frac{260 - 82.6}{260} = 1 - 0.318 = 0.682 \text{ or } 68.2\%$$

It should be mentioned here that the modern high-speed oil engine operates on a cycle for which the Otto cycle is a better basis of comparison. Also, since the Otto cycle calculation for thermal efficiency is much simpler than that of the dual-combustion cycle, then this is another reason for using the Otto cycle as a standard of comparison.

5.9 Mean effective pressure

The term work ratio is defined in section 5.3, and is shown to be a useful criterion for practical power plants. For internal-combustion engines work ratio is not such a useful concept, since the work done on and by the working fluid takes place inside one cylinder. In order to compare reciprocating engines another term is defined called the *mean effective pressure.* The mean effective pressure is defined as the height of a rectangle having the same length and area as the cycle plotted on a p–v diagram. This is illustrated for an Otto cycle in Fig. 5.14. The rectangle ABCDA is the same length as the cycle 12341, and area

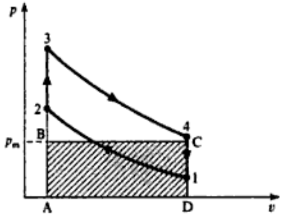


Fig. 5.14 Mean effective pressure on a p–v diagram

ABCDA is equal to area 12341. Then the mean effective pressure, p_m, is the height AB of the rectangle. The work output per kilogram of air can therefore be written as

$$-W = \text{area ABCDA} = p_m(v_1 - v_2) \tag{5.12}$$

The term $(v_1 - v_2)$ is proportional to the swept volume of the cylinder, hence it can be seen from equation (5.12) that the mean effective pressure gives a measure of the work output per swept volume. It can therefore be used to compare similar engines of different size. The mean effective pressure discussed in this section is for the air standard cycle. It will be shown in Chapter 13 that the indicated mean effective pressure of an actual engine can be measured from an indicator diagram and used to evaluate the indicated work done by the engine.

Example 5.7 Calculate the mean effective pressure for the cycle of Example 5.6.

Solution In Example 5.6 the heat supplied, Q_1, and the cycle efficiency were found to be 260 kJ/kg and 68.2% respectively. From equation (4.2)

$$\eta = \frac{-W}{Q_1}$$

therefore

$$-W = \eta Q_1 = 0.682 \times 260 = 177 \text{ kJ/kg}$$

Now from the definition of mean effective pressure, and equation (5.12), we have

$$-W = p_m(v_1 - v_2)$$

Using equation (2.5), $pv = RT$ and equation (5.8), $r_v = v_1/v_2 = 18$, then

$$v_1 - v_2 = \left(v_1 - \frac{v_1}{18}\right) = \frac{17}{18}v_1 = \frac{17}{18}\frac{RT_1}{p_1} = \frac{17 \times 287 \times 293}{18 \times 1.01 \times 10^5}$$

i.e. $\quad v_1 - v_2 = 0.786 \text{ m}^3/\text{kg}$

Then substituting,

$$-W = p_m \times 0.786 \quad \text{or} \quad p_m = -W/0.786 \text{ kJ/m}^3$$

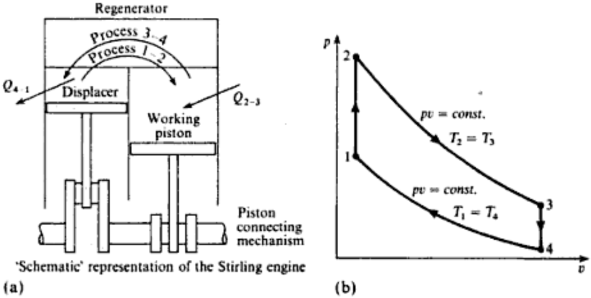
i.e. $\quad$ Mean effective pressure $= \dfrac{177 \times 10^3}{10^5 \times 0.786} = 2.25$ bar

5.10 The Stirling and Ericsson cycles

It has been shown that no cycle can have an efficiency greater than that of the Carnot cycle working between given temperature limits T_1 and T_2. Cycles which have an efficiency equal to that of the Carnot cycle have been defined and are known as the Stirling and Ericsson cycles and they are superior to the Carnot cycle in that they have higher work ratios.

The Stirling cycle is shown in the p–v diagram in Fig. 5.15(a) and is represented diagrammatically in Fig. 5.15(b): it must be emphasized that this is not a physical description of a Stirling engine but one which may help to give an understanding of the way the processes which make up the cycle are related.

Fig. 5.15 Stirling engine and the Stirling cycle



Heat is supplied to the working fluid from an external source, process 2–3, as the gas expands isothermally ($T_2 = T_3$), and heat is rejected to an external sink, process 4–1, as the gas is compressed isothermally ($T_1 = T_4$). The two isothermals are connected by the reversible constant volume processes 1–2 and 3–4 during which the temperature changes are equal to ($T_2 - T_1$). The heat rejected during process 3–4, $c_v(T_2 - T_1)$, is used to heat the gas during process 1–2, $c_v(T_2 - T_1) = c_v(T_3 - T_4)$ and this is assumed to take place ideally and reversibly in a *regenerator*. The regenerator requires a matrix of material which separates the heating and cooling gases, but allows the temperatures to change progressively by infinitesimal and corresponding amounts during the processes. This regenerative process takes place at constant volume and is internal to the cycle.

The efficiency of the Stirling cycle is obtained by considering the heat transfers between the system and the bodies external to it, i.e. a high-temperature heat supply and a low-temperature sink to which heat is rejected.

Heat supplied from the hot source, using equations (3.11) and (3.12),

$$Q_{2\text{-}3} = -W_{2\text{-}3} = RT_2 \ln\left(\frac{p_2}{p_3}\right) \text{ per unit mass of gas}$$

Similarly

$$\text{Heat } \textit{rejected} \text{ to the coldsink} = W_{4\text{-}1} = RT_1 \ln\left(\frac{p_1}{p_4}\right)$$

therefore

$$\sum Q = RT_2 \ln\left(\frac{p_2}{p_3}\right) - RT_1 \ln\left(\frac{p_1}{p_4}\right)$$

and as the cycle efficiency, $\eta = \sum Q/Q_{2\text{-}3}$, therefore

$$\eta = 1 - \frac{RT_1 \ln\left(\dfrac{p_2}{p_3}\right)}{RT_2 \ln\left(\dfrac{p_1}{p_4}\right)}$$

For the constant volume process 1–2,

$$\frac{p_2}{p_1} = \frac{T_2}{T_1} \quad \text{and for process 3–4} \quad \frac{p_3}{p_4} = \frac{T_3}{T_4} = \frac{T_2}{T_1}$$

therefore

$$\frac{p_2}{p_1} = \frac{p_3}{p_4} \quad \text{and} \quad \frac{p_2}{p_3} = \frac{p_1}{p_4}$$

therefore

$$\eta = 1 - \frac{T_1}{T_2} = \text{the Carnot efficiency}$$

This result can be deduced without formal proof as the heat supply and rejection processes take place at constant temperatures.

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{-W_{2\text{-}3} + W_{4\text{-}1}}{-W_{2\text{-}3}}$$

$$= \frac{\sum Q}{Q_{2\text{-}3}} = \text{cycle efficiency, } \eta$$

since $-W_{2\text{-}3} = Q_{2\text{-}3}$.

The practical interpretation of the ideal cycle will not be described in detail here and the reader is advised to consult the specialist literature for the mechanical arrangements employed and the performance assessments (see refs 5.2 and 5.3). Figure 5.15(b) gives a simplified representation of the engine and shows the necessity for two pistons, a working piston and a displacing piston, which in fact work in different parts of the same cylinder and not as represented. It is necessary to the ideal cycle for the pistons to move discontinuously and this is only approximated to by the mechanisms employed. The result is that the processes of the ideal cycle are not achieved and there is a considerable 'rounding off' of the ideal p–v diagram as the heating and cooling processes merge to depart considerably from the constant volume heating concept.

The attractions of the Stirling engine are that it can utilize any form of heat from conventional or indigenous fuel, solar or nuclear sources, provided the temperature created is high enough. The engines are quiet, with an efficiency equal to or better than the best internal combustion engines and with little vibration due to the nature of the drive needed to give the differential movements between the working and displacing pistons. The possible range of application of the Stirling engine is wide and includes marine use, electricity generation for peak loads and as a stand-by unit, automotive purposes, particularly in comparison with the diesel engine, and for situations when unconventional fuels or heat sources can, or must, be used. The most important applications up to now have been as an air engine and as a refrigerator; with the Stirling cycle reversed, it is capable of reaching the low temperatures of the cryogenic regions.

The Ericsson cycle is similar to the Stirling cycle except that the two isothermals are connected by constant pressure processes, as shown in Fig. 5.16.

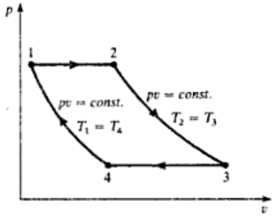


Fig. 5.16 Ericsson cycle on a p–v diagram

Problems

5.1 What is the highest cycle efficiency possible for a heat engine operating between 800 and 15 °C?

(73.2%)

5.2 Two reversible heat engines operate in series between a source at 527 °C and a sink at 17 °C. If the engines have equal efficiencies and the first rejects 400 kJ to the second, calculate:

(i) the temperature at which heat is supplied to the second engine;
(ii) the heat taken from the source;
(iii) the work done by each engine.

Assume that each engine operates on the Carnot cycle.

(208.7 °C; 664.4 kJ; 264.4 kJ; 159.2 kJ)

5.3 In a Carnot cycle operating between 307 and 17 °C the maximum and minimum pressures are 62.4 bar and 1.04 bar. Calculate the cycle efficiency and the work ratio. Assume air to be the working fluid.

(50%; 0.286)

5.4 A closed-cycle gas turbine unit operating with maximum and minimum temperatures of 760 and 20 °C has a pressure ratio of 7/1. Calculate the ideal cycle efficiency and the work ratio.

(42.7%; 0.505)

5.5 In an air standard Otto cycle the maximum and minimum temperatures are 1400 and 15 °C. The heat supplied per kilogram of air is 800 kJ. Calculate the compression ratio and the cycle efficiency. Calculate also the ratio of maximum to minimum pressures in the cycle.

(5.27/1; 48.5%; 30.65/1)

5.6 A four-cylinder petrol engine has a swept volume of 2000 cm^3, and the clearance volume in each cylinder is 60 cm^3. Calculate the air standard cycle efficiency. If the introduction conditions are 1 bar and 24 °C, and the maximum cycle temperature is 1400 °C, calculate the mean effective pressure based on the air standard cycle.

(59.1%; 5.28 bar)

5.7 Calculate the cycle efficiency and mean effective pressure of an air standard diesel cycle with a compression ratio of 15/1, and maximum and minimum cycle temperatures of 1650 °C and 15 °C respectively. The maximum cycle pressure is 45 bar.

(59.1%; 8.38 bar)

5.8 In a dual-combustion cycle the maximum temperature is 2000 °C and the maximum pressure is 70 bar. Calculate the cycle efficiency and the mean effective pressure when the pressure and temperature at the start of compression are 1 bar and 17 °C respectively. The compression ratio is 18/1.

(63.6%; 10.46 bar)

5.9 An air standard dual-combustion cycle has a mean effective pressure of 10 bar. The minimum pressure and temperature are 1 bar and 17 °C respectively, and the compression ratio is 16/1. Calculate the maximum cycle temperature when the cycle efficiency is 60%. The maximum cycle pressure is 60 bar.

(1259 °C)

References

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5.3 I Mech E Conference 1982 *Stirling Engines – Progress Towards Reality* MEP

6

Mixtures

A pure substance is defined as a substance having a constant and uniform chemical composition, and this definition can be extended to include a homogeneous mixture of gases when there is no chemical reaction taking place. The thermodynamic properties of a mixture of gases can be determined in the same way as for a single gas. The most common example of this is dry air, which is a mixture of oxygen, nitrogen, a small percentage of argon, and traces of other gases. The properties of air have been determined and it is considered as a single substance.

The mixtures to be considered in this chapter are those composed of perfect gases, and perfect gases and vapours. The properties of such mixtures are important in combustion calculations. Air and water vapour mixtures are considered later in the chapter with reference to surface condensers, but for moist atmospheric air there is a special nomenclature and this is considered in Chapter 15 on psychrometry and air-conditioning.

6.1 Dalton's law and the Gibbs–Dalton law

Consider a closed vessel of volume V at temperature T, which contains a mixture of perfect gases at a known pressure. If some of the mixture were removed, then the pressure would be less than the initial value. If the gas removed were the full amount of one of the constituents then the reduction in pressure would be equal to the contribution of that constituent to the initial total pressure. Each constituent contributes to the total pressure by an amount which is known as the *partial pressure* of the constituent. The relationship between the partial pressures of the constituents is expressed by Dalton's law, as follows:

> *The pressure of a mixture of gases is equal to the sum of the partial pressure of the constituents.*
>
> *The partial pressure of each constituent is that pressure which the gas would exert if it occupied alone that volume occupied by the mixture at the same temperature.*

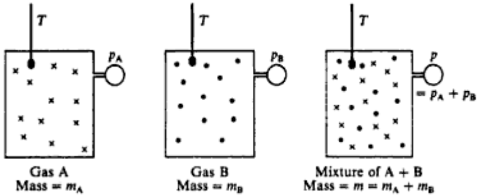


Fig. 6.1 Gas A mixing with gas B

This is expressed diagrammatically in Fig. 6.1. The gases A and B, originally occupying volume V at temperature T, are mixed in the third vessel which is of the same volume and is at the same temperature.

By the conservation of mass

$$m = m_A + m_B \tag{6.1}$$

By Dalton's law

$$p = p_A + p_B \tag{6.2}$$

Dalton's law is based on experiment and is found to be obeyed more accurately by gas mixtures at low pressures. As shown in Fig. 6.1 each constituent occupies the whole vessel. The example given in Fig. 6.1 and the relationships in equations (6.1) and (6.2) refer to a mixture of two gases, but the law can be extended to any number of gases,

i.e. $$m = m_A + m_B + m_C + \text{etc.} \quad \text{or} \quad m = \sum m_i \tag{6.3}$$

where m_i is the mass of a constituent.

Table 6.1 Analyses of air

Constituent	Chemical symbol	Analysis By volume (%)	Analysis By mass (%)	Molar mass (kg/kmol)
Oxygen	O_2	20.95	23.14	31.999
Nitrogen	N_2	78.09	75.53	28.013
Argon	Ar	0.93	1.28	39.948
Carbon dioxide	CO_2	0.03	0.05	44.010

Similarly

$$p = p_A + p_B + p_C + \text{etc.} \quad \text{or} \quad p = \sum p_i \tag{6.4}$$

where p_i is the partial pressure of a constituent.

Air is the most common mixture and since it will be referred to frequently, its composition is as given in Table 6.1. The mean molar mass of air is 28.96 kg/kmol, and the specific gas constant R is 0.2871 kJ/kg K. For approximate calculations the air is said to be composed of oxygen and 'atmospheric nitrogen' (see Table 6.2). Note: volumetric analysis is the analysis by volume; gravimetric analysis is the analysis by mass.

Table 6.2 Approximate analyses for air

	Analysis		Molar mass
Constituent	By volume (%)	By mass (%)	(kg/kmol)
Oxygen	21.0	23.3	32.0
Nitrogen	79.0	76.7	28.0

Example 6.1 A vessel of volume 0.4 m^3 contains 0.45 kg of carbon monoxide and 1 kg of air, at 15 °C. Calculate the partial pressure of each constituent and the total pressure in the vessel. The gravimetric analysis of air is to be taken as 23.3% oxygen and 76.7% nitrogen. Take the molar masses of carbon monoxide, oxygen and nitrogen as 28, 32 and 28 kg/kmol.

Solution

$$\text{Mass of oxygen present} = \frac{23.3}{100} \times 1 = 0.233 \text{ kg}$$

$$\text{Mass of nitrogen present} = \frac{76.7}{100} \times 1 = 0.767 \text{ kg}$$

From equation (2.9)

$$R = \frac{\tilde{R}}{\tilde{m}}$$

and from equation (2.6)

$$pV = mRT$$

Hence $p = \dfrac{m\tilde{R}T}{\tilde{m}V}$

or for a constituent

$$p_i = \frac{m_i \tilde{R} T}{\tilde{m}_i V}$$

The volume V is 0.4 m^3 and the temperature T is (15 + 273) = 288 K. Therefore we have for O_2

$$p_{O_2} = \frac{0.233 \times 8.3145 \times 288}{32 \times 0.4} = 43.59 \text{ kN/m}^2$$

$$= \frac{43.59 \times 10^3}{10^5} = 0.4359 \text{ bar}$$

for N_2 $$p_{N_2} = \frac{0.767 \times 8.3145 \times 288}{28 \times 0.4} = 163.99 \text{ kN/m}^2$$

$$= \frac{163.99 \times 10^3}{10^5} = 1.6399 \text{ bar}$$

for CO $p_{CO} = \dfrac{0.45 \times 8.3145 \times 288}{28 \times 0.4} = 96.21\ \text{kN/m}^2$

$$= \frac{96.21 \times 10^3}{10^5} = 0.9621\ \text{bar}$$

The total pressure in the vessel is given by equation (6.4)

$$p = \sum p_i = 0.436 + 1.640 + 0.962 = 3.038\ \text{bar}$$

i.e. Pressure in vessel = 3.038 bar

Dalton's law was reformulated by Gibbs to include a second statement on the properties of mixtures. The combined statement is known as the Gibbs–Dalton law, and is as follows:

The internal energy, enthalpy, and entropy, of a gaseous mixture are respectively equal to the sums of the internal energies, enthalpies, and entropies, of the constituents.

Each constituent has that internal energy, enthalpy, and entropy, which it would have if it occupied alone that volume occupied by the mixture at the temperature of the mixture.

This statement leads to the equations

$$mu = m_A u_A + m_B u_B + \text{etc.} \quad \text{or} \quad mu = \sum m_i u_i \tag{6.5}$$

and $$mh = m_A h_A + m_B h_B + \text{etc.} \quad \text{or} \quad mh = \sum m_i h_i \tag{6.6}$$

and $$ms = m_A s_A + m_B s_B + \text{etc.} \quad \text{or} \quad ms = \sum m_i s_i \tag{6.7}$$

6.2 Volumetric analysis of a gas mixture

The analysis of a mixture of gases is often quoted by volume as this is the most convenient for practical determinations.

Consider a volume V of a gaseous mixture at a temperature T, consisting of three constituents A, B, and C as in Fig. 6.2(a). Let each of the constituents be compressed to a pressure p equal to the total pressure of the mixture, and let the temperature remain constant. The partial volumes then occupied by the constituents will be V_A, V_B, and V_C. From equation (2.6) $pV = mRT$, therefore, referring to Fig. 6.2(a)

$$m_A = \frac{p_A V}{R_A T}$$

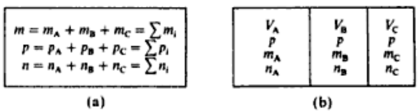


Fig. 6.2 Illustration of partial volume

and referring to Fig. 6.2(b)

$$m_A = \frac{pV_A}{R_A T}$$

Equating the two values for m_A, we have

$$\frac{p_A V}{R_A T} = \frac{pV_A}{R_A T}$$

i.e. $$p_A V = pV_A \quad \text{or} \quad V_A = \frac{p_A}{p} V$$

In general therefore,

$$V_i = \frac{p_i}{p} V \tag{6.8}$$

i.e. $$\sum V_i = \sum \frac{p_i V}{p} = \frac{V}{p} \sum p_i$$

Now from equation (6.4), $p = \sum p_i$, therefore

$$\sum V_i = V \tag{6.9}$$

Therefore the volume of a mixture of gases is equal to the sum of the volumes of the individual constituents when each exists alone at the pressure and temperature of the mixture. This is the statement of another empirical law, the law of partial volumes (sometimes called Amagat's law or Leduc's law).

The amount of substance is defined in section 2.3 and is given by equation (2.7) as $n = m/\tilde{m}$. By Avogadro's law, the amount of substance of any gas is proportional to the volume of the gas at a given pressure and temperature. Referring to Fig. 6.2(a), the volume V contains an amount of substance n of the mixture at p and T. In Fig. 6.2(b), the gas A occupies a volume V_A at p and T, and this volume contains an amount of substance n_A. Similarly there are amounts of substance n_B of gas B in volume V_B, and n_C of gas C in volume V_C. Now from equation (6.9),

$$\sum V_i = V \quad \text{or} \quad V_A + V_B + V_C = V$$

Therefore the total amount of substance in the vessel must equal the sum of the amounts of substance of the individual constituents,

i.e. $$n_A + n_B + n_C = n \quad \text{or} \quad n = \sum n_i \tag{6.10}$$

6.3 The molar mass and specific gas constant

For any gas in a gas mixture occupying a total volume of V at a temperature T, from equation (2.8) $pV = n\tilde{R}T$, and the definition of partial pressure, we have

$$p_i V = n_i \tilde{R} T \tag{6.11}$$

therefore

$$\sum(p_i V) = \sum(n_i \tilde{R} T)$$

i.e. $$V\sum p_i = \tilde{R}T\sum n_i$$

From equation (6.4), $p = \sum p_i$, hence,

$$pV = \tilde{R}T\sum n_i$$

Also from equation (6.10), $n = \sum n_i$, therefore

$$pV = n\tilde{R}T$$

The mixture therefore acts as a perfect gas, and this is the characteristic equation for the mixture. A molar mass is defined by the equation, $\tilde{m} = m/n$, where m is the mass of the mixture and n is the amount of substance of the mixture. Similarly, a specific gas constant is defined by the equation $R = \tilde{R}/\tilde{m}$. It can be assumed that a mixture of perfect gases obeys all the perfect gas laws.

To find the specific gas constant for the mixture in terms of the specific gas constants of the constituents, consider equation (2.6) both for the mixture and for a constituent,

i.e. $$pV = mRT \quad \text{and} \quad p_i V = m_i R_i T$$

Then $$\sum p_i V = \sum m_i R_i T$$

therefore

$$V\sum p_i = T\sum m_i R_i$$

Now from equation (6.4), $p = \sum p_i$, therefore

$$pV = T\sum m_i R_i \quad \text{or} \quad pV = mRT = T\sum m_i R_i$$

i.e. $$mR = \sum m_i R_i \quad \text{or} \quad R = \sum \frac{m_i}{m} R_i \qquad (6.12)$$

where m_i/m is the mass fraction of a constituent.

Example 6.2 The gravimetric analysis of air is 23.14% oxygen, 75.53% nitrogen, 1.28% argon, 0.05% carbon dioxide. Calculate the specific gas constant for air and the molar mass. Take the molar masses from Table 6.1 on p. 148.

Solution From equation (2.9), $R = \tilde{R}/\tilde{m}$, therefore

$$R_{O_2} = \frac{8.3145}{31.999} = 0.2598 \text{ kJ/kg K}$$

$$R_{N_2} = \frac{8.3145}{28.013} = 0.2968 \text{ kJ/kg K}$$

$$R_{A_r} = \frac{8.3145}{39.948} = 0.2081 \text{ kJ/kg K}$$

$$R_{CO_2} = \frac{8.3145}{44.010} = 0.1889 \text{ kJ/kg K}$$

Then using equation (6.12), $R = \sum (m_i/m)R_i$, we have

$$R = (0.2314 \times 0.2598) + (0.7553 \times 0.2968) + (0.0128 \times 0.2081) + (0.0005 \times 0.1889) = 0.2871 \text{ kJ/kg K}$$

i.e. Specific gas constant for air = 0.2871 kJ/kg K

From equation (2.9), $\tilde{m} = \tilde{R}/R$, therefore,

$$\tilde{m} = \frac{8.3145}{0.2871} = 28.960 \text{ kg/kmol}$$

i.e. Molar mass of air = 28.96 kg/kmol

When the approximate analysis for air is used (i.e. 23.3% O_2 and 76.7% N_2 by mass), it is usual practice to take R as 0.287 kJ/kg K and $\tilde{m}$ as 29 kg/kmol.

From equation (6.11), $p_i V = n_i \tilde{R} T$, and combining this with equation (2.8) applied to the mixture (i.e. $pV = n\tilde{R}T$), we have

$$\frac{p_i V}{pV} = \frac{n_i \tilde{R} T}{n \tilde{R} T}$$

i.e.
$$\frac{p_i}{p} = \frac{n_i}{n} \qquad (6.13)$$

This can be combined with equation (6.8), to give

$$\frac{p_i}{p} = \frac{n_i}{n} = \frac{V_i}{V} \qquad (6.14)$$

This is an important result which means that the molar analysis is identical with the volumetric analysis, and both are equal to the ratio of the partial pressure to the total pressure.

Another method of determining the molar mass is as follows. Applying the characteristic equation, (2.6), to each constituent and to the mixture we have $m_i = p_i V/R_i T$, and $m = pV/RT$.

From equation (6.3), $m = \sum m_i$, therefore

$$\frac{pV}{RT} = \sum \frac{p_i V}{R_i T} \quad \text{or} \quad \frac{p}{R} = \sum \frac{p_i}{R_i}$$

Using equation (2.9), $R = \tilde{R}/\tilde{m}$, and substituting, we have

$$\frac{p\tilde{m}}{\tilde{R}} = \sum \frac{p_i \tilde{m}_i}{\tilde{R}} \quad \text{or} \quad p\tilde{m} = \sum p_i \tilde{m}_i$$

i.e.
$$\tilde{m} = \sum \frac{p_i}{p} \tilde{m}_i \qquad (6.15)$$

Also using equation (6.14)

$$\tilde{m} = \sum \frac{V_i}{V} \tilde{m}_i \qquad (6.16)$$

and $\tilde{m} = \sum \frac{n_i}{n} \tilde{m}_i$ (6.17)

Example 6.3 The gravimetric analysis of air is 23.14% oxygen, 75.53% nitrogen, 1.28% argon, and 0.05% carbon dioxide. Calculate the analysis by volume and the partial pressure of each constituent when the total pressure is 1 bar.

Solution From equation (6.14) the analysis by volume, V_i/V, is the same as the fraction n_i/n. Also from equation (2.7), $n_i = m_i/\tilde{m}_i$, therefore considering 1 kg of mixture we have the tabular solution shown in Table 6.3.

Table 6.3 Solution for Example 6.3

Constituent	m_i (kg)	$\tilde{m}_i$ (kg/kmol)	$n_i = m_i/\tilde{m}_i$ (kmol)	$n_i/n = V_i/V$ (%)
Oxygen	0.2314	31.999	0.00723	$\frac{0.00723}{0.03452} \times 100 = 20.95$
Nitrogen	0.7553	28.013	0.02696	$\frac{0.02696}{0.03452} \times 100 = 78.09$
Argon	0.0128	39.948	0.00032	$\frac{0.00032}{0.03452} \times 100 = 0.93$
Carbon dioxide	0.0005	44.010	0.00001	$\frac{0.00001}{0.03452} \times 100 = 0.03$
		$n = \sum n_i =$	$\overline{0.03452}$	

From equation (6.14), $p_i/p = V_i/V = n_i/n$, therefore, $p_i = (n_i/n)p$, hence using the volume fractions from Table 6.3,

for O_2 $p_{O_2} = 0.2095 \times 1 = 0.2095$ bar

for N_2 $p_{N_2} = 0.7809 \times 1 = 0.7809$ bar

for Ar $p_{A_r} = 0.0093 \times 1 = 0.0093$ bar

for CO_2 $p_{CO_2} = 0.0003 \times 1 = 0.0003$ bar

Example 6.4 A mixture of 1 kmol CO_2 and 3.5 kmol of air is contained in a vessel at 1 bar and 15 °C. The volumetric analysis of air can be taken as 21% oxygen and 79% nitrogen. Calculate for the mixture:

(i) the masses of CO_2, O_2, and N_2, and the total mass;
(ii) the percentage carbon content by mass;
(iii) the molar mass and the specific gas constant for the mixture;
(iv) the specific volume of the mixture.

Take the molar masses of carbon, oxygen and nitrogen as 12 kg/kmol, 32 kg/kmol and 28 kg/kmol respectively.

Solution (i) From equation (6.14), $n_i = (V_i/V)n$, we have

$$n_{O_2} = 0.21 \times 3.5 = 0.735 \text{ kmol}$$

and $$n_{N_2} = 0.79 \times 3.5 = 2.765 \text{ kmol}$$

From equation (2.7), $m_i = n_i \tilde{m}_i$, therefore

$$m_{CO_2} = 1 \times 44 = 44 \text{ kg}$$

$$m_{O_2} = 0.735 \times 32 = 23.55 \text{ kg}$$

and $$m_{N_2} = 2.765 \times 28 = 77.5 \text{ kg}$$

$$\text{Total mass, } m = m_{O_2} + m_{N_2} + m_{CO_2}$$

$$= 23.55 + 77.5 + 44 = 145.05 \text{ kg}$$

(ii) The molar mass of carbon is 12 kg/kmol, therefore there are 12 kg of carbon present in 1 kmol of carbon dioxide,

i.e. $$\text{Percentage carbon in mixture} = \frac{12 \times 100}{145.05} = 8.27\% \text{ by mass}$$

(iii) From equation (6.10), $n = \sum n_i$, then

$$n = n_{CO_2} + n_{O_2} + n_{N_2} = 1 + 0.735 + 2.765 = 4.5 \text{ kmol}$$

Then using equation (6.17),

$$\tilde{m} = \sum \left(\frac{n_i}{n} \tilde{m}_i \right)$$

we have

$$\tilde{m} = \left(\frac{1}{4.5} \times 44 \right) + \left(\frac{0.735}{4.5} \times 32 \right) + \left(\frac{2.765}{4.5} \times 28 \right) = 32.2 \text{ kg/kmol}$$

i.e. Molar mass of mixture = 32.2 kg/kmol

From equation (2.9), $R = \tilde{R}/\tilde{m}$, we have

$$R = \frac{8.3145}{32.2} = 0.2581 \text{ kJ/kg K}$$

i.e. Specific gas constant for the mixture = 0.2581 kJ/kg K

(iv) From equation (2.5), $pv = RT$, therefore

$$v = \frac{RT}{p} = \frac{0.2581 \times 288 \times 10^3}{1 \times 10^5} = 0.7435 \text{ m}^3/\text{kg}$$

where $T = 15 + 273 = 288$ K.
i.e. specific volume of the mixture at 1 bar and 15 °C is 0.7435 m³/kg.

Example 6.5 A mixture of H_2 and O_2 is to be made so that the ratio of H_2 to O_2 is 2 to 1 by volume. Calculate the mass of O_2 required and the volume of the container, per kilogram of H_2, if the pressure and temperature are 1 bar and 15 °C respectively. Take the molar masses of hydrogen and oxygen as 2 kg/kmol and 32 kg/kmol.

Solution Let the mass of O_2 per kilogram of H_2 be x.

From equation (2.7), $n_i = m_i/\tilde{m}_i$, therefore

$$n_{H_2} = \frac{1}{2} = 0.5\ \text{kmol} \quad \text{and} \quad n_{O_2} = \frac{x}{32}\ \text{kmol}$$

From equation (6.14), $V_i/V = n_i/n$, therefore

$$\frac{V_{H_2}}{V_{O_2}} = \frac{n_{H_2}}{n_{O_2}} \quad \text{and} \quad \frac{V_{H_2}}{V_{O_2}} = 2 \quad \text{(given)}$$

i.e.
$$\frac{0.5}{x/32} = 2 \quad \text{therefore } x = \frac{32 \times 0.5}{2} = 8\ \text{kg}$$

i.e. Mass of oxygen per kilogram of hydrogen = 8 kg

The total amount of substance in the vessel per kilogram of H_2 is

$$n = n_{H_2} + n_{O_2} = 0.5 + \frac{x}{32} = 0.5 + \frac{8}{32} = 0.5 + 0.25 = 0.75\ \text{kmol}$$

Then from equation (2.8),

$$pV = n\tilde{R}T$$

therefore

$$V = \frac{0.75 \times 8.3145 \times 288 \times 10^3}{1 \times 10^5} = 17.96\ \text{m}^3$$

Example 6.6 A vessel contains a gaseous mixture of composition by volume, 80% H_2 and 20% CO. It is desired that the mixture should be made in the proportion 50% H_2 and 50% CO by removing some of the mixture and adding some CO. Calculate per kilomole of mixture the mass of mixture to be removed, and the mass of CO to be added. The pressure and temperature in the vessel remain constant during the procedure.

Take the molar mass of hydrogen and carbon monoxide as 2 kg/kmol and 28 kg/kmol.

Solution Since the pressure and temperature remain constant, then the amount of substance in the vessel remains the same throughout. Therefore the amount of substance of mixture removed is equal to the amount of substance of CO added.

Let x kg of mixture be removed and y kg of CO be added.

For the mixture, from equation (6.16)

$$\tilde{m} = \sum \frac{V_i}{V} \tilde{m}_i$$

therefore,

$$\tilde{m} = (0.8 \times 2) + (0.2 \times 28) = 7.2 \text{ kg/kmol}$$

Then using equation (2.7), $n = m/\tilde{m}$, we have

$$\text{amount of substance of mixture removed} = \frac{x}{7.2} \text{ kmol}$$

$$\text{amount of substance of CO added} = \frac{y}{28} \text{ kmol}$$

and $\quad x/7.2 = y/28$

From equation (6.14), $V_i/V = n_i/n$, therefore

$$\text{amount of substance of } H_2 \text{ in the mixture removed} = 0.8 \times \frac{x}{7.2} = \frac{x}{9} \text{ kmol}$$

and $\quad$ amount of substance of H_2 initially $= 0.8 \times 1 = 0.8$ kmol

Hence $\quad$ amount of substance of H_2 remaining in vessel $= \left(0.8 - \frac{x}{9}\right)$ kmol

But 1 kmol of the new mixture is 50% H_2 and 50% CO, therefore

$$0.8 - \frac{x}{9} = 0.5$$

i.e. $\quad x = (0.8 - 0.5) \times 9 = 2.7$ kg

i.e. $\quad$ Mass of mixture removed = 2.7 kg

Also since $x/7.2 = y/28$, therefore

$$y = \frac{28}{7.2} \times x = \frac{28 \times 2.7}{7.2} = 10.5 \text{ kg}$$

i.e. $\quad$ Mass of CO added = 10.5 kg

6.4 Specific heat capacities of a gas mixture

It was shown in section 6.1 that as a consequence of the Gibbs–Dalton law the internal energy of a mixture of gases is given by equation (6.5), $mu = \sum m_i u_i$. Also for a perfect gas from equation (2.14), $u = c_v T$. Hence substituting we have

$$mc_v T = \sum m_i c_{v_i} T$$

therefore

$$mc_v = \sum m_i c_{v_i}$$

or $$c_v = \sum \frac{m_i}{m} c_{v_i} \qquad (6.18)$$

Similarly from equation (6.6), $mh = \sum m_i h_i$, and from equation (2.18), $h = c_p T$, therefore

$$mc_p T = \sum m_i c_{p_i} T$$

therefore

$$mc_p = \sum m_i c_{p_i}$$

or $$c_p = \sum \frac{m_i}{m} c_{p_i} \tag{6.19}$$

From equations (6.18) and (6.19)

$$c_p - c_v = \sum \frac{m_i}{m} c_{p_i} - \sum \frac{m_i}{m} c_{v_i} = \sum \frac{m_i}{m}(c_{p_i} - c_{v_i})$$

Using equation (2.17), $c_{p_i} - c_{v_i} = R_i$, therefore

$$c_p - c_v = \sum \frac{m_i}{m} R_i$$

Also from equation (6.12), $R = \sum \frac{m_i}{m} R_i$, therefore for the mixture

$$c_p - c_v = R$$

The equations (2.20), (2.21), and (2.22), can be applied to a mixture of gases,

$$\gamma = \frac{c_p}{c_v}; \qquad c_v = \frac{R}{\gamma - 1}; \qquad c_p = \frac{\gamma R}{\gamma - 1}$$

It should be noted that γ must be determined from equation 2.20; there is no weighted mean expression as there is for R, c_v, and c_p.

Example 6.7 The gas in an engine cylinder has a volumetric analysis of 12% CO_2, 11.5% O_2, and 76.5% N_2. The temperature at the beginning of expansion is 1000 °C and the gas mixture expands reversibly through a volume ratio of 7 to 1, according to a law $pv^{1.25}$ = constant. Calculate the work done and the heat flow per unit mass of gas. The values of c_p for the constituents averaged over the temperature are as follows: c_p for CO_2 = 1.271 kJ/kg K; c_p for O_2 = 1.110 kJ/kg K; c_p for N_2 = 1.196 kJ/kg K.

Solution From equation (2.7) $m_i = n_i \tilde{m}_i$, therefore a conversion from volume fraction to mass fraction is as given in Table 6.4. Then using equation (6.19) and the mass fractions from Table 6.4

$$c_p = \sum \frac{m_i}{m} c_{p_i}$$

therefore

$$c_p = (0.174 \times 1.271) + (0.121 \times 1.110) + (0.705 \times 1.196)$$
$$= 1.199 \text{ kJ/kg K}$$

Table 6.4 Solution for Example 6.7

Constituent	n_i (kmol)	$\tilde{m}_i$ (kg/kmol)	$m_i = n_i\tilde{m}_i$ (kg)	m_i/m
Carbon dioxide	0.120	44	5.28	5.28/30.36 = 0.174
Oxygen	0.115	32	3.68	3.68/30.36 = 0.121
Nitrogen	0.765	28	21.40	21.40/30.36 = 0.705
			$m = \sum m_i =$ 30.36	

From equation (6.12), $R = \sum(m_i/m)R_i$, and from equation (2.9), $R_i = \tilde{R}/\tilde{m}_i$, therefore

$$R = \left(0.174 \times \frac{8.3145}{44}\right) + \left(0.121 \times \frac{8.3145}{32}\right) + \left(0.705 \times \frac{8.3145}{28}\right)$$

$$= 0.274 \text{ kJ/kg K}$$

Then from equation (2.17), $c_p - c_v = R$, we have

$$c_v = 1.199 - 0.274 = 0.925 \text{ kJ/kg K}$$

The work done per kg of gas can be obtained from equation (3.20)

$$W = \frac{R(T_2 - T_1)}{n - 1}$$

T_2 can be found using equation (3.28)

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1} = \left(\frac{1}{7}\right)^{0.25}$$

$$T_2 = \frac{T_1}{7^{0.25}} = \frac{1273}{1.627} = 782.6 \text{ K}$$

where $T_1 = 1000 + 273 = 1273$ K. Therefore

$$W = \frac{0.274(782.6 - 1273)}{1.25 - 1} = -537.5 \text{ kJ/kg}$$

i.e. Work done *by* the gas mixture = +537.5 kJ/kg

Also from equation (2.16), for unit mass, $u_2 - u_1 = c_v(T_2 - T_1)$, therefore

$$u_2 - u_1 = 0.925(782.6 - 1273) = -453.6 \text{ kJ/kg}$$

Finally, from the non-flow energy equation (1.4), $Q + W = (u_2 - u_1)$,

i.e. $Q - 537.5 = -453.6$ therefore $Q = 83.9$ kJ/kg

i.e. Heat supplied = 83.9 kJ/kg

Example 6.8 Calculate for the data of Example 6.7 the change of entropy per kilogram of mixture.

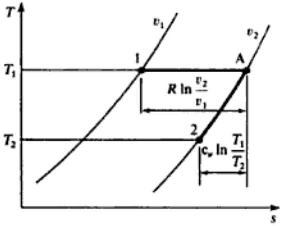


Fig. 6.3 T–s diagram for Example 6.8

Solution Referring to Fig. 6.3, the change of entropy between state 1 and state 2 can be found by imagining the process replaced by two other processes, 1 to A and A to 2. This method is described in section 4.4.

For isothermal process 1 to A, from equation (4.12)

$$s_A - s_1 = R \ln\left(\frac{v_2}{v_1}\right) = 0.274 \times \ln 7 = 0.533 \text{ kJ/kg K}$$

For the constant volume process A to 2

$$s_A - s_2 = c_v \int_2^A \frac{dT}{T} = c_v \ln\left(\frac{T_1}{T_2}\right) = 0.925 \times \ln\left(\frac{1273}{782.6}\right)$$

i.e. $\quad s_A - s_2 = 0.450 \text{ kJ/kg K}$

Then by subtraction,

$$s_2 - s_1 = 0.533 - 0.450 = 0.083 \text{ kJ/kg K}$$

It is often convenient to use amount of substance in problems on mixtures, and to define heat capacities expressed in terms of the amount of substance. These are known as *molar heat capacities*, and are denoted by $\tilde{c}_p$ and $\tilde{c}_v$. Molar heat capacities are defined as follows:

$$\tilde{c}_p = \tilde{m}c_p \quad \text{and} \quad \tilde{c}_v = \tilde{m}c_v \tag{6.20}$$

From equation (2.17), $c_p - c_v = R$, therefore

$$\tilde{c}_p - \tilde{c}_v = \tilde{m}c_p - \tilde{m}c_v = \tilde{m}R$$

Also from equation (2.9), $\tilde{m}R = \tilde{R}$, hence

$$\tilde{c}_p - \tilde{c}_v = \tilde{R} \tag{6.21}$$

From equation (2.15)

$$U = mc_vT$$

Also from equation (2.7), $m = n\tilde{m}$, and from equation (6.20), $\tilde{m}c_v = \tilde{c}_v$, therefore,

$$U = n\tilde{c}_vT \tag{6.22}$$

Similarly

$$H = n\tilde{c}_p T \tag{6.23}$$

By the Gibbs–Dalton law,

$$U = \sum U_i \quad \text{and} \quad H = \sum H_i$$

therefore

$$n\tilde{c}_v T = \sum n_i \tilde{c}_{v_i} T \quad \text{and} \quad n\tilde{c}_p T = \sum n_i \tilde{c}_{p_i} T$$

i.e.

$$\tilde{c}_v = \sum \frac{n_i}{n} \tilde{c}_{v_i} \tag{6.24}$$

and

$$\tilde{c}_p = \sum \frac{n_i}{n} \tilde{c}_{p_i} \tag{6.25}$$

Example 6.9 A producer gas has the following volumetric analysis: 29% CO, 12% H_2, 3% CH_4, 4% CO_2, 52% N_2. Calculate the values of $\tilde{c}_p$, $\tilde{c}_v$, c_p, and c_v for the mixture. The values of $\tilde{c}_p$ for the constituents are as follows: for CO, $\tilde{c}_p = 29.27$ kJ/kmol K; for H_2, $\tilde{c}_p = 28.89$ kJ/kmol K; for CH_4, $\tilde{c}_p = 35.80$ kJ/kmol K; for CO_2, $\tilde{c}_p = 37.22$ kJ/kmol K; for N_2, $\tilde{c}_p = 29.14$ kJ/kmol K.

The molar masses may be taken as follows: for H_2, 2 kg/kmol; for CH_4, 16 kg/kmol; for CO_2, 44 kg/kmol; for N_2, 28 kg/kmol.

Solution From equation (6.25),

$$\tilde{c}_p = \sum \frac{n_i}{n} \tilde{c}_{p_i}$$

Therefore,

$$\tilde{c}_p = (0.29 \times 29.27) + (0.12 \times 23.89) + (0.03 \times 35.80) + (0.04 \times 37.22) + (0.52 \times 29.14)$$

i.e.

$$\tilde{c}_p = 29.6707 \text{ kJ/kmol K}$$

From equation (6.21),

$$\tilde{c}_p - \tilde{c}_v = \tilde{R}$$

therefore

$$\tilde{c}_v = \tilde{c}_p - \tilde{R} = 29.6707 - 8.3145 = 21.3562 \text{ kJ/kmol K}$$

i.e.

$$\tilde{c}_v = 21.3562 \text{ kJ/kmol K}$$

The molar mass can be found from equation (6.17), i.e.

$$\tilde{m} = \sum \frac{n_i}{n} \tilde{m}$$

$$= (0.29 \times 28) + (0.12 \times 2) + (0.03 \times 16) + (0.04 \times 44) + (0.52 \times 28)$$

Table 6.5 Properties of some common gases at 300K

Gas	c_p (kJ/kg K)	c_v	γ	$\tilde{c}_p$ (kJ/kmol K)	$\tilde{c}_v$	$\tilde{m}$ (kg/kmol)	R (kJ/kg K)
Diatomic							
Carbon monoxide (CO)	1.0410	0.7442	1.399	29.158	20.845	28.010	0.2968
Hydrogen (H_2)	14.3230	10.1987	1.404	28.875	20.561	2.016	4.1243
Nitrogen (N_2)	1.0400	0.7432	1.399	29.134	20.819	28.013	0.2968
Oxygen (O_2)	0.9182	0.6584	1.395	29.382	21.068	31.999	0.2598
Monatomic							
Argon (Ar)	0.5203	0.3122	1.666	20.786	12.472	39.950	0.2081
Helium (He)	5.1930	3.1159	1.666	20.788	12.473	4.003	2.0771
Triatomic							
Carbon dioxide (CO_2)	0.8457	0.6568	1.288	37.219	28.906	44.010	0.1889
Sulphur dioxide (SO_2)	0.6448	0.5150	1.252	41.306	32.991	64.060	0.1298
Hydrocarbons							
Ethane (C_2H_6)	1.7668	1.4903	1.186	53.128	44.813	30.070	0.2765
Methane (CH_4)	2.2316	1.7132	1.303	35.795	27.480	16.040	0.5184
Propane (C_3H_8)	1.6915	1.5029	1.126	74.578	66.263	44.090	0.1886

i.e. $\tilde{m} = 25.16$ kg/kmol

Then from equation (6.20)

$$c_p = \frac{\tilde{c}_p}{\tilde{m}} = \frac{29.6707}{25.16} = 1.1793 \text{ kJ/kg K}$$

and

$$c_v = \frac{\tilde{c}_v}{\tilde{m}} = \frac{21.3562}{25.16} = 0.8488 \text{ kJ/kg K}$$

Values of γ, c_p, c_v, $\tilde{c}_p$, $\tilde{c}_v$, $\tilde{m}$, and R at 300 K for some of the more common gases are shown in Table 6.5.

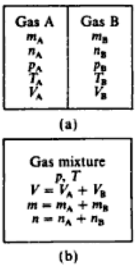


Fig. 6.4 Mixing of two gases initially separate

6.5 Adiabatic mixing of perfect gases

Consider two gases A and B separated from each other in a closed vessel by a thin diaphragm, as shown in Fig. 6.4(a). If the diaphragm is punctured or removed, then the gases mix as in Fig. 6.4(b), and each then occupies the total volume, behaving as if the other gas were not present. This process is equivalent to a free expansion of each gas, and is irreversible. The process can be simplified by the assumption that it is adiabatic; this means that the vessel is perfectly thermally insulated and therefore there will be an increase in entropy of the system. In section 4.5 it is shown that there is always an increase in entropy of a thermally isolated system which undergoes an irreversible process.

It is shown in section 3.5 that in a free expansion process the internal energy initially is equal to the internal energy finally. In this case, from equation (6.22)

$$U_1 = n_A\tilde{c}_{v_A}T_A + n_B\tilde{c}_{v_B}T_B$$

and $$U_2 = (n_A\tilde{c}_{v_A} + n_B\tilde{c}_{v_B})T$$

Extending this result to any number of gases,

$$U_1 = \sum n_i\tilde{c}_{v_i}T_i \quad \text{and} \quad U_2 = T\sum n_i\tilde{c}_v$$

Then $$U_1 = U_2$$

i.e. $$\sum n_i\tilde{c}_{v_i}T_i = T\sum n_i\tilde{c}_{v_i}$$

i.e. $$T = \frac{\sum n_i\tilde{c}_{v_i}T_i}{\sum n_i\tilde{c}_{v_i}} \tag{6.26}$$

Example 6.10 A vessel of 1.5 m^3 capacity contains oxygen at 7 bar and 40 °C. The vessel is connected to another vessel of 3 m^3 capacity containing carbon monoxide at 1 bar and 15 °C. A connecting valve is opened and the gases mix adiabatically. Calculate:

(i) the final temperature and pressure of the mixture;
(ii) the change in entropy of the system.

For oxygen, $\tilde{c}_v = 21.07$ kJ/kmol K; for carbon monoxide, $\tilde{c}_v = 20.86$ kJ/kmol K.

Solution (i) From equation (2.8)

$$n = \frac{pV}{\tilde{R}T}$$

Therefore

$$n_{O_2} = \frac{7 \times 10^5 \times 1.5}{8.3145 \times 313 \times 10^3} = 0.4035 \quad \text{where } T_{O_2} = 40 + 273 = 313 \text{ K}$$

and

$$n_{CO} = \frac{1 \times 10^5 \times 3}{8.3145 \times 288 \times 10^3} = 0.1253 \quad \text{where } T_{CO} = 15 + 273 = 288 \text{ K}$$

Before mixing

$$U_1 = \sum(n_i\tilde{c}_{v_i}T_i) = (0.4035 \times 21.07 \times 313) + (0.1253 \times 20.86 \times 288)$$

i.e. $$U_1 = 3413.8 \text{ kJ}$$

After mixing

$$U_2 = T\sum(n_i\tilde{c}_{v_i}) = T\{(0.4035 \times 21.07) + (0.1253 \times 20.86)\}$$

i.e. $$U_2 = 11.118 \times T$$

For adiabatic mixing, $U_1 = U_2$, therefore

$$3413.8 = 11.118 \times T \quad \text{therefore } T = \frac{3413.8}{11.118} = 307\ \text{K}$$

i.e. Temperature of mixture = 307 − 273 = 34 °C

From equation (2.8),

$$p = \frac{n\tilde{R}T}{V}$$

Therefore

$$p = \frac{(0.4035 + 0.1253) \times 8.3145 \times 307 \times 10^3}{(1.5 + 3.0) \times 10^5} = 3\ \text{bar}$$

i.e. Pressure after mixing = 3 bar

(ii) The change of entropy of the system is equal to the change of entropy of the oxygen plus the change of entropy of the carbon monoxide; this follows from the Gibbs–Dalton law.

Referring to Fig. 6.5, the change of entropy of the oxygen can be calculated by replacing the process undergone by the oxygen by the two processes 1 to A and A to 2.

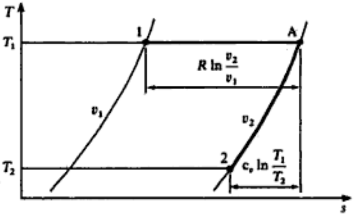


Fig. 6.5 *T–s* diagram for oxygen for Example 6.10

For an isothermal process from 1 to A, from equation (4.13), we have

$$s_A - s_1 = R \ln\left(\frac{V_A}{V_1}\right) \quad \text{or} \quad S_A - S_1 = mR \ln\left(\frac{V_A}{V_1}\right)$$

i.e. $$S_A - S_1 = n\tilde{R} \ln\left(\frac{V_A}{V_1}\right) = 0.4035 \times 8.3145 \times \ln\left(\frac{4.5}{1.5}\right) = 3.686\ \text{kJ/K}$$

At constant volume from A to 2,

$$s_A - s_2 = c_v \int_2^A \frac{dT}{T} = c_v \ln\left(\frac{T_1}{T_2}\right) \quad \text{or} \quad S_A - S_2 = mc_v \ln\left(\frac{T_1}{T_2}\right)$$

$$S_A - S_2 = n\tilde{c}_v \ln\left(\frac{T_1}{T_2}\right) = 0.4035 \times 21.07 \times \ln\left(\frac{313}{307}\right) = 0.1683\ \text{kJ/K}$$

therefore

$$S_2 - S_1 = 3.686 - 0.168 = 3.518 \text{ kJ/K}$$

Referring to Fig. 6.6, the change of entropy of the carbon monoxide can be found in a similar way to the above,

i.e. $$S_2 - S_1 = (S_B - S_1) + (S_2 - S_B)$$

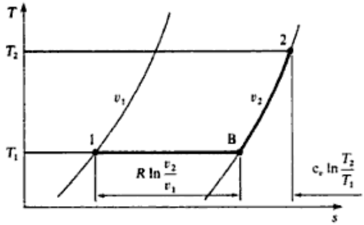


Fig. 6.6 *T–s* diagram for carbon monoxide for Example 6.10

therefore

$$S_2 - S_1 = n\tilde{R} \ln\left(\frac{V_B}{V_1}\right) + n\tilde{c}_v \ln\left(\frac{T_2}{T_1}\right)$$

$$= \left\{0.1253 \times 8.314 \times \ln\left(\frac{4.5}{3}\right)\right\}$$

$$+ \left\{0.1253 \times 20.86 \times \ln\left(\frac{307}{288}\right)\right\}$$

therefore

$$S_2 - S_1 = 0.590 \text{ kJ/K}$$

Hence the change of entropy of the whole system is given by

$$(S_2 - S_1)_{system} = (S_2 - S_1)_{O_2} + (S_2 - S_1)_{CO}$$

i.e. Change of entropy of system = 3.518 + 0.590 = 4.108 kJ/K

Another form of mixing is that which occurs when streams of fluid meet to form a common stream in steady flow. This is shown diagrammatically in Fig. 6.7. The steady-flow energy equation can be applied to the mixing section, and changes in kinetic and potential energy are usually negligible,

i.e. $$\dot{m}_A h_{A_1} + \dot{m}_B h_{B_1} + \dot{Q} + \dot{W} = \dot{m}_A h_{A_2} + \dot{m}_B h_{B_2}$$

For adiabatic flow $Q = 0$, and also $W = 0$ in this case, therefore

$$\dot{m}_A h_{A_1} + \dot{m}_B h_{B_1} = \dot{m}_A h_{A_2} + \dot{m}_B h_{B_2}$$

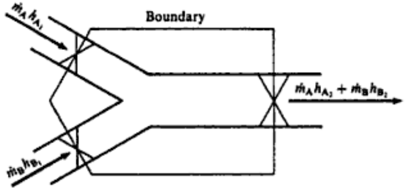


Fig. 6.7 Mixing of two fluid streams

From equation (2.18), $h = c_p T$, hence

$$\dot{m}_A c_{p_A} T_A + \dot{m}_B c_{p_B} T_B = \dot{m}_A c_{p_A} T + \dot{m}_B c_{p_B} T$$

For any number of gases this becomes

$$\sum(\dot{m}_i c_{p_i} T_i) = T \sum(\dot{m}_i c_{p_i})$$

i.e.

$$T = \frac{\sum(\dot{m}_i c_{p_i} T_i)}{\sum(\dot{m}_i c_{p_i})} \qquad (6.27)$$

Also, since from equation (6.20), $\tilde{c}_p = \tilde{m} c_p$, and $\tilde{m} = m/n$ from equation (2.7), then

$$n\tilde{c}_p = mc_p$$

Hence,

$$T = \frac{\sum(n_i \tilde{c}_{p_i} T_i)}{\sum(n_i \tilde{c}_{p_i})} \qquad (6.28)$$

Equation (6.27) or (6.28) represents one condition which must be satisfied in an adiabatic mixing process of perfect gases in steady flow. In a particular problem some other information must be known (e.g. the final pressure or specific volume) before a complete solution is possible. To find the change of entropy in such a process the procedure is as described above for adiabatic mixing by a free expansion. The entropy change of each gas is found and the results added together.

6.6 Gas and vapour mixtures

Consider a vessel of fixed volume which is maintained at a constant temperature as shown in Fig. 6.8(a). The vessel is evacuated and the absolute pressure is therefore zero. In Fig. 6.8(b) a small quantity of water is introduced into the vessel and it evaporates to occupy the whole volume. For a small quantity of water introduced, the pressure in the vessel will be less than the saturation pressure corresponding to the temperature of the vessel. At this condition of pressure and temperature the vessel will be occupied by superheated vapour.

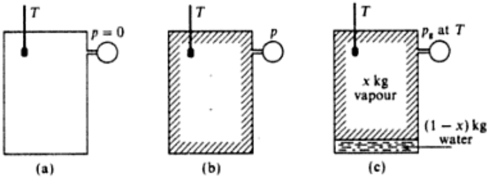


Fig. 6.8 Liquid introduced into an evacuated vessel

As more water is introduced the pressure increases and the water continues to evaporate until such a condition is reached that the volume can hold no more vapour. Any additional water introduced into the vessel after this will not evaporate but will exist as water, the condition being as in Fig. 6.8(c), which shows the vapour in contact with its liquid. Per kilogram of water introduced, the vessel can be thought of as containing either $(1 - x)$ kg of water plus x kg of dry saturated vapour, or as containing 1 kg of wet steam of dryness fraction x.

During the entire process of evaporation the temperature remains constant. If the temperature is now raised by the addition of heat, then more vapour will evaporate and the pressure in the vessel will increase. Eventually the vessel will contain a superheated vapour as before, but at a higher pressure and temperature.

The vessel in Fig. 6.8 is considered to be initially evacuated, but the water would evaporate in exactly the same way if the vessel contained a gas or a mixture of gases. As stated in the Gibbs–Dalton law, each constituent behaves as if it occupies the whole vessel at the temperature of the vessel. When a little water is sprayed into a vessel containing a gas mixture, then the vapour formed will exert the saturation pressure corresponding to the temperature of the vessel, and this is the partial pressure of the vapour in the mixture. (It must be remembered that the vapour is only saturated when it is in contact with its liquid.)

When a mixture contains a saturated vapour, then the partial pressure of the vapour can be found from tables at the temperature of the mixture. This assumes that a saturated vapour obeys the Gibbs–Dalton law; this is only a good approximation at low values of the total pressure.

Example 6.11

(a) A vessel of 0.3 m^3 capacity contains air at 0.7 bar and 75 °C. The vessel is maintained at this temperature as water is injected into it. Calculate the mass of water to be injected so that the vessel is just filled with saturated vapour.

(b) If injection now continues until a total mass of 0.7 kg of water is introduced, calculate the new total pressure in the vessel.

(c) The vessel is now heated until all the water in it just evaporates. Calculate:

(i) the total pressure for this condition;
(ii) the heat to be supplied.

Solution

(a) The subscripts s, w, and a will be used for steam, water, and air respectively.

At 75 °C, the saturation pressure $p_g = 0.3855$ bar and $v_g = 4.133\ m^3/kg$.

Therefore

$$\text{Mass of vapour occupying } 0.3\ m^3 = \frac{0.3}{4.133} = 0.0726\ kg$$

i.e. Mass of water to be injected = 0.0726 kg

(b) By Dalton's law, equation (6.2), $p = p_a + p_s$,

i.e. Total pressure in vessel = 0.7 + 0.3855 = 1.0855 bar

Note that the dry vapour is assumed to act as a perfect gas, hence the vapour and the air are assumed to occupy the same volume while each exerts its partial pressure.

When a total mass of 0.7 kg of water has been injected into the vessel it will exist partly as dry saturated vapour (say m_s kg) and partly as water (say m_w kg, where $m_w = (0.7 - m_s)$) in such proportions that the mixture occupies the total volume of 0.3 m³, therefore

$$(m_s \times 4.133) + (0.7 - m_s) \times 0.001\,026 = 0.3$$

where 0.001 026 m³/kg is the specific volume of water.

i.e. $m_s(4.133 - 0.001\,026) = 0.3 - (0.7 \times 0.001\,026)$

$$4.132 \times m_s = 0.2993 \quad \text{therefore } m_s = \frac{0.2993}{4.132} = 0.0724\ kg$$

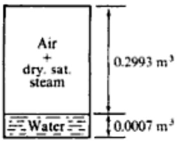


Fig. 6.9 Conditions in vessel for part (b) of Example 6.11

Note that the volume of water is negligibly small compared to the volume of the air–vapour mixture

$$m_w = 0.7 - 0.0724 = 0.6276\ kg$$

The volume occupied by the dry vapour = 0.0724 × 4.133 = 0.2993 m³. The vessel may be assumed to contain air, dry saturated steam, and water, as shown in Fig. 6.9.

Since $T_1 = T_2$, we can write

$$p_{a_1} V_{a_1} = p_{a_2} V_{a_2}$$

therefore

$$p_{a_2} = 0.7 \times \frac{0.3}{0.2993} = 0.7017\ bar$$

i.e. Total pressure = $p_a + p_s$ = 0.7017 + 0.3855 = 1.0872 bar

(c) (i) The water can be completely evaporated by raising the temperature to a value such that the total volume is occupied by saturated steam and air. This condition is reached when the steam has a specific volume v_g, such that, $0.7 \times v_g = 0.3$,

i.e. $$v_g = \frac{0.3}{0.7} = 0.4286\ m^3/kg$$

From tables the saturation pressure at $v_g = 0.4286\ m^3/kg$ is, by interpolating,

$$p = 4 + \left(\frac{0.4623 - 0.4286}{0.4623 - 0.4139}\right) \times (4.5 - 4.0) = 4.35\ \text{bar}$$

The air now occupies the volume of $0.3\ m^3$ while exerting its partial pressure p_{a_2} at the new temperature. The new temperature is that saturation temperature corresponding to the pressure of 4.35 bar.

From tables by interpolation at 4.35 bar

$$t = 143.6 + \frac{0.35}{0.5} \times 4.3 = 146.6\,^\circ\text{C} \quad \text{therefore } T = 146.6 + 273 = 419.6\ \text{K}$$

Then for the air

$$\frac{p_{a_2}}{T_{a_2}} = \frac{p_{a_1}}{T_{a_1}} \quad \text{therefore } p_{a_2} = 0.7 \times \frac{419.6}{348} = 0.8439\ \text{bar}$$

where $T_{a_1} = 75 + 273 = 348$ K,

i.e. Total pressure in vessel = 4.35 + 0.8439 = 5.194 bar

(ii) From the non-flow energy equation

$$Q + W = U_2 - U_1$$

In this case $W = 0$, therefore $Q = (U_2 - U_1)$. Then

$$U_1 = m_{w_1}u_{w_1} + m_a u_{a_1} + m_{s_1}u_{s_1}$$

and

$$U_2 = m_a u_{a_2} + m_{s_2}u_{s_2}$$

For a perfect gas, from equation (2.15), $U = mc_v T$, therefore

$$Q = m_{s_2}u_{s_2} - m_{s_1}u_{s_1} - m_{w_1}u_{w_1} + m_a c_v(T_2 - T_1)$$

Then taking u_s and u_w from tables, and substituting for

$$m_a = \frac{p_a V}{R_a T} = \frac{0.7 \times 10^5 \times 0.3}{0.287 \times 348 \times 10^3} = 0.2102\ \text{kg}$$

we have

$$Q = (0.7 \times 2556.8) - (0.0724 \times 2475.3)$$
$$- (0.6276 \times 313.5) + 0.2102 \times 0.718(419.6 - 348)$$

i.e. Heat supplied = 1789.8 − 179.2 − 196.8 + 10.8 = 1424.6 kJ

Example 6.12 The products of combustion of a fuel have a volumetric analysis of CO_2 8%, H_2O 15%, O_2 5.5%, and N_2 71.5%. If the total pressure is 1.4 bar, calculate the temperature to which the gas must be cooled at constant pressure for condensation of the H_2O just to commence.

Solution From equation (6.14)

$$\text{Partial pressure of } H_2O = \frac{n_i}{n} \times p = 0.15 \times 1.4 = 0.21 \text{ bar}$$

The saturation temperature corresponding to 0.21 bar is 61.15 °C, i.e. the gas must be cooled to 61.15 °C for condensation of the H_2O to commence.

6.7 The steam condenser

The condenser is an essential part of any steam power plant. The temperature at which condensation occurs is in the order of 25 to 40 °C, the corresponding saturation pressures being 0.031 66 and 0.073 75 bar. The shell and tube type condenser is a vessel in which this low pressure is maintained by a pump, and the steam condenses on the outside of tubes through which cold water is flowing. This type is called a surface condenser. There will be some leakage of air into the condenser, both through the glands and from air dissolved in the feedwater which comes out of solution and is carried into the condenser by the steam. This air impairs the condenser performance since it reduces the heat transfer from the steam to the cooling water.

The condenser contains a mixture of steam, air, and water. The air must be pumped out of the condenser continually to maintain the vacuum, and the air which is pumped out carries with it some of the steam. This results in a loss of feedwater to the boiler. This loss has to be made up by the addition of cold water. Another effect of the presence of air is that the condensate is undercooled (i.e. cooled to a temperature below the saturation temperature), which means that more heat has to be supplied to the water in the boiler than if no undercooling had occurred.

The pressure in the condenser is approximately constant throughout and steam and air enter the condenser in fixed proportions when steady conditions prevail. As some of the steam is condensed the partial pressure of the remaining steam decreases, and hence the partial pressure of the air increases to maintain the same total pressure. At reduced partial pressures the steam has a saturation temperature which is below that of the incoming steam. Hence condensation proceeds at progressively lower temperatures.

Some condensers are designed to make up for the deficiencies of the simple type. Two of these are indicated in Figs 6.10(a) and 6.10(b). In Fig. 6.10(a) most of the condensation is carried out on the main bank of tubes and the air is drawn over another, smaller, bank which is shielded from the main bank and is called the air cooler. Here further condensation takes place at a lower temperature with a subsequent saving in feedwater, and a smaller pump is required for the condenser. In Fig. 6.10(b) the air-cooling tubes are in the centre of the condenser and the air is pumped away from this region. The incoming steam passes all round the bank of tubes and some is drawn upwards to the centre. In doing so it meets the undercooled condensate which has been formed and reheates it, hence reducing the amount of undercooling.

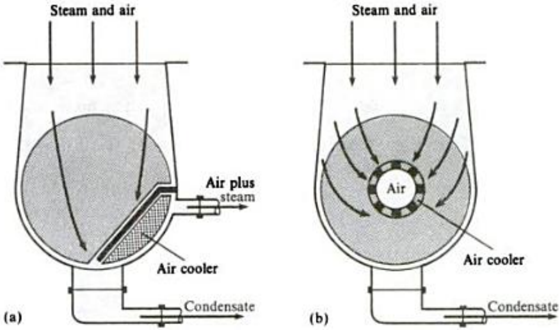


Fig. 6.10 Two arrangements for air extraction in a condenser

Example 6.13 A surface condenser is required to deal with 20000 kg of steam per hour, and the air leakage is estimated at 0.3 kg per 1000 kg of steam. The steam enters the condenser dry saturated at 38 °C. The condensate is extracted at the lowest point of the condenser at a temperature of 36 °C. The condensate loss is made up with water at 7 °C. It is required to find the saving in condensate and the saving in heat supplied in the boiler, by fitting a separate air extraction pump which draws the air over an air cooler. Assume that the air leaves the cooler at 27 °C. The pressure in the condenser can be assumed to remain constant.

Solution At entry, mass of air per kilogram of steam = 0.3/1000 kg.

At 38 °C the saturation pressure is 0.066 24 bar and $v_g = 21.63\ \mathrm{m^3/kg}$.

For 1 kg of steam the volume is 21.63 m³, and this must be the volume occupied by 0.3/1000 kg of air when exerting its partial pressure,

$$\text{Partial pressure of air} = \frac{m_a R_a T}{V} = \frac{0.3 \times 0.287 \times 311 \times 10^3}{1000 \times 21.63 \times 10^5}$$

$$= 1.2 \times 10^{-5}\ \text{bar}$$

This is negligibly small and may be neglected.

Condensate extraction: the saturation pressure at 36 °C is 0.0594 bar, and $v_g = 23.97\ \mathrm{m^3/kg}$. The total pressure in the condenser is 0.066 24 bar, hence

$$0.066\,24 = 0.0594 + p_a \quad \text{therefore } p_a = 0.006\,84\ \text{bar}$$

The mass of air removed per hour is

$$\frac{20\,000 \times 03}{1000} = 6\ \text{kg/h}$$

Hence the volume of air removed per hour is

$$\frac{mRT}{p} = \frac{6 \times 0.287 \times 309 \times 10^3}{0.006\,84 \times 10^5} = 778\ \mathrm{m^3/h}$$

The mass of steam associated with the air removed is therefore given by

$$\frac{778}{23.97} = 32.45 \text{ kg/h}$$

Separate extraction: the saturation pressure at 27 °C is 0.035 64 bar and $v_g = 38.81 \text{ m}^3/\text{kg}$.

The air partial pressure is 0.066 24 − 0.035 64 = 0.0306 bar. Therefore the volume of air removed is

$$\frac{mRT}{p} = \frac{6 \times 0.287 \times 300 \times 10^3}{0.0306 \times 10^5} = 168.9 \text{ m}^3/\text{h}$$

therefore

$$\text{Steam removed} = \frac{168.9}{38.81} = 4.35 \text{ kg/h}$$

Hence the saving in condensate by using the separate extraction method is given by 32.45 − 4.35 = 28.1 kg/h.

Also, the saving in heat to be supplied in the boiler is approximately 28.1 × 4.182(36 − 7)/3600 = 0.95 kW, where the mean specific heat of the water is 4.182 kJ/kg K.

Example 6.14 For the data of Example 6.13 calculate the percentage reduction in air pump capacity by using the separate extraction method. If the temperature rise of the cooling water is 5.5 K, calculate the mass flow of cooling water required.

Solution

$$\text{Air pump capacity without air cooler} = 778 \text{ m}^3/\text{h}$$

$$\text{Air pump capacity with the air cooler} = 168.9 \text{ m}^3/\text{h}$$

Therefore

$$\text{Percentage reduction in capacity} = \left(\frac{778 - 168.9}{778}\right) \times 100$$

$$= 78.3\%$$

The system to be analysed is shown in Fig. 6.11. Let suffixes s, a, and c denote steam, air, and condensate respectively. Applying the steady-flow energy equation and neglecting changes in kinetic energy, we have

$$Q + \dot{m}_{s_1}h_{s_1} + \dot{m}_{a_1}h_{a_1} = (\dot{m}_{s_2}h_{s_2} + \dot{m}_{a_2}h_{a_2}) + \dot{m}_c h_c$$

$$\dot{m}_{a_1} = \dot{m}_{a_2} = 6 \text{ kg/h}; \qquad \dot{m}_{s_1} = 20\,000 \text{ kg/h}; \qquad \dot{m}_{s_2} = 4.35 \text{ kg/h}$$

$$\dot{m}_c = 20\,000 - 4.35 = 20\,000 \text{ kg/h approx.}$$

$$h_{a_1} - h_{a_2} = c_p(T_1 - T_2) \quad \text{(from equation (2.18))}$$

i.e.

$$Q = (4.35 \times 2550.3) + \{6 \times 1.005(38 - 27)\}$$
$$+ (20\,000 \times 150.7) - (20\,000 \times 2570.1)$$

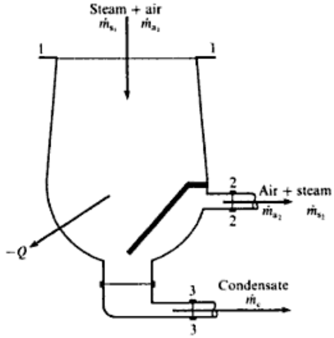


Fig. 6.11 Condenser system for Example 6.14

therefore

$$Q = -48.38 \times 10^6 \text{ kJ/h} = -13\,439 \text{ kW}$$

where $h_c = h_f$ at 36 °C = 150.7 kJ/kg,

i.e. Heat rejected = +13 439 kW

The mass of cooling water required for a 5.5 K rise in temperature is $48.38 \times 10^6/(5.5 \times 4.182) = 2.1 \times 10^6$ kg/h, approximately.

Unless a very large natural supply of cooling water is available for large steam plants, means must be found to cool the cooling water after use. This can be done by passing the cooling water through a cooling tower; cooling towers are considered in Section 15.5.

Problems

(For values of $\tilde{m}$, R, $\tilde{c}_p$, $\tilde{c}_v$, etc. which are necessary in the following problems, refer to Table 6.5 on p. 162; take values of $\tilde{m}$ to the nearest whole number.)

6.1 A mixture of carbon monoxide and oxygen is to be prepared in the proportion of 7 kg to 4 kg in a vessel of 0.3 m³ capacity. If the temperature of the mixture is 15 °C, determine the pressure to which the vessel is subject. If the temperature is raised to 40 °C, what will then be the pressure in the vessel?

(29.94 bar; 32.54 bar)

6.2 For the mixture of Problem 6.1 calculate the volumetric analysis, the molar mass and the characteristic gas constant. Calculate also the total amount of substance in the mixture.

(33.3% O_2; 66.7% CO; 29.3 kg/kmol; 0.283 kJ/kg K; 0.375 kmol)

6.3 An exhaust gas is analysed and is found to contain, by volume, 78% N_2, 12% CO_2, and 10% O_2. What is the corresponding gravimetric analysis? Calculate the molar mass of the mixture, and the density if the temperature is 550 °C and the total pressure is 1 bar.

(72% N_2, 17.4% CO_2, 10.6% O_2; 30.33 kg/kmol; 0.443 kg/m^3)

6.4 A vessel of 3 m^3 capacity contains a mixture of nitrogen and carbon dioxide, the analysis by volume showing equal quantities of each. The temperature is 15 °C and the total pressure is 3.5 bar. Determine the mass of each constituent.

(6.14 kg N_2; 9.65 kg CO_2)

6.5 The mixture of Problem 6.4 is to be changed so that it is 70% CO_2 and 30% N_2 by volume. Calculate the mass of mixture to be removed and the mass of CO_2 to be added to give the required mixture at the same temperature and pressure as before.

(6.31 kg; 7.72 kg CO_2)

6.6 In a mixture of methane (CH_4) and air there are three volumes of oxygen to one volume of methane. From initial conditions of 1 bar and 95 °C the gas is compressed reversibly and adiabatically through a volume ratio of 5. Assuming that air contains only oxygen and nitrogen, calculate:

(i) the values of c_p, c_v, $\tilde{c}_p$, $\tilde{c}_v$, R and γ for the mixture;
(ii) the final pressure and temperature of the mixture;
(iii) the work input per unit mass of mixture.

(1.057 kJ/kg K, 0.761 kJ/kg K, 29.60 kJ/kmol K, 21.31 kJ/kmol K, 0.297 kJ/kg K, 1.389; 9.35 bar, 415.3 °C; 243.8 kJ/kg)

6.7 A mixture is made up of 25% N_2, 35% O_2, 20% CO_2, and 20% CO by volume. Calculate:

(i) the molar mass of the mixture;
(ii) $\tilde{c}_p$ and $\tilde{c}_v$ for the mixture;
(iii) γ for the mixture;
(iv) the partial pressure of each constituent when the total pressure is 1.5 bar;
(v) the density of the mixture at 1.5 bar and 15 °C.

(32.6 kg/kmol; 30.84, 22.53 kJ/kmol K; 1.37; 0.375, 0.525, 0.3, 0.3 bar; 2.04 kg/m^3)

6.8 Two vessels are connected by a pipe in which there is a valve. One vessel of 0.3 m^3 contains air at 7 bar and 32 °C, and the other of 0.03 m^3 contains oxygen at 21 bar and 15 °C. The valve is opened and the two gases are allowed to mix. Assuming that the system is well lagged, calculate:

(i) the final temperature of the mixture;
(ii) the final pressure of the mixture;
(iii) the partial pressure of each constituent;
(iv) the volumetric analysis of the mixture;
(v) the values of c_p, c_v, R, $\tilde{m}$, and γ for the mixture;
(vi) the increase of entropy of the system per kilogram of mixture;
(vii) the change in internal energy and enthalpy of the mixture per kilogram if the vessel is cooled to 10 °C.

Assume that air consists only of oxygen and nitrogen.

(27.9 °C; 8.27 bar; 3.31, 4.96 bar; 60% N_2, 40% O_2; 0.987, 0.709 kJ/kg K; 0.278 kJ/kg K; 29.91 kg/mol; 1.392; 0.183 kJ/kg K; 12.69, 17.67 kJ/kg)

6.9 Air and carbon monoxide are mixed in the proportion 3 to 1 by mass. The CO is supplied at 4 bar and 15 °C, and the air is supplied at 7 bar and 32 °C. The two constituents are passed in steady flow through non-return valves to mix adiabatically at a pressure of 1 bar. Calculate:

(i) the final temperature of the mixture;

(ii) the partial pressure of each constituent of the mixture;
(iii) the increase of entropy per kilogram of mixture;
(iv) the volume flow of mixture for a flow of 1 kg/min of CO;
(v) the velocity of the mixture if the area of the pipe downstream of the mixing section is 0.1 m^2

(27.7 °C; 0.256, 0.156, 0.588 bar; 0.689 kJ/kg K; 3.49 m^3/min; 0.582 m/s)

6.10 Ammonia in air is a toxic mixture when the ammonia is 0.55% by volume. Calculate how much leakage from an ammonia compressor can be tolerated per 1000 m^3 of space. The pressure is 1 bar and the temperature is 15 °C. The molar mass of ammonia (NH_3) is 17 kg/kmol, and it may be assumed to act as a perfect gas in this case.

(3.91 kg)

6.11 A vessel of 0.3 m^3 capacity contains a mixture of air and steam which is 0.75 dry. If the pressure is 7 bar and the temperature is 116.9 °C, calculate the mass of water present, the mass of dry saturated vapour, and the mass of air.

(0.102 kg; 0.307 kg; 1.394 kg)

6.12 If the vessel of problem 6.11 is cooled to 100 °C calculate:
(i) the mass of vapour condensed;
(ii) the final pressure in the vessel;
(iii) the heat rejected.

(0.128 kg; 5.99 bar; 297 kJ)

6.13 A closed vessel of volume 3 m^3 contains air saturated with water vapour at 38 °C and a vacuum pressure of 660 mm of mercury. The vacuum falls to 560 mm of mercury and the temperature falls to 26.7 °C. Calculate the mass of air that has leaked in and the quantity of vapour that has condensed. Take the barometric pressure as 760 mm Hg.

(0.583 kg; 0.0627 kg)

6.14 The air in a cylinder fitted with a piston is saturated with water vapour. The volume is 0.3 m^3, the pressure is 3.5 bar and the temperature is 60.1 °C. The mixture is compressed to 5.5 bar, the temperature remaining constant. Calculate:
(i) the masses of air and vapour present initially;
(ii) the mass of vapour condensed on compression.

(1.036 kg; 0.0392 kg; 0.0148 kg)

6.15 The temperature in a vessel is 36 °C and the proportion by mass of air to dry saturated steam is 0.1. What is the pressure in the vessel in bar and in mm of mercury vacuum? The barometric pressure is 760 mm Hg.

(0.0631 bar; 712.7 mm Hg)

6.16 A surface condenser is fitted with separate air and condensate outlets. A portion of the cooling surface is screened from the incoming steam and the air passes over these screened tubes to the air extraction and becomes cooled below the condensate temperature. The condenser receives 20 000 kg/h of steam dry saturated at 36.2 °C. At the condensate outlet the temperature is 34.6 °C, and at the air extraction the temperature is 29 °C. The volume of air plus vapour leaving the condenser is 3.8 m^3/min. Assuming constant pressure throughout the condenser calculate:
(i) the mass of air removed per 10 000 kg of steam;
(ii) the mass of steam condensed in the air cooler per minute;
(iii) the heat rejected to the cooling water.
Neglect the partial pressure of the air at inlet to the condenser.

(2.63 kg; 0.5 kg/min; 13 451 kW)

7

Combustion

The ideal cycles previously considered use fluids which remain unchanged chemically as they pass through the various processes of the cycle. In practical engines and power plants the source of heat is the chemical energy of substances called fuels. This energy is released during the chemical reaction of the fuel with oxygen. The fuel elements combine with oxygen in an oxidation process which is rapid and is accompanied by the evolution of heat.

The combustion process takes place in a controlled manner in some form of combustion chamber after initiation of combustion by some means (e.g. in a petrol engine the combustion is started by an electric spark). The most convenient source of oxygen supply is that of the atmosphere which contains oxygen and nitrogen and traces of other gases. Normally no attempt is made to separate out the oxygen from the atmosphere, and the nitrogen, etc. accompanies the oxygen into the combustion chamber.

Nitrogen does not oxidize easily and is inert as far as the combustion process is concerned, but it acts as a moderator in that it absorbs some of the heat of combustion and so limits the maximum temperature reached. As combustion proceeds the oxygen is progressively used up and the proportion of nitrogen plus products of combustion to the available oxygen increases. For a given amount of fuel there is a definite amount of oxygen, and therefore air, which is required for the complete combustion of a given fuel. To ensure complete combustion it is usual to supply air in excess of the amount required for chemically correct combustion. The oxygen not consumed in the reaction passes into the exhaust with the products of combustion.

Internal-combustion engines are run on liquid fuels which are grouped as 'petrols' (known as gasoline in the USA), and diesel oils, or gaseous fuels, commonly used in combined heat and power plant; gas turbines are run mainly on kerosene although natural gas is now commonly used. Engines burning solid fuels have been built but are mainly experimental. In the many and diverse applications in industry, solid, liquid, and gaseous fuels are used. Generalization is not possible on the selection of fuels, since the fuel used and its necessary firing equipment depend on the particular application, the practical circumstances, and economic considerations.

7.1 Basic chemistry

It is necessary to understand the construction and use of chemical formulae, before combustion problems can be considered. This involves elementary concepts which have been met before by most students, but a brief explanation will be given here.

Atoms. Chemical elements cannot be divided indefinitely and the smallest particle which can take part in a chemical change is called an atom. If an atom is split as in a nuclear reaction, the divided atom does not retain the original chemical properties.

Molecules. Elements are seldom found to exist naturally as single atoms. Some elements have atoms which exist in pairs, each pair forming a molecule (e.g. oxygen), and the atoms of each molecule are held together by strong inter-atomic forces. The isolation of a molecule of oxygen would be tedious, but possible; the isolation of an atom of oxygen would be a different prospect.

The molecules of some substances are formed by the mating up of atoms of different elements. For example, water (which is chemically the same as ice and steam) has a molecule which consists of two atoms of hydrogen and one atom of oxygen.

The atoms of different elements have different masses and these values are important when a quantitative analysis is required. The actual masses are infinitesimally small, and the ratios of the masses of atoms are used. These ratios are given by the relative atomic masses quoted on a scale which defines the atomic mass of isotope 12 of carbon as 12 (see Ch. 2, p. 40). The *relative atomic mass* of a substance is the mass of a single entity of the substance relative to a single entity of carbon-12. Table 7.1 gives the relative atomic masses of some common elements rounded off to give values accurate enough for most purposes.

Table 7.1 Relative atomic and molecular masses of some common substances

Element	Oxygen	Hydrogen	Carbon	Sulphur	Nitrogen
Atomic symbol	O	H	C	S	N
Relative atomic mass	16	1	12	32	14
Molecular grouping	O_2	H_2	C	S	N_2
Relative molecular mass (rounded)	32	2	12	32	28
Accurate values	31.999	2.016	12	32.030	28.013

Relative molecular masses are based on the relative masses of the atoms which constitute the molecule. In chemical formulae one atom of an element is represented by the symbol for the element, i.e. an atom of hydrogen is written as H, and other examples are given in Table 7.1. If a substance exists as a molecule containing, say, two atoms, as for hydrogen, it is written as H_2. Two molecules of hydrogen is written as $2H_2$, etc. Table 7.1 includes relative molecular masses, rounded off, and, for comparison, the accurate values.

Table 7.2 Compounds and their relative molecular masses

Compound	Formula	Relative molecular mass
Water, steam	H_2O	$(2 \times 1) + (1 \times 16) = 18$
Carbon monoxide	CO	$(1 \times 12) + (1 \times 16) = 28$
Carbon dioxide	CO_2	$(1 \times 12) + (2 \times 16) = 44$
Sulphur dioxide	SO_2	$(1 \times 32) + (2 \times 16) = 64$
Methane	CH_4	$(1 \times 12) + (4 \times 1) = 16$
Ethane	C_2H_6	$(2 \times 12) + (6 \times 1) = 30$
Propane	C_3H_8	$(3 \times 12) + (8 \times 1) = 44$
n-Butane	C_4H_{10}	$(4 \times 12) + (10 \times 1) = 58$
Ethylene	C_2H_4	$(2 \times 12) + (4 \times 1) = 28$
Propylene	C_3H_6	$(3 \times 12) + (6 \times 1) = 42$
n-Pentane	C_5H_{12}	$(5 \times 12) + (12 \times 1) = 72$
Benzene	C_6H_6	$(6 \times 12) + (6 \times 1) = 78$
Toluene	C_7H_8	$(7 \times 12) + (8 \times 1) = 92$
n-Octane	C_8H_{18}	$(8 \times 12) + (18 \times 1) = 114$

Some of the other substances met in combustion work are given in Table 7.2 to illustrate the calculations of the relative molecular mass from the relative atomic masses of the elements.

7.2 Fuels

The most important fuel elements are carbon and hydrogen, and most fuels consist of these and sometimes a small amount of sulphur. The fuel may contain some oxygen and a small quantity of incombustibles (e.g. water vapour, nitrogen, or ash).

Coal is the most important solid fuel and the various types are divided into groups according to their chemical and physical properties. An accurate chemical analysis by mass of the important elements in the fuel is called the *ultimate analysis*, the elements usually included being carbon, hydrogen, nitrogen, and sulphur. The main groups are shown in Table 7.3, and their ultimate analyses are given. The analyses are typical but may vary from one sample to another within the group, and hence can be taken only as a guide. Another analysis of coal, also shown in Table 7.3 called the *proximate analysis*, gives the percentages of inherent moisture, volatile matter, and combustible solid (called fixed carbon). The fixed carbon is found as a remainder by deducting the percentages of the other quantities. The volatile matter includes the water derived from the chemical decomposition of the coal (not to be confused with free, or inherent moisture), the combustible gases (e.g. hydrogen, methane, ethane, etc.), and tar (i.e. a complex mixture of hydrocarbons and other organic compounds). The procedures for both analyses are given in ref. 7.1; see also ref. 7.2 and a concise treatment in ref. 7.3.

Most liquid fuels are hydrocarbons which exist in the liquid phase at atmospheric conditions. Petroleum oils are complex mixtures of sometimes hundreds of different fuels, but the necessary information to the engineer is the relative proportions of carbon, hydrogen, etc. as given by the ultimate analysis. Table 7.4 gives the ultimate analyses of some liquid fuels.

Table 7.3 Analysis of solid fuels

Ultimate analysis

Fuel	Rank	Percentage by mass of dry fuel					
		C	H	O	N	S	Mineral matter
Anthracite	101	88.2	2.7	1.7	1.0	1.2	5.2
Medium-rank coal	401	81.8	4.9	4.4	1.8	1.9	5.2
Low-rank coal	902	75.0	4.6	10.7	1.6	2.1	6.0
Coke	—	90.0	0.4	1.9	—	—	7.7

Proximate analysis on a mineral matter-free basis

Fuel	Percentage by mass of fuel		
	Inherent moisture	Volatile matter	Fixed carbon
Anrhtacite	2	6	92
Medium-rank coal	3	39	58
Low-rank coal	10	42	48

Table 7.4 Analyses of liquid fuels

Fuel	Carbon	Hydrogen	Sulphur	Ash, etc.
100-octane petrol	85.1	14.9	0.01	—
Motor petrol	85.5	14.4	0.1	—
Benzole	91.7	8.0	0.3	—
Kerosene (paraffin)	86.3	13.6	0.1	—
Diesel oil	86.3	12.8	0.9	—
Light fuel oil	86.2	12.4	1.4	—
Heavy fuel oil	86.1	11.8	2.1	—
Residual fuel oil	88.3	9.5	1.2	1.0

Table 7.5 Analysis by volume of a typical natural gas

Methane CH_4	Ethane C_2H_6	Propane C_3H_8	Butane C_4H_{10}	Nitrogen N_2	Carbon dioxide CO_2
92.6%	3.6%	0.8%	0.3%	2.6%	0.1%

Gaseous fuels are chemically the simplest of the three groups. The main gaseous fuel in use occurs naturally but other gaseous fuels may be manufactured by the various treatments of coal. Carbon monoxide is an important gaseous fuel which is a constituent of other gas mixtures, and is also a product of the incomplete combustion of carbon. A typical analysis of a natural gas is given in Table 7.5. The table gives the analyses by volume, each constituent having been measured by volume at atmospheric pressure and temperature. The volumetric analysis is the same as the molar analysis (see equation (6.14)).

Fuels are tested according to standardized procedures and for further information ref. 7.2 should be consulted.

7.3 Combustion equations

Proportionate masses of air and fuel enter the combustion chamber where the chemical reaction takes place, and from which the products of combustion pass to the exhaust. By the conservation of mass the mass flow remains constant (i.e. total mass of products equals total mass of reactants), but the reactants are chemically different from the products, and the products leave at a higher temperature. The total number of atoms of each element concerned in the combustion remains constant, but the atoms are rearranged into groups having different chemical properties. This information is expressed in the chemical equation which shows:

(i) the reactants and the products of combustion;
(ii) the relative quantities of the reactants and products.

The two sides of the equation must be consistent, each having the same number of atoms of each element involved. It should not be assumed that if an equation can be written, that the reaction it represents is inevitable or even possible. For possibility and direction the reaction has to be considered with reference to the Second Law of Thermodynamics. For the present the only concern is known combustion equations.

The equation shows the number of molecules of each reactant and product. The amount of substance, introduced in section 2.3, is proportional to the number of molecules, hence the relative numbers of molecules of the reactants and the products give the molar, and therefore the volumetric, analysis of the gaseous constituents.

As stated earlier the oxygen supplied for combustion is usually provided by atmospheric air, and it is necessary to use accurate and consistent analyses of air by mass and by volume. It is usual in combustion calculations to take air as 23.3% O_2, 76.7% N_2 by mass, and 21% O_2, 79% N_2 by volume. The small traces of other gases in dry air are included in the nitrogen, which is sometimes called 'atmospheric nitrogen'.

Consider the combustion equation for hydrogen:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{7.1}$$

This tells us that

(i) hydrogen reacts with oxygen to form steam or water;
(ii) two molecules of hydrogen react with one molecule of oxygen to give two molecules of steam or water,

i.e. $\quad 2 \text{ volumes } H_2 + 1 \text{ volume } O_2 \rightarrow 2 \text{ volumes } H_2O$

The H_2O may be a liquid or a vapour depending on whether the product has been cooled sufficiently to cause condensation. The proportions by mass are obtained by using relative atomic masses,

i.e. $\quad 2H_2 + O_2 \rightarrow 2H_2O$

therefore

$$2 \times (2 \times 1) + (2 \times 16) \rightarrow 2 \times \{(2 \times 1) + 16\}$$

i.e. $4\,\text{kg}\,H_2 + 32\,\text{kg}\,O_2 \rightarrow 36\,\text{kg}\,H_2O$

or $1\,\text{kg}\,H_2 + 8\,\text{kg}\,O_2 \rightarrow 9\,\text{kg}\,H_2O$

The same proportions are obtained by writing equation (7.1) as $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, and this is sometimes done.

It will be noted from equation (7.1) that the total volume of the reactants is 2 volumes H_2 + 1 volume O_2 = 3 volumes. The total volume of the product is only 2 volumes. There is therefore a volumetric contraction on combustion.

Since oxygen is accompanied by nitrogen if air is supplied for the combustion, then this nitrogen should be included in the equation. As nitrogen is inert as far as the chemical reaction is concerned, it will appear on both sides of the equation.

With 1 kmol of oxygen there are 79/21 kmol of nitrogen, hence equation (7.1) becomes

$$2H_2 + O_2 + \frac{79}{21}N_2 \rightarrow 2H_2O + \frac{79}{21}N_2 \qquad (7.2)$$

Similar equations can be found for the combustion of carbon. There are two possibilities to consider:

(i) The complete combustion of carbon to carbon dioxide

$$C + O_2 \rightarrow CO_2 \qquad (7.3)$$

and including the nitrogen

$$C + O_2 + \frac{79}{21}N_2 \rightarrow CO_2 + \frac{79}{21}N_2 \qquad (7.4)$$

Considering the volumes of reactants and products

$$0 \text{ volume C} + 1 \text{ volume } O_2 + \frac{79}{21} \text{ volumes } N_2$$

$$\rightarrow 1 \text{ volume } CO_2 + \frac{79}{21} \text{ volumes } N_2$$

The volume of carbon is written as zero since the volume of a solid is negligible in comparison with that of a gas.

By mass

$$12\,\text{kg C} + (2 \times 16)\,\text{kg}\,O_2 + \frac{79}{21}(2 \times 14)\,\text{kg}\,N_2$$

$$\rightarrow \{12 + (2 \times 16)\}\,\text{kg}\,CO_2 + \frac{79}{21}(2 \times 14)\,\text{kg}\,N_2$$

i.e. $12\,\text{kg C} + 32\,\text{kg}\,O_2 + 105.3\,\text{kg}\,N_2 \rightarrow 44\,\text{kg}\,CO_2 + 105.3\,\text{kg}\,N_2$

or $1\,\text{kg C} + \frac{32}{12}\,\text{kg}\,O_2 + \frac{105.3}{12}\,\text{kg}\,N_2 \rightarrow \frac{44}{12}\,\text{kg}\,CO_2 + \frac{105.3}{12}\,\text{kg}\,N_2$

(ii) The incomplete combustion of carbon. This occurs when there is an insufficient supply of oxygen to burn the carbon completely to carbon dioxide,

i.e. $$2C + O_2 \rightarrow 2CO \tag{7.5}$$

$$2C + O_2 + \frac{79}{21}N_2 \rightarrow 2CO + \frac{79}{21}N_2 \tag{7.6}$$

By mass

$$(2 \times 12)\,\text{kg C} + (2 \times 16)\,\text{kg } O_2 + \frac{79}{21}(2 \times 14)\,\text{kg } N_2$$
$$\rightarrow 2(12 + 16)\,\text{kg CO} + \frac{79}{21}(2 \times 14)\,\text{kg } N_2$$

i.e. $$24\,\text{kg C} + 32\,\text{kg } O_2 + 105.3\,\text{kg } N_2 \rightarrow 56\,\text{kg CO} + 105.3\,\text{kg } N_2$$

or $$1\,\text{kg C} + \frac{32}{24}\,\text{kg } O_2 + \frac{105.3}{24}\,\text{kg } N_2 \rightarrow \frac{56}{24}\,\text{kg CO} + \frac{105.3}{24}\,\text{kg } N_2$$

If a further supply of oxygen is available then the combustion can continue to completion

$$2CO + O_2 + \frac{79}{21}N_2 \rightarrow 2CO_2 + \frac{79}{21}N_2 \tag{7.7}$$

By mass,

$$56\,\text{kg CO} + 32\,\text{kg } O_2 + 105.3\,\text{kg } N_2 \rightarrow 88\,\text{kg } CO_2 + 105.3\,\text{kg } N_2$$

or $$1\,\text{kg CO} + \frac{32}{56}\,\text{kg } O_2 + \frac{105.3}{56}\,\text{kg } N_2 \rightarrow \frac{88}{56}\,\text{kg } CO_2 + \frac{105.3}{56}\,\text{kg } N_2$$

7.4 Stoichiometric air–fuel ratio

A stoichiometric mixture of air and fuel is one that contains just sufficient oxygen for the complete combustion of the fuel. A mixture which has an excess of air is termed a *weak mixture*, and one which has a deficiency of air is termed a *rich mixture*. The percentage of excess air is given by the following:

Percentage excess air

$$= \frac{\text{actual A/F ratio} - \text{stoichiometric A/F ratio}}{\text{stoichiometric A/F ratio}} \tag{7.8}$$

where A denotes air and F denotes fuel.

For gaseous fuels the ratios are expressed by volume and for solid and liquid fuels the ratios are expressed by mass. Equation (7.8) gives a positive result when the mixture is weak, and a negative result when the mixture is rich. For boiler plant the mixture is usually greater than 20% weak; for gas turbines it can be as much as 300% weak. Petrol engines have to meet various conditions of load and speed, and operate over a wide range of mixture strengths. The following definition is used:

$$\text{Mixture strength} = \frac{\text{stoichiometric A/F ratio}}{\text{actual A/F ratio}} \qquad (7.9)$$

The working values range between 80% (weak) and 120% (rich) (see section 13.6).

Where fuels contain some oxygen (e.g. ethyl alcohol C_2H_6O) this oxygen is available for the combustion process, and so the fuel requires a smaller supply of air.

7.5 Exhaust and flue gas analysis

The products of combustion are mainly gaseous. When a sample is taken for analysis it is usually cooled down to a temperature which is below the saturation temperature of the steam present. The steam content is therefore not included in the analysis, which is then quoted as the analysis of the dry products. Since the products are gaseous, it is usual to quote the analysis by volume. An analysis which includes the steam in the exhaust is called a wet analysis. The following examples illustrate the principles covered in this chapter up to this point.

Example 7.1 A sample of dry anthracite has the following composition by mass.

C 90%; H 3%; O 2.5%; N 1%; S 0.5%; ash 3%

Calculate:
(i) the stoichiometric A/F ratio;
(ii) the A/F ratio and the dry and wet analysis of the products of combustion by mass and by volume, when 20% excess air is supplied.

Solution (i) Each constituent is taken separately and the amount of oxygen required for complete combustion is found from the relevant chemical equation. Carbon:

$$C + O_2 \rightarrow CO_2 \qquad 12\,\text{kg C} + 32\,\text{kg}\,O_2 \rightarrow 44\,\text{kg}\,CO_2$$

i.e. $$\text{Oxygen required} = 0.9 \times \frac{32}{12} = 2.4\,\text{kg/kg coal}$$

where the carbon content is 0.9 kg per kilogram of coal

$$\text{Carbon dioxide produced} = 0.9 \times \frac{44}{12} = 3.3\,\text{kg}\,CO_2$$

Hydrogen (H):

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad 2\,\text{kg}\,H_2 + 16\,\text{kg}\,O_2 \rightarrow 18\,\text{kg}\,H_2O$$

or $$1\,\text{kg}\,H_2 + 8\,\text{kg}\,O_2 \rightarrow 9\,\text{kg}\,H_2O$$

i.e. $$\text{Oxygen required} = 0.03 \times 8 = 0.24\,\text{kg/kg coal}$$

and $$\text{Steam produced} = 0.03 \times 9 = 0.27\,\text{kg/kg coal}$$

Sulphur:

$$S + O_2 \rightarrow SO_2 \qquad 32\text{ kg S} + 32\text{ kg } O_2 \rightarrow 64\text{ kg } SO_2$$

or

$$1\text{ kg S} + 1\text{ kg } O_2 \rightarrow 2\text{ kg } SO_2$$

i.e. Oxygen required = 0.005 kg/kg coal

Sulphur dioxide produced = 2 × 0.005 = 0.01 kg/kg coal

These results are tabulated in Table 7.6; the oxygen in the fuel is shown as a negative quantity in the column 'oxygen required'.

Table 7.6 Solution for Example 7.1(i)

Constituent	Mass fraction	Oxygen required (kg/kg coal)	Product mass (kg/kg coal)
Carbon (C)	0.900	2.400	3.30 (CO_2)
Hydrogen (H)	0.030	0.240	0.27 (H_2O)
Sulphur (S)	0.005	0.005	0.01 (SO_2)
Oxygen (O)	0.025	−0.025	—
Nitrogen (N)	0.010	—	0.01 (N_2)
Ash	0.030	—	—
		2.620	

From Table 7.6:

O_2 required per kilogram of coal = 2.62 kg

therefore

$$\text{Air required per kilogram of coal} = \frac{2.62}{0.233} = 11.245\text{ kg}$$

where air is assumed to contain 23.3% O_2 by mass.

i.e. stoichiometric air–fuel ratio = 11.245.

(ii) For an air supply which is 20% in excess, using equation (7.8),

$$\text{Actual A/F ratio} = 11.245 + \left(\frac{20}{100} \times 11.245\right) = 1.2 \times 11.245$$

$$= 13.494/1$$

Therefore

N_2 supplied = 0.767 × 13.494 = 10.350 kg

Also O_2 supplied = 0.233 × 13.494 = 3.144 kg

In the products, then, we have

N_2 = 10.350 + 0.01 = 10.360 kg

and excess O_2 = 3.144 − 2.620 = 0.524 kg

The products are entered in Table 7.7 and the analysis by volume is obtained. In column 3 the percentage by mass is given by 100 times the mass of each product divided by the total mass of 14.464 kg. In column 5 the amount of substance per kilogram of coal is given by equation (2.7), $n_i = m_i/\tilde{m}_i$. The total of 0.4764 in column 5 gives the total amount of substance of wet products per kilogram of coal, and by subtracting the amount of substance of H_2O from this total, the total amount of substance of the dry products is obtained as 0.4616. Column 6 gives the proportion of each constituent of column 5 expressed as a percentage of the total amount of substance of the wet products. Similarly column 7 gives the percentage by volume of the dry products.

Table 7.7 Solution for Example 7.1(ii)

Product	m_i (kg/kg coal)	m_i/m (%)	$\tilde{m}_i$ (kg/kmol)	$n_i = m_i/\tilde{m}_i$	Wet n_i/n (%)	Dry n_i/n (%)
1	2	3	4	5	6	7
CO_2	3.300	22.82	44	0.0750	15.74	16.25
H_2O	0.270	1.87	18	0.0150	3.15	--
SO_2	0.010	0.07	64	0.0002	0.04	0.04
O_2	0.524	3.62	32	0.0164	3.44	3.55
N_2	10.360	71.63	28	0.3700	77.63	80.16
	14.464	100.01		0.4766 (wet)	100.00	100.00
				(0.4616) (dry)		

Example 7.2 The analysis of a supply of gas is as follows: H_2 49.4%; CO 18%; CH_4 20%; C_4H_8 2%; O_2 0.4% N_2 6.2%; CO_2 4%. Calculate:

(i) the stoichiometric A/F ratio;

(ii) the wet and dry analysis of the products of combustion if the actual mixture is 20% weak.

Solution (i) The example is solved by a similar tabular method to Example 7.1; a specimen calculation is shown more fully as follows.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

i.e. $$1\ \text{kmol}\ CH_4 + 2\ \text{kmol}\ O_2 \rightarrow 1\ \text{kmol}\ CO_2 + 2\ \text{kmol}\ H_2O$$

There are 0.2 kmol of CH_4 for 1 kmol gas, hence

$$0.2\,\text{kmol}\,CH_4 + (0.2 \times 2)\text{kmol}\,O_2 \rightarrow 0.2\,\text{kmol}\,CO_2 + (0.2 \times 2)\text{kmol}\,H_2O$$

Therefore the oxygen required for the CH_4 in the gas is 0.4 kmol/kmol gas. The results are summarized in Table 7.8; the oxygen in the gas, (0.004 kmol/kmol of gas) is included in column 4 as a negative quantity. From Table 7.8,

$$\text{Air required} = \frac{0.853}{0.21} = 4.062\ \text{kmol/kmol gas}$$

Table 7.8 Results for Example 7.2

1	2 kmol/kmol fuel	3 Combustion equation	4 O_2 kmol/kmol fuel	5 Products kmol/kmol fuel CO_2	6 Products kmol/kmol fuel H_2O
H_2	0.494	$2H_2 + O_2 \rightarrow 2H_2O$	0.247	—	0.494
CO	0.18	$2CO + O_2 \rightarrow 2CO_2$	0.09	0.18	—
CH_4	0.2	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	0.4	0.2	0.4
C_4H_8	0.02	$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$	0.12	0.08	0.08
O_2	0.004	—	−0.004	—	—
N_2	0.062	—	—	—	—
CO_2	0.04	—	—	0.04	—
		Total	0.853	0.50	0.974

where air is assumed to contain 21% oxygen by volume,

i.e. Stoichiometric A/F ratio = 4.062 by volume

(ii) For a mixture which is 20% weak, using equation (7.8),

$$\text{Actual A/F ratio} = 4.062 + (0.2 \times 4.062)$$

$$= 1.2 \times 4.062 = 4.874 \text{ by volume}$$

$$\text{Associated nitrogen} = 0.79 \times 4.874 = 3.851 \text{ kmol/kmol gas}$$

$$\text{Excess oxygen} = (0.21 \times 4.874) - 0.853$$

$$= 0.1706 \text{ kmol/kmol gas}$$

Total amount of nitrogen in products

$$= 3.851 + 0.062 = 3.913 \text{ kmol/kmol gas}$$

The analysis by volume of the wet and dry products is then as shown in Table 7.9

Table 7.9 Solution for Example 7.2

Product	kmol/kmol fuel	% by vol. (dry)	% by vol. (wet)
CO_2	0.50	10.90	9.0
H_2O	0.974	—	17.5
O_2	0.171	3.72	3.08
N_2	3.912	85.4	70.4
Total wet	5.557	100.02	99.98
$-H_2O$	0.974		
Total dry	4.583		

Example 7.3 Ethyl alcohol is burned in a petrol engine. Calculate:

(i) the stoichiometric A/F ratio;
(ii) the A/F ratio and the wet and dry analyses by volume of the exhaust gas for a mixture strength of 90%;

(iii) the A/F ratio and the wet and dry analyses by volume of the exhaust gas for a mixture strength of 120%.

Solution (i) The equation for the combustion of ethyl alcohol is as follows:

$$C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Since there are two atoms of carbon in each mole of C_2H_6O then there must be 2 mol of CO_2 in the products, giving two atoms of carbon on each side of the equation. Similarly, since there are six atoms of hydrogen in each mole of ethyl alcohol then there must be 3 mol of H_2O in the products, giving six atoms of hydrogen on each side of the equation. Then balancing the atoms of oxygen, it is seen that there are $\{(2 \times 2) + 3\} = 7$ atoms on the right-hand side of the equation, hence seven atoms must appear on the left-hand side of the equation. There is one atom of oxygen in the ethyl alcohol, therefore a further six atoms of oxygen must be supplied, and hence 3 mol of oxygen are required as shown. Since the O_2 is supplied as air, the associated N_2 must appear in the equation,

i.e. $$C_2H_6O + 3O_2 + \left(3 \times \frac{79}{21}\right)N_2 \rightarrow 2CO_2 + 3H_2O + \left(3 \times \frac{79}{21}\right)N_2$$

1 kmol of fuel has a mass of $(2 \times 12) + (6 + 16) = 46$ kg; 3 kmol of oxygen have a mass of $(3 \times 32) = 96$ kg.

Therefore

$$O_2 \text{ required per kg of fuel} = \frac{96}{46} = 2.087 \text{ kg}$$

Therefore

$$\text{Stoichiometric A/F ratio} = \frac{2.087}{0.233} = 8.957/1$$

(ii) Considering a mixture strength of 90% then, from equation (7.9),

$$0.9 = \frac{\text{stoichiometric A/F ratio}}{\text{actual A/F ratio}}$$

Therefore

$$\text{Actual A/F ratio} = \frac{8.957}{0.9} = 9.952/1$$

This means that 1/0.9 times as much air is supplied as is necessary for complete combustion. The exhaust will therefore contain $(1/0.9) - 1 = 0.1/0.9$ of the stoichiometric oxygen,

$$C_2H_6O + \frac{1}{0.9}\left\{3O_2 + \left(3 \times \frac{79}{21}\right)N_2\right\}$$

$$\rightarrow 2CO_2 + 3H_2O + \left(\frac{0.1}{0.9} \times 3\right)O_2 + \left(\frac{1}{0.9} \times 3 \times \frac{79}{21}\right)N_2$$

i.e. the products are

$$2 \text{ kmol } CO_2 + 3 \text{ kmol } H_2O + 0.333 \text{ kmol } O_2 + 12.540 \text{ kmol } N_2$$

$$\text{The total amount of substance} = 2 + 3 + 0.333 + 12.540 = 17.873 \text{ kmol}$$

Hence wet analysis is

$$\frac{2}{17.873} \times 100 = 11.19\% \; CO_2; \quad \frac{3}{17.873} \times 100 = 16.79\% \; H_2O$$

$$\frac{0.333}{17.873} \times 100 = 1.86\% \; O_2; \quad \frac{12.540}{17.873} \times 100 = 70.16\% \; N_2$$

$$\text{The total dry amount of substance} = 2 + 0.333 + 12.540 = 14.873 \text{ kmol}$$

Hence the dry analysis is

$$\frac{2}{14.873} \times 100 = 13.45\% \; CO_2; \quad \frac{0.333}{14.873} \times 100 = 2.24\% \; O_2;$$

$$\frac{12.540}{14.873} \times 100 = 84.31\% \; N_2$$

(iii) Considering a mixture strength of 120%, then from equation (7.9),

$$1.2 = \frac{\text{stoichiometric A/F ratio}}{\text{actual A/F ratio}}$$

Therefore

$$\text{Actual A/F ratio} = \frac{8.957}{1.2} = 7.47/1$$

This means that 1/1.2 of the stoichiometric air is supplied. The combustion cannot be complete, as the necessary oxygen is not available. It is usual to assume that all the hydrogen is burned to H_2O, since hydrogen atoms have a greater affinity for oxygen than carbon atoms. The carbon in the fuel will burn to CO and CO_2, but the relative proportions have to be determined. Let there be a kmol CO_2 and b kmol CO in the products. Then the combustion equation is as follows:

$$C_2H_6O + \frac{1}{1.2}\left\{3O_2 + \left(3 \times \frac{79}{21}\right)N_2\right\}$$

$$\rightarrow aCO_2 + bCO + 3H_2O + \left(\frac{1}{1.2} \times 3 \times \frac{79}{21}\right)N_2$$

To find a and b a balance of the carbon and the oxygen atoms can be made, i.e. Carbon balance: $2 = a + b$

Oxygen balance: $1 + \left(2 \times \frac{1}{1.2} \times 3\right) = 2a + b + 3$

Subtracting the equations gives

$$a = 1 \quad \text{and then} \quad b = 2 - 1 = 1$$

i.e. the products are

$$(1\ \text{kmol}\ CO_2) + (1\ \text{kmol}\ CO) + (3\ \text{kmol}\ H_2) + (9.405\ \text{kmol}\ N_2)$$
$$= 1 + 1 + 3 + 9.405 = 14.405\ \text{kmol}$$

Hence wet analysis is

$$\frac{1}{14.405} \times 100 = 6.94\%\ CO_2; \qquad \frac{1}{14.405} \times 100 = 6.94\%\ CO$$

$$\frac{3}{14.405} \times 100 = 20.83\%\ H_2; \qquad \frac{9.405}{14.405} \times 100 = 65.29\%\ N_2$$

$$\text{The total dry amount of substance} = 1 + 1 + 9.405 = 11.405\ \text{kmol}$$

Hence dry analysis is

$$\frac{1}{11.405} \times 100 = 8.77\%\ CO_2; \qquad \frac{1}{11.405} \times 100 = 8.77\%\ CO$$

$$\frac{9.405}{11.405} \times 100 = 82.46\%\ N_2$$

Example 7.4 For the stoichiometric mixture of Example 7.3, calculate:

(i) the volume of the mixture per kilogram of fuel at a temperature of 65 °C and a pressure of 1.013 bar;
(ii) the volume of the products of combustion per kilogram of fuel after cooling to a temperature of 120 °C at a pressure of 1 bar.

Solution (i) As before

$$C_2H_6O + 3O_2 + \left(3 \times \frac{79}{21}\right)N_2 \rightarrow 2CO_2 + 3H_2O + \left(3 \times \frac{79}{21}\right)N_2$$

Therefore

$$\text{Total amount of substance reactants} = 1 + 3 + \left(3 \times \frac{79}{21}\right) = 15.286\ \text{kmol}$$

From equation (2.8), $pV = n\tilde{R}T$, therefore

$$V = \frac{15.286 \times 10^3 \times 8.3145 \times 338}{10^5 \times 1.013} = 424.06\ \text{m}^3/\text{kmol of fuel}$$

where $T = 65 + 273 = 338$ K.

In 1 kmol of fuel there are $(2 \times 12) + (6 + 16) = 46$ kg, therefore

$$\text{Volume of reactants per kilogram of fuel} = \frac{424.06}{46} = 9.219\ \text{m}^3$$

(ii) When the products are cooled to 120 °C the H_2O exists as steam, since the temperature is well above the saturation temperature corresponding to the partial pressure of the H_2O. (This must be so since the saturation temperature corresponding to the total pressure is 99.6 °C, and saturation temperature decreases with pressure.) The total amount of substance of the products is

$$2 + 3 + \left(3 \times \frac{79}{21}\right) = 16.286\ \text{kmol}$$

From equation (2.8), $pV = n\tilde{R}T$, therefore

$$V = \frac{16.286 \times 10^3 \times 8.3145 \times 393}{10^5 \times 1} = 532.15\ \text{m}^3/\text{kmol of fuel}$$

where $T = 120 + 273 = 393$ K.

i.e. $$\text{Volume of products per kg of fuel} = \frac{532.15}{46} = 11.57\ \text{m}^3$$

Example 7.5 If the products in Example 7.4 are cooled to 15 °C at constant pressure, calculate the amount of water which will condense per kilogram of fuel.

Solution At 15 °C, since some condensation has taken place, the steam remaining is dry saturated, being in contact with its liquid. The saturation pressure at 15 °C is 0.01704 bar, and this is the partial pressure of the dry saturated steam.

Then using equation (6.14)

$$\frac{V_i}{V} = \frac{n_i}{n} = \frac{p_i}{p}$$

For the steam

$$\frac{n_s}{n} = \frac{0.01704}{1} = 0.01704$$

From Example 7.4 the total amount of substance of dry products is $(16.286 - 3) = 13.286$ kmol, therefore

$$\frac{n_s}{n_s + 13.286} = 0.01704 \quad \text{therefore } n_s = \left(\frac{0.01704 \times 13.286}{1 - 0.01704}\right) = 0.2303$$

i.e. amount of substance of dry saturated steam remaining at 15 °C is 0.2303 kmol, therefore amount of substance of water condensed is $(3 - 0.2303) = 2.77$ kmol. Also 1 kmol of H_2O contains $(2 + 16) = 18$ kg, therefore mass of water condensed is (2.77×18) kg/kmol fuel

i.e. $$\text{Mass of water condensed per kilogram of fuel} = \frac{2.77 \times 18}{46} = 1.084 \text{ kg}$$

Any problem in combustion can be solved using the amount of substance. The following examples illustrate the method for a solid and for a gaseous fuel; these examples should be compared with the method used in Examples 7.1 and 7.2.

Example 7.6 The gravimetric analysis of a sample of coal is given as 80% C, 12% H, and 8% ash. Calculate the stoichiometric A/F ratio and the analysis of the products by volume.

Solution

1 kg of coal contains 0.8 kg C and 0.12 kg H

$$1 \text{ kg of coal contains } \frac{0.8}{12} \text{ kmol C and } 0.12 \text{ kmol H}$$

Let the oxygen required for complete combustion be x kmol, the nitrogen supplied with the oxygen is then $x \times 79/21 = 3.76x$ kmol.

For 1 kg of coal the combustion equation is therefore as follows:

$$\frac{0.8}{12}C + 0.12H + xO_2 + 3.76xN_2 \rightarrow aCO_2 + bH_2O + 3.76xN_2$$

Then Carbon balance: $\frac{0.8}{12} = a$ or $a = 0.067$ kmol

Hydrogen balance: $0.12 = 2b$ or $b = 0.060$ kmol

Oxygen balance: $2x = 2a + b$

i.e. $x = a + b/2 = 0.067 + 0.030 = 0.097$ kmol

The mass of 1 kmol of oxygen is 32 kg, therefore the mass of O_2 supplied per kilogram of coal is 32×0.097 kg,

$$\text{Stoichiometric A/F ratio} = \frac{32 \times 0.097}{0.233} = 13.3/1$$

$$\text{Total amount of substance of products} = a + b + 3.76x$$
$$= 0.067 + 0.06 + (3.76 \times 0.097)$$
$$= 0.492 \text{ kmol}$$

Hence wet analysis is

$$\frac{0.067}{0.492} \times 100 = 13.6\%\ CO_2; \qquad \frac{0.06}{0.492} \times 100 = 12.2\%\ H_2$$

$$\frac{0.365}{0.492} \times 100 = 74.2\%\ N_2$$

Example 7.7 A gas engine is supplied with natural gas of the following composition: CH_4 93%; C_2H_6 3%; N_2 3%; CO 1%. If the A/F ratio is 30 by volume, calculate the analysis of the dry products of combustion. It can be assumed that the stoichiometric A/F ratio is less than 30.

Solution Since we are told that the actual air–fuel ratio is greater than the stoichiometric it follows that excess air has been supplied. The products will therefore consist of CO_2, H_2O, O_2, and N_2. The combustion equation can be written as follows:

$$0.93CH_4 + 0.03C_2H_6 + 0.01CO + 0.03N_2 + (0.21 \times 30)O_2 + (0.79 \times 30)N_2 \rightarrow aCO_2 + bH_2O + cO_2 + dN_2$$

Then Carbon balance: $0.93 + (2 \times 0.03) + 0.01 = a$ or $a = 1$
Hydrogen balance: $(4 \times 0.93) + (6 \times 0.03) = 2b$ or $b = 1.95$
Oxygen balance: $0.01 + (0.21 \times 30) = 2a + b + 2c$

Therefore

$$c = \{6.31 - 2 - (2 \times 1.95)\}/2 = 0.205$$

Nitrogen balance: $0.03 + (0.79 \times 30) = d$ or $d = 23.73$

i.e. Total amount of substance of dry products $= 1 + 0.205 + 23.73 = 24.935$ kmol

Then analysis by volume is

$$\frac{1}{24.935} \times 100 = 4.01\ CO_2; \quad \frac{0.205}{24.935} \times 100 = 0.82\%\ O_2$$

$$\frac{23.73}{24.935} \times 100 = 95.17\%\ N_2$$

7.6 Practical analysis of combustion products

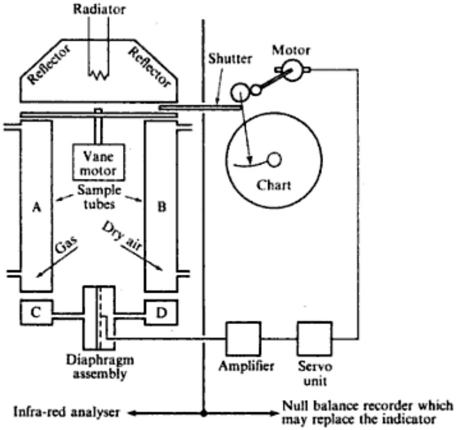
The experimental investigation of a combustion process requires the analysis of the products of combustion. The most basic method is to take a sample of the gas and analyse it chemically as in an Orsat apparatus for example (see ref. 7.2). Modern instrumentation now provides a quicker, more accurate, and continuous means of analysis. Some of the methods used are summarized below, but manufacturers' catalogues should be consulted for details of actual instruments since improvements are continually being made to the measuring systems.

Non-dispersive infra-red (NDIR)

In this method the concentration of the constituent gas is measured by recording its 'optical' absorption in the infra-red spectrum. The mixture is continuously examined by being drawn through a tube, the inside of which is subject to radiation from an infra-red source, each gas absorbing on a particular waveband of the radiation. Full descriptions of infra-red analysis and other methods are given in ref. 7.4.

One particular instrument is shown diagrammatically in Fig. 7.1. The gas being analysed is passed through tube A and dry air is passed through tube B. The chambers C and D contain pure samples of the constituents to be detected. Radiation from nichrome elements is passed through tubes A and B and thence to chambers C and D where it is absorbed. The subsequent heating of the gases in C and D causes an increase in pressure in the two chambers; C and D are separated by a thin metal diaphragm which, together with an insulated, perforated plate, forms a capacitor.

Fig. 7.1 Non-dispersive infra-red gas analyser



If the constituent being sought is not present in tube A then equal amounts of radiation will be absorbed in C and D, which will be heated equally and there will be no pressure difference across the diaphragm. If the constituent is present in A, it will absorb some of the radiation admitted, and the rest will pass on to chamber C. The radiation absorbed in C will then be less than in D so that a greater pressure will be reached in D than in C, and the diaphragm will be displaced. This displacement causes a change in capacitance of the capacitor and a current is produced which is amplified to give a reading on a microammeter. The microammeter scale is calibrated to give the corresponding concentration of the constituent in the gas being analysed.

To avoid zero errors the radiation is cut off from both tubes simultaneously and allowed to fall on them simultaneously, by means of a vane which rotates at a low frequency. The pressure changes are then related to the temperature changes produced by the differential absorption in C and D.

To provide a continuously recording instrument as shown in the right-hand part of Fig. 7.1, a 'null' balance recorder is employed. The principle is that the pressure difference created should be nullified by cutting off from the vessel B a sufficient amount of radiation to balance that absorbed in A. This is done by means of a shutter driven by a servo-motor which receives a signal from the detector unit. A recording pen is linked to the balancing shutter mechanism and records on a circular chart.

Another NDIR instrument uses photoacoustic detection: a sample is drawn into a closed cell where infra-red light of the correct frequency is absorbed by the gas to be measured; the pressure increases and decreases because the light is pulsing and the pressure wave is detected by a microphone in the cell wall; the acoustic information is processed by a computer and can be printed or plotted as required; an optical filter carousel is then turned so that infra-red light of a low frequency enters the cell so that the next constituent can be measured. The instrument is manufactured by Brüel and Kjaer of Denmark.

The NDIR instruments are calibrated against accurately prepared samples of gas mixtures. This method is suitable for carbon monoxide, carbon dioxide, sulphur and nitrogen compounds, methane and other hydrocarbons, and organic vapours. Oxygen, hydrogen, nitrogen, argon, chlorine, and helium, do not absorb infra-red radiation and so will not be detected by this type of instrument.

CO_2 and O_2 recorders

Boiler-house engineers require a continuous indication of the quality of the combustion process in the plant under their control. This enables comparisons to be made and a falling-off in efficiency becomes immediately apparent. For continuous firing a continuous record is required, and digital instruments are available with in-built microchips which enable boiler efficiency to be obtained directly from individual readings of temperature, and percentage by volume of CO_2 and O_2. The variations and applications of these instruments are many, and are made to suit particular requirements. The general principles only will be dealt with here.

CO_2 measurement by thermal conductivity variations

The CO_2 content of a flue gas is an important criterion of efficient and economic combustion, and is important in observing the regulations governing smoke emission.

When a heated wire is placed in a gaseous atmosphere it loses heat by radiation, convection and conduction. If the losses by radiation and convection are kept constant, the total heat loss is dependent on the heat loss by conduction, which varies with the constituents of the gas since each has a different and characteristic thermal conductivity. If a constant heat input is supplied to the wire there is an equilibrium temperature for each mixture, and if the CO_2 content alone is varied, then its concentration will be indicated by a measurement of the temperature of the wire. In an actual instrument the heat loss from the wire is mainly by conduction, the other means (e.g. convection, radiation, end cooling, diffusion) account for about 1% each of the total loss. The convection loss is reduced by mounting the wire vertically. The instrument is calibrated against mixtures of known composition.

The sample of gas is passed over an electrically heated platinum wire in a cell which forms one arm of a Wheatstone bridge. In another arm of the bridge is a similar cell containing air. A difference in CO_2 content between the two cells causes a difference in temperature between the two wires and hence a difference in resistance. The out-of-balance potential of the bridge is measured by a recording potentiometer, calibrated to give the CO_2 content directly.

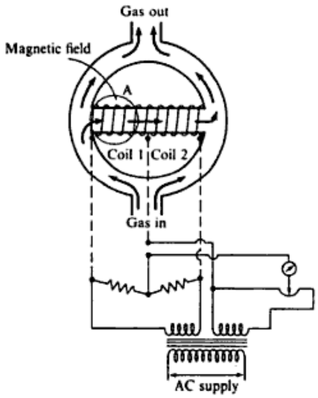
Oxygen measurement by magnetic means

Gases may be classified in two groups:

(i) diamagnetic gases which seek the weakest part of a magnetic field;
(ii) paramagnetic gases which seek the strongest part of a magnetic field.

Most gases are diamagnetic, but oxygen is paramagnetic, and this property of oxygen can be utilized in measuring the oxygen content of gas mixtures. Referring to Fig. 7.2 the gas sample is introduced into the analysis cell and passes through the annulus as shown. The horizontal cross-tube carries two identical platinum windings, coils 1 and 2, which are connected in adjacent arms of a Wheatstone bridge, and are heated by the applied voltage. The winding at A is traversed by a magnetic field of high intensity from a large permanent magnet. When the gas sample passes the end of the tube the oxygen is drawn into the cross-tube. It is heated and its paramagnetic property decreases due

Fig. 7.2 Paramagnetic analyser



to the increase in temperature as it passes through the tube. The induction of fresh cool oxygen continues, hence a continuous flow is established. The result is that the two windings are cooled by different amounts, the resistance changes and the bridge goes out of balance. The resulting electromotive force (emf) is measured by a potentiometer, and since this is proportional to the oxygen content, the reading gives the oxygen content of the mixture.

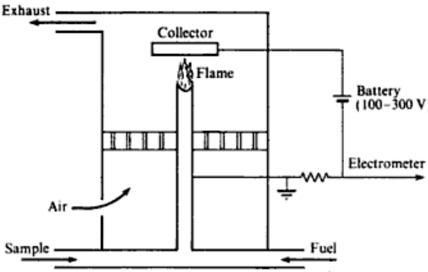
Zirconia cell

An absolute method of measurement of oxygen may be obtained using a zirconia cell; the output of the cell is directly related to the oxygen concentration of the gas sample (see ref. 7.5).

Flame ionization detector (FID)

This is a method used for detecting the hydrocarbon (HC) content of the exhaust from internal combustion (IC) engines; Fig. 7.3 shows a diagram of a typical system. The sample to be analysed is mixed with a special burner fuel which may be hydrogen, hydrogen plus helium, or hydrogen plus nitrogen. A polarizing voltage exists between the burner and the collector which causes a migration of ions in the flame and so a current to flow in the collector circuit. The current is proportional to the rate of ion formation which depends on the HC concentration in the gases and is detected by a suitable electrometer and displayed as an analogue output. The FID gives a rapid, accurate, and continuous reading of total HC concentration for levels as low as one part in 10^9.

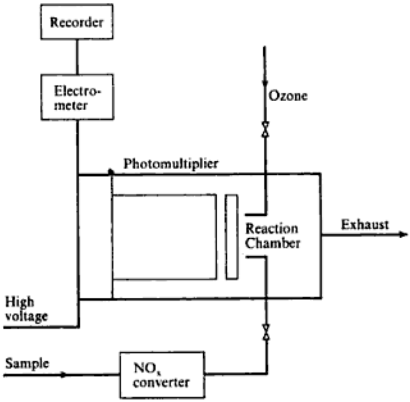
Fig. 7.3 Flame ionization detector



Chemiluminescent analyser

This method is preferred to NDIR for the analysis of the oxides of nitrogen found in the exhaust of IC engines; a diagram of a chemiluminescent analyser is shown in Fig. 7.4. The nitrous oxides, NO_x, are converted to NO before analysis by passing the gas sample over a heated catalyst such as stainless steel,

Fig. 7.4
Chemiluminescent analyser



graphite, or molybdenum at about 600 °C. The sample is now mixed with ozone where the reaction gives NO_2 and O_2; some of the NO_2 contains an excess of energy within its atoms and this NO_2 then changes to the ground state with the emission of light (chemiluminescence) which is amplified then measured by a photomultiplier tube and the signal displayed as an analogue reading of the NO_x content of the original sample.

Results of the analysis

An analysis will show whether or not the combustion is complete. For instance the presence of CO will indicate that the combustion is not complete, and if an oxygen reading is obtained this will mean that excess air has been supplied. Both CO and O_2 may appear in the analysis as a result of incomplete combustion and dissociation (see section 7.7). Quantitatively the dry product analysis can be used to calculate the A/F ratio. This method of obtaining the A/F ratio is not so reliable as direct measurement of the air consumption and fuel consumption of the engine. More caution is required when analysing the products of combustion of a solid fuel since some of the products do not appear in the flue gases (e.g. ash and unburnt carbon). The residual solid must be analysed as well in order to determine the carbon content, if any. With an engine using petrol or diesel fuel the exhaust may include unburnt particles of carbon and this quantity will not appear in the analysis. The exhaust from internal combustion engines may contain also some CH_4 and H_2 due to incomplete combustion. The CH_4 content is approximately 0.22% of the dry products and the H_2 content is of the order of half the CO content.

Considerable care is required in combustion calculations as inaccuracies are caused due to taking small differences between quantities and then using these as ratios. The use which can be made of the dry analysis is illustrated by the following problems.

Example 7.8 An analysis of the dry exhaust from an engine running on benzole shows a CO_2 content of 15%, but no CO. Assuming that the remainder of the exhaust contains only oxygen and nitrogen, calculate the A/F ratio of the engine and the dry and wet volumetric analyses of the products of combustion.

The ultimate analysis of benzole is 90% C and 10% H.

Solution There are many different methods used in combustion analysis. The following method is recommended; its algebraic approach makes it less confusing than some other methods; it also lends itself more easily to a computer solution.

Consider 1 kg of fuel:

$$\left\{\frac{0.9}{12}\mathrm{C} + 0.1\mathrm{H}\right\} + A\left(\frac{0.233}{32}\mathrm{O}_2 + \frac{0.767}{28}\mathrm{N}_2\right)$$

$$\rightarrow B\{0.15\mathrm{CO}_2 + a\mathrm{O}_2 + (1 - 0.15 - a)\mathrm{N}_2\} + b\mathrm{H}_2\mathrm{O}$$

where A is the A/F ratio on a mass basis; B the amount of substance of dry exhaust gas per kilogram of fuel, kmol/kg; a the fraction by volume of oxygen in the dry exhaust gas; b the amount of substance of steam per kilogram of fuel, kmol/kg. A brief explanation of the above equation is given below.

Left-hand side of the equation. There are (0.9/12) kmol C and 0.1 kmol H in 1 kg of fuel. A kg of air per kg of fuel contains $0.233A$ kg of oxygen and hence contains (0.233/32) kmol of oxygen; similarly there are (0.767/28) kmol of nitrogen in A kg of air for every kilogram of fuel.

Right-hand side of the equation. There are 0.15 kmol CO_2 for 1 kmol of dry exhaust gas (given in the example), hence there are $0.15B$ kmol CO_2 per kilogram of fuel since there are B kmol dry exhaust gas per kilogram of fuel.

Similarly, there are Ba kmol oxygen in the products per kilogram of fuel; the nitrogen in the dry exhaust gas is obtained by difference, i.e. $(1 - 0.15 - a)$.

There are four unknowns in the above equation and four equations may be obtained from the mass balances on carbon, oxygen, nitrogen and hydrogen.

Carbon balance: $0.9/12 = 0.15B$ therefore $B = 0.5$

Hydrogen balance: $0.1 = 2b$ therefore $b = 0.05$

Oxygen balance: $0.233A/32 = 0.15B + Ba + b/2$

i.e. $a = 0.01456A - 0.2$ [1]

Nitrogen balance: $0.767A/28 = B(0.85 - a)$

i.e. $a = 0.85 - 0.05479A$ [2]

Solving equations [1] and [2] for A we have

$$0.01456A - 0.2 = 0.85 - 0.05479A$$

therefore

$$A = 15.14$$

i.e. A/F ratio = 15.14

The value of a can then be found from either equation [1] or equation [2] as 0.02. Hence the complete dry exhaust gas volumetric analysis is given by 15% CO_2, 20% O_2, 65% N_2. The wet volumetric analysis can be found by totalling the amount of substance of wet products and taking the appropriate ratios,

i.e. Total amount of substance of wet products

$$= (0.5 \times 0.15)CO_2 + (0.5 \times 0.2)O_2 + (0.5 \times 0.65)N_2 + 0.05\ H_2$$

$$= 0.55\ \text{kmol/kg fuel}$$

Then the wet volumetric analysis is as follows:

$$\frac{0.5 \times 0.15}{0.55} \times 100 = 13.64\%\ CO_2, \qquad \frac{0.5 \times 0.2}{0.55} \times 100 = 18.18\%\ O_2,$$

$$\frac{0.5 \times 0.65}{0.55} \times 100 = 59.09\%\ N_2, \qquad \frac{0.05}{0.55} \times 100 = 9.09\%\ H_2$$

Example 7.9 The analysis of the dry exhaust gas from an internal combustion engine gave 12% CO_2, 2% CO, 4% CH_4, 1% H_2, 4.5% O_2, 76.5% N_2. Calculate the proportions by mass of carbon to hydrogen in the fuel, assuming it to be a pure hydrocarbon, and the A/F ratio used.

Solution Let the unknown mass fraction of carbon in the fuel be x kg per kilogram of fuel. Then we can write the combustion equation as follows:

$$\frac{x}{12}C + (1 - x)H + A\left(\frac{0.233}{32}O_2 + \frac{0.767}{28}N_2\right)$$

$$\rightarrow B\{0.12CO_2 + 0.02CO + 0.04CH_4$$

$$+ 0.01H_2 + 0.045O_2 + 0.765N_2\} + aH_2O$$

As in Example 7.8 there are four unknowns and four possible equations.

Carbon balance: $x/12 = B(0.12 + 0.02 + 0.04)$

$$x = 2.16B \qquad [1]$$

Hydrogen balance: $(1 - x) = (4 \times 0.04)B + (2 \times 0.01)B + 2a$

$$a = 0.5 - 0.5x - 0.09B \qquad [2]$$

Oxygen balance: $\dfrac{0.233A}{32} = B\left(0.12 + \dfrac{0.02}{2} + 0.045\right) + \dfrac{a}{2}$

$$a = 0.01456A - 0.35B \qquad [3]$$

Nitrogen balance: $0.767A/28 = 0.765B$

$$A = 27.927B \qquad [4]$$

Equating [2] and [3] we have

$$0.5 - 0.5x - 0.09B = 0.01456A - 0.35B$$

$$A = 34.341 - 34.341x + 17.857B$$

Then using equation [4]

$$34.341 - 34.341x + 17.857B = 27.927B$$
$$B = 3.41 - 3.41x$$

Substituting in [1]

$$x = 7.366 - 7.366x$$

i.e. $x = 0.8805$

The composition of the fuel is therefore 88.05% C, 11.95% H.

Also, $B = 3.41 \times 0.1195 = 0.4075$

Then in equation [4],

$$A = 27.927 \times 0.4075 = 11.38$$

i.e. A/F ratio = 11.38

7.7 Dissociation

It is found that during adiabatic combustion the maximum temperature reached is lower than that expected on the basis of elementary calculation. One important reason for this is that the *exothermic* combustion process can be reversed to some extent if the temperature is high enough. The reversed process is an *endothermic* one, i.e. energy is absorbed. In a real process the reaction proceeds in both directions simultaneously and chemical equilibrium is reached when the rate of break-up of product molecules is equal to their rate of formation. This is represented for the combustion of carbon monoxide and hydrogen respectively by the equations

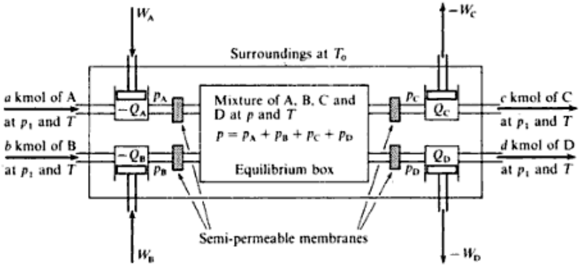
$$2CO + O_2 \rightleftharpoons 2CO_2 \quad \text{and} \quad 2H_2 + O_2 \rightleftharpoons 2H_2O$$

Both of these reactions can take place simultaneously in the same combustion process. The proportions of the constituents adjust themselves to satisfy the equilibrium conditions and their actual values depend on the particular pressure and temperature. The presence of CO and H_2 means that there is further energy to be released on their reaction with O_2 so the maximum temperature reached cannot be as high as that expected on the basis of complete combustion. As the combustion proceeds and the temperature level falls, due to expansion and/or subsequent heat loss, the amount of dissociation decreases (it is significant at temperatures > 1500 K) and combustion proceeds to completion. However, since the energy is released at lower temperatures and, in a positive expansion cylinder, at a lower effective compression ratio the efficiency of the process is reduced.

The condition of equilibrium during a reversible combustion process can be studied by means of a conceptual device known as the 'Van't Hoff equilibrium box' as shown in Fig. 7.5. Consider the general reversible combustion process

$$a \text{ kmol } A + b \text{ kmol } B \rightleftharpoons c \text{ kmol } C + d \text{ kmol } D$$

Fig. 7.5 Van't Hoff equilibrium box



which occurs at a fixed temperature T and a pressure, p, in the equilibrium box. The reactants A and B are each initially at p_1 and T and the products C and D are each finally at p_1 and T. As the process is reversible some energy transfer will take place in the form of work and this is allowed for by the inclusion of isothermal compressors and expanders. The equilibrium box contains a mixture of gases A, B, C and D at total pressure p and temperature T and to allow reversible mass flow of the constituents the pressure of each constituent at entry to the box must be equal to its partial pressure in the box. The pressure adjustments are made by the isothermal expanders and compressors and each constituent enters or leaves through a *semi-permeable membrane*. Some substances permit one gas to pass through but prevent other gases, e.g. a glowing aluminium sheet allows hydrogen to pass through but not other gases. It is assumed here that such substances are available for gases A, B, C and D.

The process may proceed equally well in either direction but it is illustrated here as going from left to right in the equation and in Fig. 7.5. With a reversal of the process the heat and work transfers would be reversed in direction.

The work input during an isothermal expansion by a perfect gas between states 1 and 2 is given by

$$W = mRT\ln\left(\frac{p_2}{p_1}\right) = n\tilde{R}T\ln\left(\frac{p_2}{p_1}\right)$$

and this can be applied to each of the compressors and expanders in the system of Fig. 7.5

$$W_A = \text{work input on A} = a\tilde{R}T\ln\left(\frac{p_A}{p_1}\right) = \tilde{R}T\ln\left(\frac{p_A}{p_1}\right)^a$$

$$W_B = \text{work input on B} = b\tilde{R}T\ln\left(\frac{p_B}{p_1}\right) = \tilde{R}T\ln\left(\frac{p_B}{p_1}\right)^b$$

$$W_C = \text{work input on C} = c\tilde{R}T\ln\left(\frac{p_1}{p_C}\right) = -\tilde{R}T\ln\left(\frac{p_C}{p_1}\right)^c$$

$$W_D = \text{work input on D} = d\tilde{R}T\ln\left(\frac{p_1}{p_D}\right) = -\tilde{R}T\ln\left(\frac{p_D}{p_1}\right)^d$$

Therefore the net work *output* of the system

$$-W = -W_A - W_B - W_C - W_D$$

i.e.

$$-W = \tilde{R}T\left\{-\ln\left(\frac{p_A}{p_1}\right)^a - \ln\left(\frac{p_B}{p_1}\right)^b + \ln\left(\frac{p_C}{p_1}\right)^c + \ln\left(\frac{p_D}{p_1}\right)^d\right\}$$

$$= \tilde{R}T\left\{\ln\frac{p_C^c p_D^d}{p_A^a p_B^b} + \ln p_1^{a+b-c-d}\right\}$$

Suppose that in a second similar system in the same surroundings the pressure in the equilibrium box is p' then it will have a net work output, $-W'$, given by

$$-W' = \tilde{R}T\left\{\ln\frac{(p'_C)^c(p'_D)^d}{(p'_A)^a(p'_B)^b} + \ln p_1^{a+b-c-d}\right\}$$

where $\quad p' = p'_A + p'_B + p'_C + p'_D$

It is proposed that $-W \neq -W'$ and this statement is to be investigated. Suppose $-W > -W'$, then the second system can be reversed, as shown in Fig. 7.6, and a single system formed by using the work output from the first system, $-W$, to provide the work input for the second system reversed.

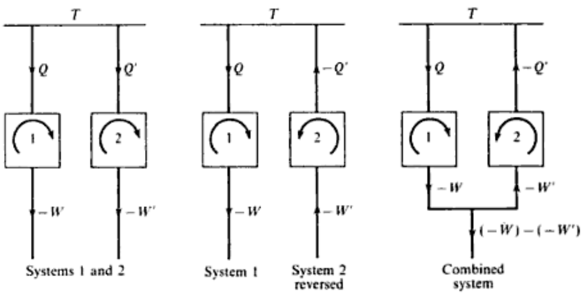


Fig. 7.6 Hypothetical (impossible) combination of two systems

The result is a single system giving a net output of work $(-W) - (-W')$ while exchanging heat with a single source at temperature T. This is a contradiction of the Second Law of Thermodynamics, thus the proposition that $W \neq W'$ is not true so that $W = W'$, therefore

$$\frac{p_C^c p_D^d}{p_A^a p_B^b} = \frac{(p'_C)^c(p'_D)^d}{(p'_A)^a(p'_B)^b} = K$$

where K is the *thermal equilibrium* or *dissociation* constant and has been shown to be independent of the pressure in the equilibrium box. A standard thermodynamic equilibrium constant, $K^\ominus$, can be defined in dimensionless form by referring each partial pressure to a pressure of 1 bar,

i.e. $$K^\ominus = \ln\left(\frac{p_C}{p^\ominus}\right)^c + \ln\left(\frac{p_D}{p^\ominus}\right)^d - \ln\left(\frac{p_A}{p^\ominus}\right)^a - \ln\left(\frac{p_B}{p^\ominus}\right)^b$$

or in general

$$\ln K^\ominus = \sum_i \ln(p_i/p^\ominus)^{\gamma_i} \tag{7.10}$$

where γ_i is the stoichiometric coefficient, taken as positive for the products and negative for the reactants. The thermodynamic equilibrium constant $K^\ominus$ is a function of temperature and values of $\ln K^\ominus$ are tabulated against temperature for each reaction equation, see ref. 7.6. As the partial pressures of the constituents are proportional to the molar proportions then $K^\ominus$ is an indication of the ratio of products to reactants and so is a measure of the amount of dissociation. If $K^\ominus$ is large then the proportion of product is high and the amount of dissociation is small.

The above general expression for $K^\ominus$, equation (7.10), will now be applied to particular important reactions. For example the combustion of carbon monoxide to carbon dioxide can be written as

$$CO + \tfrac{1}{2}O_2 \rightleftharpoons CO_2$$

with molar proportions for CO, O_2 and CO_2 of 1, 0.5, and 1. Thus K can be written as

$$\ln K^\ominus = \ln\left\{\frac{p_{CO_2}(p^\ominus)^{1/2}}{p_{CO}(p_{O_2})^{1/2}}\right\} \tag{7.11}$$

For the combustion of hydrogen the equation is

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O$$

with molar proportions 1, 0.5, and 1. The equilibrium constant then becomes

$$K^\ominus = \frac{p_{H_2O}(p^\ominus)^{1/2}}{p_{H_2}(p_{O_2})^{1/2}} \tag{7.12}$$

In the combustion of hydrocarbon fuels both of the above reactions may occur simultaneously and another equilibrium constant can be defined by dividing

$$\frac{p_{H_2O}(p^\ominus)^{1/2}}{p_{H_2}(p_{O_2})^{1/2}} \quad \text{by} \quad \frac{p_{CO_2}(p^\ominus)^{1/2}}{p_{CO}(p_{O_2})^{1/2}}$$

giving $$K^\ominus = \frac{p_{H_2O}p_{CO}}{p_{H_2}p_{CO_2}} \tag{7.13}$$

which is also tabulated, see ref. 7.6, and can be used to form another equation in the analysis.

It is readily seen that dissociation as described introduces an added complexity into the analysis of the combustion process but the complication does not end there. The conditions of equilibrium must be satisfied at any particular temperature and also the energy balance for the process must be satisfied. The temperature reached will depend on the amount of fuel burned, the proportions of the constituents and their thermodynamic properties, all of which are also dependent on pressure or temperature. Thus several conditions have to be satisfied before any particular state in the process can be determined and it is necessary to establish a sufficient number of equations to complete the analysis. This is discussed more fully in section 7.8 and for the immediate purpose it will be assumed that the energy requirements have been met in the process and only the dissociation effects are required.

The analysis of combustion may be extended to include the formation of nitric oxide, $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$, which occurs at high temperature and the dissociation of H_2O vapour into hydrogen and hydroxyl, $\frac{1}{2}H_2 + OH \rightleftharpoons H_2O$, as well as into its constituent gases. There may also be the dissociation of molecules of oxygen, hydrogen and nitrogen into atoms. These aspects of combustion are detailed and involve small proportions of the charge. It has been stated previously that recombination occurs as the temperature falls so that combustion is completed with a loss in efficiency of the cycle such that less work output is obtained than expected. The completion of combustion requires the absence of low-temperature quenching conditions, which may arrest the process, and a sufficiency of time for the reaction to be completed.

The importance of the analysis of combustion increases with advancing engine technology as typified in the petrol engine. This engine includes the extremes of combustion conditions starting from a complex chemical fuel and a mixture of air, water vapour and residual exhaust gas. The pressure and temperature levels passed through are large and the duration of a cycle is only a fraction of a second. The cylinders are water-cooled usually and sudden exhausting of gas is provided for. Under these conditions the exhaust gas can have a complex analysis and some of the constituents are responsible for the polluting of the atmosphere with undesirable and irritating results.

Example 7.10 A combustible mixture of carbon monoxide and air which is 10% rich is compressed to a pressure of 8.28 bar and a temperature of 282 °C. The mixture is ignited and combustion occurs adiabatically at constant volume. When the maximum temperature is attained analysis shows 0.228 kmol of CO present for 1 kmol of CO supplied. Show that the maximum temperature reached is 2695 °C.

Solution For stoichiometric conditions

$$CO + \tfrac{1}{2}O_2 + (3.76 \times \tfrac{1}{2}N_2) \rightarrow CO_2 + (3.76 \times \tfrac{1}{2}N_2)$$

$$CO + 0.5O_2 + 1.88N_2 \rightarrow CO_2 + 1.88N_2$$

$$\text{Actual A/F ratio} = \text{stoichiometric A/F ratio} \times \frac{100}{110}$$

$$= \text{stoichiometric A/F ratio}/1.1$$

Therefore the actual reactants are

$$CO + (0.5O_2 + 1.88N_2)/1.1$$

With dissociation there will be some break up of CO_2 giving CO and O_2 in the products such that

$$CO + (0.5O_2 + 1.88N_2)/1.1 = aCO_2 + bCO + cO_2 + (1.88/1.1)N_2$$

The question states that $b = 0.228$, therefore

$$CO + 0.455O_2 + 1.709N_2 \rightarrow aCO_2 + 0.228CO + cO_2 + 1.709N_2$$

Carbon balance: $1 = a + 0.228$ therefore $a = 0.772$
Oxygen balance: $1 + (2 \times 0.455) = 2a + 0.228 + 2c$ therefore $c = 0.069$

For the reaction $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$

$$K^\ominus = \frac{p_{CO_2}(p^\ominus)^{1/2}}{p_{CO}(p_{O_2})^{1/2}}$$

and $$p_{CO_2} = \frac{a}{n_2}p_2, \quad p_{CO} = \frac{b}{n_2}p_2, \quad p_{O_2} = \frac{c}{n_2}p_2$$

therefore

$$K^\ominus = \frac{a}{b}\sqrt{\left\{\frac{n_2 p^\ominus}{c p_2}\right\}} \qquad [1]$$

where p_2 = the total pressure at the required temperature and n_2 = total amount of substance of products

$$n_2 = a + b + c + 1.709 = 0.772 + 0.228 + 0.069 + 1.709$$
$$= 2.778 \text{ kmol}$$

At ignition

$$p_1 = 8.28 \text{ bar} \quad \text{and} \quad T_2 = 273 + 282 = 555 \text{ K}$$

$$p_1 V = n_1 \tilde{R} T_1 \quad \text{and} \quad p_2 V = n_2 \tilde{R} T_2 \quad \text{and} \quad V = \text{constant}$$

therefore

$$p_2 = p_1 \frac{n_2}{n_1}\frac{T_2}{T_1}$$

where n_1 = amount of substance of reactants = $1 + 0.455 + 1.709 = 3.164$. Then, assuming that $T_2 = 273 + 2695 = 2968$ K, we have

$$p_2 = 8.28 \times \frac{2.778}{3.164} \times \frac{2968}{555} = 38.88 \text{ bar}$$

Substituting in equation [1],

$$K^\ominus = \frac{0.772}{0.228}\sqrt{\left\{\frac{2.778 \times 1}{0.069 \times 38.88}\right\}} = 3.446$$

therefore

$$\ln K^{\ominus} = 1.237$$

From tables, ref. 7.6, it is seen by interpolation that $\ln K^{\ominus} = 1.235$ for this reaction at 2968 K showing the assumed value to be true. The corresponding pressure was calculated at 38.88 bar.

Example 7.11 A mixture of heptane (C_7H_{16}) and air which is 10% rich is initially at a pressure of 1 bar and temperature 100 °C, and is compressed through a volumetric ratio of 6 to 1. It is ignited and adiabatic combustion proceeds at constant volume. The maximum temperature reached is 2627 °C and at this temperature the equilibrium constants are

$$\frac{p_{H_2O}p_{CO}}{p_{CO_2}p_{H_2}} = 7.01 \quad \text{and} \quad \frac{p_{CO_2}(p^{\ominus})^{1/2}}{p_{CO}(p_{O_2})^{1/2}} = 4.49$$

If the constituents of the gas are CO_2, CO, H_2O, H_2, O_2 and N_2 show that approximately 30% of the carbon has burned incompletely.

Solution The processes are shown in Fig. 7.7 and for a 10% rich mixture

$$C_7H_{16} + \frac{10}{11}\{11O_2 + (11 \times 3.76)N_2\}$$
$$\rightarrow aCO_2 + bCO + cH_2O + dH_2 + eO_2 + (10 \times 3.76)N_2$$

$$C_7H_{16} + 10O_2 + 37.6N_2$$
$$\rightarrow aCO_2 + bCO + cH_2O + dH_2 + eO_2 + 37.6N_2$$

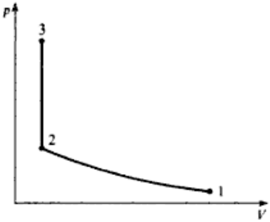


Fig. 7.7 Pressure–volume diagram for Example 7.11

Then,

Carbon balance: $a + b = 7$ [1]

Hydrogen balance: $c + d = 8$ [2]

Oxygen balance: $a + \frac{b}{2} + \frac{c}{2} + e = 10$ [3]

Amount of substance initially, $n_1 = 1 + 10 + 37.6 = 48.6$; amount of substance finally, $n_3 = a + b + c + d + e + 37.6$. Also,

$$p_1V_1 = n_1\tilde{R}T_1 \quad \text{and} \quad p_3V_3 = n_3\tilde{R}T_3$$

and combining these gives

$$\frac{p_3}{n_3} = \frac{p_1}{n_1}\frac{V_1}{V_3}\frac{T_3}{T_1} = \frac{1}{48.6} \times \frac{6}{1} \times \frac{2900}{373} = 0.958 \text{ bar/kmol}$$

where $T_1 = 273 + 100 = 373$ K, and $T_2 = 273 + 2627 = 2900$ K.
The partial pressures are given by equation 6.14 as

$$p_{CO_2} = \frac{a}{n_3}p_3 \qquad p_{CO} = \frac{b}{n_3}p_3$$

$$p_{H_2O} = \frac{c}{n_3}p_3 \qquad p_{H_2} = \frac{d}{n_3}p_3 \qquad p_{O_2} = \frac{e}{n_3}p_3$$

The example gives

$$\frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = 7.01 \qquad \frac{p_{CO_2}(p^{\ominus})^{1/2}}{p_{CO}(p_{O_2})^{1/2}} = 4.49$$

therefore

$$\frac{bc}{ad} = 7.01 \qquad [4]$$

and $$\frac{a}{b\,e^{1/2}}\left(\frac{n_3}{p_3}\right)^{1/2} = 4.49 \qquad [5]$$

The proportion of carbon burned incompletely is given as 0.3, so that 0.3 of the initial 7 atoms of carbon burn to give b CO.

i.e. $b/7 = 0.3$ therefore $b = 2.1$

Then from equation [1], $a = 7 - 2.1 = 4.9$. Substituting in [4] gives

$$\frac{c}{d} = 7.01 \times \frac{a}{b} = 7.01 \times \frac{4.9}{2.1} = 16.36$$

From equation [2]

$$c + d = 8 \quad \text{therefore } 16.36d + d = 8 \qquad d = \frac{8}{17.36} = 0.461$$

and $$c = 16.36 \times 0.461 = 7.539$$

From equation [3]

$$e = 10 - a - \frac{b}{2} - \frac{c}{2} = 10 - 4.9 - \frac{2.1}{2} - \frac{7.539}{2} = 0.280$$

substituting in equation [5] gives

$$\frac{a}{b\,e^{1/2}}\left(\frac{n_3}{p_3}\right)^{1/2} = \frac{4.9}{2.1}\left(\frac{1}{0.28 \times 0.958}\right)^{1/2} = 4.51$$

which gives sufficient agreement to the 4.49 quoted showing that approximately 30% of carbon was burned to CO.

7.8 Internal energy and enthalpy of reaction

Previous consideration of the combustion process has not included the energy released during the process and final temperatures attained. It is evident, however, that such a process must obey the First Law of Thermodynamics. Applications of this law to other processes have been for pure substances, or those that can be considered to be so, with the stipulation that their thermodynamic state is defined by two independent properties. In the type of process now considered there is the potential chemical energy of the fuel to be included which is released during the change from reactants to products.

It is an experimental fact that the energy released on the complete combustion of unit mass of a fuel depends on the temperature at which the process is carried out. Thus such quantities quoted are related to temperature. It will be shown that if the energy release is known for a fuel at one temperature it can be calculated at other temperatures.

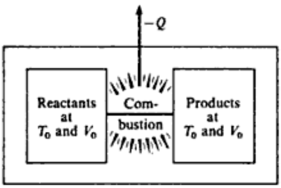
The combustion process is defined as taking place from reactants at a state identified by the reference temperature T_0 and another property, either pressure or volume, to products at the same state. If the process is carried out at constant volume then the non-flow energy equation, $Q + W = (U_2 - U_1)$, can be applied to give

$$Q = U_{P_0} - U_{R_0} \quad \text{or} \quad -Q = U_{R_0} - U_{P_0} \tag{7.14}$$

where $W = 0$ for constant volume combustion, $U_1 = U_{R_0}$ the internal energy of the reactants which is a mixture of fuel and air at T_0, and $U_2 = U_{P_0}$ the internal energy of the products of combustion at T_0.

The change in internal energy does not depend on the path between the two states but only on the initial and final values and is given by the quantity, $-Q$, the heat transferred to the surroundings during the process. This is illustrated in Fig. 7.8 and also the property diagram of Fig. 7.9.

Fig. 7.8 Combustion at reference conditions



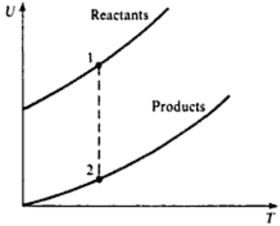
The heat supplied, Q, is called the *internal energy of reaction at* T_0 and is denoted by ΔU_0,

$$\text{i.e.} \quad Q = \Delta U_0 = U_{P_0} - U_{R_0} \tag{7.15}$$

The molar internal energy of reaction at a standard pressure of 1 bar is defined as $\Delta \tilde{u}^{\ominus} = \Delta U_0/n$, where n is the amount of substance of the fuel.

As the internal energy of the reactants includes the potential chemical energy,

Fig. 7.9 U–T diagram for combustion at a reference temperature



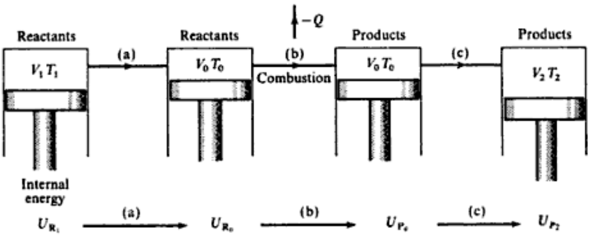
and since heat is transferred *from* the system, it is evident that as defined ΔU_0 is a negative quantity.

For real constant volume combustion processes the initial and final temperatures will be different from the reference temperature T_0. For analytical purposes the change in internal energy between reactants at state 1 to products at state 2 can be considered in three stages:

(a) the change for the reactants from state 1 to the reference temperature T_0;
(b) the constant volume combustion process from reactants to products at T_0;
(c) the change for the products from T_0 to state 2.

The complete process can be conceived as taking place in a piston-cylinder device as indicated in Fig. 7.10.

Fig. 7.10 Combustion between states 1 and 2



Thus the change in internal energy between states 1 and 2, $(U_2 - U_1)$, can be written more explicitly as, $(U_{P_2} - U_{R_1})$, to show the chemical change involved and this can be further expanded for analytical purposes:

$$U_{P_2} - U_{R_1} = (U_{P_2} - U_{P_0}) + (U_{P_0} - U_{R_0}) + (U_{R_0} - U_{R_1})$$

therefore

$$U_{P_2} - U_{R_1} = \underbrace{(U_{P_2} - U_{P_0})}_{\substack{\text{Products}\\ \text{(c)}}} + \underbrace{\Delta U_0}_{\text{(b)}} + \underbrace{(U_{R_0} - U_{R_1})}_{\substack{\text{Reactants}\\ \text{(a)}}} \tag{7.16}$$

The non-flow energy equation applied to a process involving combustion and work gives

$$Q + W = U_{P_2} - U_{R_1}$$

It can be seen that the expression for $U_{P_2} - U_{R_1}$ has been conveniently split up to give a term $U_{P_2} - U_{P_0}$ which requires the product mixture to be regarded as a single substance or a summation of single substance constituents, a similar term for the reactants and the quantity ΔU_0 previously defined. The values of internal energy for the constituents of the mixtures remain to be determined. These are functions of temperature and the most accurate method is to use tabulated values such as those of ref. 7.6. In some cases it is a good approximation to calculate changes in internal energy assuming the gaseous constituents to be perfect using an average value of c_v for the temperature range involved. If the temperature range is T_1 to T_2 then the value of c_v at $T = (T_1 + T_2)/2$ can be used, this assumes a linear change in c_v with temperature, but if the temperature range is large the result may not be accurate enough and tabulated values of the properties are required. The tables of ref. 7.6 give the values of $\tilde{u}$ and $\tilde{h}$, with $\tilde{h} = 0$ at the normal reference temperature of 25 °C = 298.15 K; $\tilde{u}$ and $\tilde{h}$ are virtually independent of pressure.

The changes in internal energy for the reactants $(U_{R_0} - U_{R_1})$ and for the products $(U_{P_2} - U_{P_0})$ can be calculated from the following expressions:

$$U_{R_0} - U_{R_1} = \sum_R n_i(\tilde{u}_{i_0} - \tilde{u}_{i_1}) \tag{7.17}$$

where Σ_R denotes the summation for all the constituents of the reactants denoted by i, $\tilde{u}_i$ is the tabulated value of the internal energy for the constituent at the required temperature T_0 or T_1, and n_i the amount of substance of the constituent.

Alternatively if a mass base is used for the tabulated values or calculation

$$U_{R_0} - U_{R_1} = \sum_R m_i(u_{i_0} - u_{i_1}) \tag{7.18}$$

where u_i is the internal energy per unit mass.

In terms of the specific heats which are average values for the required temperature range

$$U_{R_0} - U_{R_1} = \sum_R m_i c_{v_i}(T_0 - T_1) = (T_0 - T_1) \sum_R m_i c_{v_i} \tag{7.19}$$

and similar expressions for the products are

$$U_{P_2} - U_{P_0} = \sum_P n_i(\tilde{u}_{i_2} - \tilde{u}_{i_0}) \tag{7.20}$$

$$U_{P_2} - U_{P_0} = \sum_P m_i(u_{i_2} - u_{i_0}) \tag{7.21}$$

$$U_{P_2} - U_{P_0} = \sum_P m_i c_{v_i}(T_2 - T_0) = (T_2 - T_0) \sum_P m_i c_{v_i} \tag{7.22}$$

Note that $n_i \tilde{c}_{v_i} = m_i c_{v_i}$.

The process has been analysed on the basis of a non-flow process which involves combustion at constant volume. A similar analysis can be made for a steady-flow or constant pressure combustion process in which the changes in enthalpy are important

$$H_{P_2} - H_{R_1} = \underset{\text{Products}}{(H_{P_2} - H_{P_0})} + \Delta H_0 + \underset{\text{Reactants}}{(H_{R_0} - H_{R_1})} \tag{7.23}$$

where ΔH_0 = *enthalpy of reaction* at T_0 and

$$\Delta H_0 = H_{P_0} - H_{R_0} \text{ and is always negative} \tag{7.24}$$

The molar enthalpy of reaction is defined as $\Delta \tilde{h}^\ominus = \Delta H_0/n$ at 1 bar where n is the amount of substance of the fuel.

The expressions for the change in enthalpy of reactants and products are

$$H_{R_0} - H_{R_1} = \sum_R n_i(\tilde{h}_{i_0} - \tilde{h}_{i_1}) \tag{7.25}$$

$$H_{R_0} - H_{R_1} = \sum_R m_i(h_{i_0} - h_{i_1}) \tag{7.26}$$

and if mean specific heats are used

$$H_{R_0} - H_{R_1} = \sum_R m_i c_{p_i}(T_0 - T_1) = (T_0 - T_1)\sum_R m_i c_{p_i} \tag{7.27}$$

$$H_{P_2} - H_{P_0} = \sum_P n_i(\tilde{h}_{i_2} - \tilde{h}_{i_0}) \tag{7.28}$$

$$H_{P_2} - H_{P_0} = \sum_P m_i(h_{i_2} - h_{i_0}) \tag{7.29}$$

and if mean specific heats are used

$$H_{P_2} - H_{P_0} = \sum_P m_i c_{p_i}(T_2 - T_0) = (T_2 - T_0)\sum_P m_i c_{p_i} \tag{7.30}$$

Note that $n_i \tilde{c}_{p_i} = m_i c_{p_i}$.

Values of molar enthalpy, $\Delta \tilde{h}^\ominus$, referred to a pressure of 1 bar are given in ref. 7.6 for some common reactions.

For example,

Reaction	$\Delta \tilde{h}^\ominus$ at 25 °C (298.15 K) (kJ/kmol)
$C(sol) + O_2 \rightarrow CO_2$	−393 520
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	−282 990
$C_6H_6(vap) + 7\frac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O(liq)$	−3 301 397

It will be noted that the state of the fuel is given if it is solid (sol), liquid (liq) or vapour (vap) if this is required. If H_2O is a product of the combustion then it is necessary to know the state, liquid or vapour, at the end of the process by which $\Delta \tilde{h}^\ominus$ was determined. If $\Delta \tilde{h}_0$ is known for a particular fuel with the H_2O formed in the liquid state the value of $\Delta \tilde{h}_0$ with the H_2O in the vapour state can be calculated.

Example 7.12 For benzene vapour (C_6H_6) at 25 °C $\Delta\tilde{h}_0$ is −3 301 397 kJ/kmol with the H_2O in the liquid phase. Calculate $\Delta\tilde{h}_0$ for the H_2O in the vapour phase.

Solution If the H_2O remains as a vapour the heat transferred to the surroundings will be less than that when the vapour condenses, by the amount due to the change in enthalpy of the vapour during condensation at the reference temperature.

$$\Delta\tilde{h}_0(\text{vap}) = \Delta\tilde{h}_0(\text{liq}) + m_s h_{fg_0}$$

where m_s is the mass of H_2O formed for 1 kmol of fuel; h_{fg_0} is the change in enthalpy of steam between saturated liquid and saturated vapour at the reference temperature T_0 and is 2441.8 kJ/kg at 25 °C.

For the reaction

$$C_6H_6 + 7\tfrac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$$

Therefore 3 kmol of H_2O are formed on combustion of 1 kmol of C_6H_6; 3 kmol of $H_2O = 3 \times 18 = 54$ kg H_2O.

$$\Delta\tilde{h}_0(\text{vap}) = -3\,301\,397 + (54 \times 2441.8)$$

$$= -3\,169\,540 \text{ kJ/kmol}$$

In the equations for the change in internal energy and enthalpy for reactants and products, and for ΔU_0 and ΔH_0, if a change in state takes place (e.g. from liquid fuel to vapour), a term describing this process must be included.

Nothing has been said of the air–fuel ratio for combustion during the determination of ΔU_0 or ΔH_0. Consideration will show that this does not matter provided there is sufficient air to ensure complete combustion. Excess oxygen, like the nitrogen present, starts and finishes at the reference temperature T_0 and so suffers no change in internal energy or enthalpy, thus not affecting ΔU_0 or ΔH_0.

From the definition of the enthalpy of a perfect gas

$$H = U + pV = U + n\tilde{R}T$$

So if we are concerned only with gaseous mixtures in the reaction then for products and reactants

$$H_{P_0} = U_{P_0} + n_P\tilde{R}_0T_0 \quad \text{and} \quad H_{R_0} = U_{R_0} + n_R\tilde{R}_0T_0$$

where n_P and n_R are the amounts of substance of products and reactants respectively, and the temperature is the reference temperature T_0.

Then, using equations (7.15) and (7.24), we have

$$\Delta H_0 = \Delta U_0 + (n_P - n_R)\tilde{R}T_0 \qquad (7.31)$$

If there is no change in the amount of substance during the reaction, or if the reference temperature is absolute zero, then ΔH_0 and ΔU_0 will be equal.

Example 7.13 Calculate the specific internal energy of reaction for the combustion of benzene (C_6H_6) vapour at 25 °C given that $\Delta\tilde{h}_0 = -3\,169\,540$ kJ/kmol and the H_2O is in the vapour phase.

Solution The combustion equation is

$$C_6H_6 + 7\tfrac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O(\text{vap})$$

$$n_R = 1 + 7.5 = 8.5, \qquad n_P = 6 + 3 = 9$$

From equation (7.31)

$$\Delta U_0 = \Delta H_0 - (n_P - n_R)\tilde{R}T_0$$

$$= -(3\,169\,540 \times 1) - \left\{(9 - 8.5) \times 8.3145 \times 298\right\}$$

where $T_0 = 273 + 25 = 298$ K

i.e. $\Delta U_0 = -3\,169\,540 - 1239 = -3\,170\,779$ kJ

(note that ΔU_0 is negligibly different from ΔH_0)

$$1 \text{ kmol of } C_6H_6 = (6 \times 12) + (6 \times 1) = 78 \text{ kg}$$

therefore

$$\Delta u_0 = -\frac{3\,170\,779}{78} = -40\,651 \text{ kJ/kg}$$

Change in reference temperature

It has already been mentioned that the internal energy and enthalpy of reaction depend on the temperature at which the reaction occurs. This is due to the change in enthalpy and internal energy of the reactants and products with temperature.

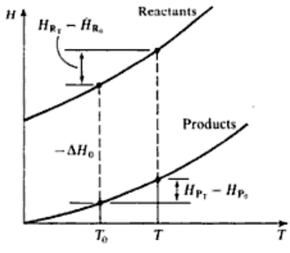
It can be seen from the property diagram of Fig. 7.11 that the enthalpy of reaction at temperature T, ΔH_T can be obtained from ΔH_0 at T_0 by the relationship

$$-\Delta H_T = -\Delta H_0 + (H_{R_T} - H_{R_0}) - (H_{P_T} - H_{P_0}) \qquad (7.32)$$

where $H_{R_T} - H_{R_0}$ = increase in enthalpy of the reactants from T_0 to T

and $H_{P_T} - H_{P_0}$ = increase in enthalpy of the products from T_0 to T

Fig. 7.11 *H–T* diagram for combustion



Example 7.14 For carbon monoxide at 60 °C, $\Delta\tilde{h}$ is given as −282 990 kJ/kmol. Calculate $\Delta\tilde{h}$ at 2800 K given that the molar enthalpies of the gases concerned are as given in Table 7.10.

Table 7.10 Molar enthalpies of gases for Example 7.14

	Molar enthalpy/(kJ/kmol)	
Gas	At 60 °C	At 2800 K
Carbon monoxide	1018	86 115
Oxygen	1036	90 144
Carbon dioxide	1368	140 440

Solution The reaction equation is

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

Also, taking values from Table 7.10, and using equations (7.25) and (7.28)

$$H_{R_0} = (1 \times 1018) + (0.5 \times 1036) = 1536 \text{ kJ}$$

$$H_{R_T} = (1 \times 86\,115) + (0.5 \times 90\,144) = 131\,187 \text{ kJ}$$

$$H_{P_0} = 1 \times 1368 = 1368 \text{ kJ}$$

$$H_{P_T} = 1 \times 140\,440 = 140\,440 \text{ kJ}$$

Then using equation (7.32)

$$-\Delta H_T = -\Delta H_0 + (H_{R_T} - H_{R_0}) - (H_{P_T} - H_{P_0})$$

$$= (1 \times 282\,990) + (131\,187 - 1536) - (140\,440 - 1368)$$

$$= 273\,569 \text{ kJ}$$

i.e. $\Delta\tilde{h} = -273\,569$ kJ/kmol CO

The property diagram and real processes

The property diagram of U against T has already been referred to and is shown in Fig. 7.12(a); a diagram of H against T is shown in Fig. 7.12(b). The diagrams can be used effectively to demonstrate real processes of interest. The solid lines indicate the property variations with T if the constituents are gaseous. If reactants or products contain a liquid component then the property lines will be modified as shown by the dotted lines. It can be seen by inspection that the effect of condensation of the H_2O in the products is to increase ΔU_0 and ΔH_0.

In processes 1–A, $T_A = T_0$ and there is a maximum energy transfer to the surroundings ΔU_T or ΔH_T.

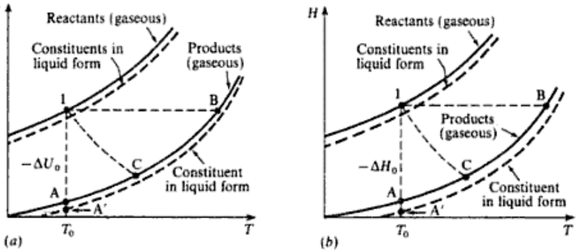


Fig. 7.12 $U-T$ and $H-T$ diagrams for combustion

In processes 1–B the internal energy, or enthalpy, initially and finally is the same so that the increase in temperature is a maximum and the combustion process is adiabatic.

In 1–C the processes are general with heat transfer and possibly work transfer.

Process 1–A′ in Fig. 7.12(a) corresponds to the constant volume bomb calorimeter test and in Fig. 7.12(b) 1–A′ corresponds to the steady-flow combustion Boys' calorimeter test. Both of these tests are discussed later in section 7.12.

In a general non-flow or steady-flow process the initial state (1) and final state (2) will be different and neither will be at the reference temperature T_0. The quantities of interest are $U_2 - U_1$, and $H_2 - H_1$ for the respective processes. It can be seen readily from Fig. 7.13 that

$$U_2 - U_1 = -(U_1 - U_2) = -\{-\Delta U_0 - (U_{R_0} - U_{R_1}) - (U_{P_2} - U_{P_0})\}$$

$$U_2 - U_1 = U_{P_2} - U_{R_1} = (U_{P_2} - U_{P_0}) + \Delta U_0 + (U_{R_0} - U_{R_1})$$

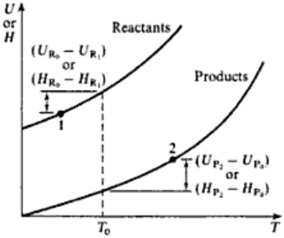


Fig. 7.13 Energy-absolute temperature diagram between stages 1 and 2

This is equation (7.16) repeated. A corresponding expression is obtained for $H_2 - H_1$.

The principles dealt with in this section will now be applied to typical problems.

Example 7.15 A combustible mixture of carbon monoxide and air which is 10% rich is compressed to a pressure of 8.28 bar and a temperature of 282 °C. The mixture is ignited and combustion occurs adiabatically at constant volume. Calculate the maximum temperature and pressure reached assuming that no dissociation takes place. At the reference temperature of 25 °C, $\Delta \tilde{h}_0^{\ominus}$ for CO is $-282\,990$ kJ/kmol.

Solution For stoichiometric conditions

$$CO + \tfrac{1}{2}O_2 + (3.76 \times \tfrac{1}{2})N_2 \rightarrow CO_2 + (3.76 \times \tfrac{1}{2})N_2$$

$$CO + 0.5O_2 + 1.88N_2 \rightarrow CO_2 + 1.88N_2$$

and for a mixture strength of 110%

$$\text{Actual A/F ratio} = \text{stoichiometric A/F ratio} \times \frac{100}{110}$$

$$= \text{stoichiometric A/F ratio}/1.1$$

Therefore, for the actual conditions,

$$CO + (0.5O_2 + 1.88N_2)/1.1 \rightarrow aCO_2 + bCO + 1.71N_2$$

Then,

Carbon balance: $1 = a + b$ [1]

Oxygen balance: $1 + (0.5 \times 2)/1.1 = 2a + b$

i.e. $1.909 = 2a + b$ [2]

From equation [1] and [2]

$$a = 0.909 \quad \text{and} \quad b = 0.091$$

therefore

$$CO + 0.455O_2 + 1.709N_2 \rightarrow 0.909CO_2 + 0.091CO + 1.709N_2$$

Also for the reaction

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$n_R = 1 + 0.5 = 1.5 \quad \text{and} \quad n_P = 1$$

therefore

$$\Delta U_0 = \Delta H_0 - (n_P - n_R)\tilde{R}T_0$$

$$= (-282\,990 \times 1) - \{(1 - 1.5) \times 8.3145 \times 298\}$$

$$= -282\,990 + 1239 = -281\,751 \text{ kJ}$$

i.e. $\Delta \tilde{u}_0^{\ominus} = -281\,751$ kJ/kmol

The non-flow process is defined by

$$Q + W = (U_2 - U_1)$$

Also $Q = 0$; $W = 0$ at constant volume; $U_1 = U_R$, $U_2 = U_{P_2}$, therefore

$$(U_{P_2} - U_{R_1}) = 0$$

$$(U_{P_2} - U_{P_0}) + (U_{P_0} - U_{R_0}) + (U_{R_0} - U_{R_1}) = 0$$

$$(U_{P_2} - U_{P_0}) + \Delta U_0 + (U_{R_0} - U_{R_1}) = 0 \quad [3]$$

The values of molar internal energies for the various gases can be read from the tables of ref. 7.6. Then

At 298.15 K $\quad U_{R_0} = -2479 - (0.455 \times 2479) - (1.709 \times 2479)$

$= -7844$ kJ

At 555 K $\quad U_{R_1} = 2984.6 + (0.455 \times 3233.1) + (1.709 \times 2944.2)$

$= 9487$ kJ

At 298.15 K $\quad U_{P_0} = -(0.909 \times 2479) - (0.091 \times 2479) - (1.709 \times 2479)$

$= -6716$ kJ

Substituting in [3],

$$(U_{P_2} + 6716) - (0.909 \times 281\,751) + (-7844 - 9487) = 0$$

Note: there are 0.091 kmol CO in the products therefore only $(1 - 0.091) = 0.909$ kmol of CO releases energy of reaction,

i.e. $\quad U_{P_2} = 266\,727$ kJ

To find the temperature of products a trial-and-error method is now necessary.

At T_2 $\quad U_{P_2} = \{0.909 \times (\tilde{u}_2 \text{ for } CO_2)\} + \{0.091 \times (\tilde{u}_2 \text{ for } CO)\}$

$+ \{1.709 \times (\tilde{u}_2 \text{ for } N_2)\}$

Try $T_2 = 3200$ K

$$U_{P_2} = (0.909 \times 138\,720) + (0.091 \times 74\,391) + (1.709 \times 73\,555)$$

$$= 258\,572 \text{ kJ}$$

This compares with the figure of 266 727 kJ calculated above, hence the actual temperature of the products is slightly greater than 3200 K; a second guess from tables gives a value of 3280 K.

The temperature calculated in Example 7.15 is that which would be obtained by adiabatic combustion of the mixture. This temperature would not be attained in practice due to the effect of dissociation; this was discussed in section 7.7 and the inclusion of this effect is illustrated in Example 7.16.

Example 7.16 Calculate the final temperature for the mixture defined in Example 7.15 including the effect of dissociation.

Solution The proportions of the constituents depend on the temperature so the combustion equation is written as

$$CO + 0.455O_2 + 1.709N_2 \rightarrow aCO_2 + bCO + cO_2 + 1.709N_2$$

and b and c can be expressed in terms of a by an atomic balance.

Carbon balance: $1 = a + b$ therefore $b = 1 - a$
Oxygen balance: $1 + (0.455 \times 2) = 2a + b + 2c$

$$1.91 = 2a + b + 2c$$

i.e. $2c = 1.91 - 2a - (1 - a)$

therefore

$$c = 0.455 - 0.5a$$

and

$$CO + 0.455O_2 + 1.709N_2$$
$$\rightarrow aCO_2 + (1-a)CO + (0.455 - 0.5a)O_2 + 1.709N_2$$

The energy equation can be written as previously

$$(U_{P_2} - U_{P_0}) + \Delta U_0 + (U_{R_0} - U_{R_1}) = 0$$

Using the values calculated in Example 7.15,

$$U_{P_0} = -(a \times 2479) - \{(1-a) \times 2479\}$$
$$- \{(0.455 - 0.5a) \times 2479\} - [1.709 \times 2479]$$
$$= -(3.164 - 0.5a) \times 2479 \text{ kJ}$$

$$\Delta U_0 = -a \times 281\,751 \text{ kJ}$$

$$U_{R_0} = -7844 \text{ kJ} \qquad U_{R_1} = 9487 \text{ kJ}$$

Substituting,

$$U_{P_2} + \{(3.164 - 0.5a) \times 2479\} - 281\,751a - 17\,331 = 0$$

therefore

$$U_{P_2} = 9487 + 282\,991a \qquad [1]$$

A second equation is derived using the equilibrium constant for the reaction

$$K^\ominus = \frac{p_{CO_2}}{p_{CO}}\left\{\frac{p}{p_{O_2}}\right\}^{1/2}_{1/2} = \frac{a}{(1-a)}\left\{\frac{n_2}{(0.455 - 0.5a)p_2}\right\}^{1/2}$$

where p_2 is the pressure of the mixture after combustion and n_2 the number of kmol of the products. Now

$$p_1 V = n_1 R T_1 \quad \text{and} \quad p_2 V = n_2 R T_2$$

$$\frac{n_2}{p_2} = \frac{T_1}{T_2}\frac{n_1}{p_1} = \frac{555}{T_2} \times \frac{(1 + 0.455 + 1.709)}{8.28} = \frac{212.08}{T_2} \text{ kmol/bar}$$

Substituting in the expression for K gives

$$K^\ominus = \frac{a}{(1-a)}\left\{\frac{212.08}{(0.455 - 0.5a)T_2}\right\}^{1/2} \qquad [2]$$

When the value of T_2 is known then U_{P_2} can be found by reading off $\tilde{u}$ for each of the products and multiplying by the amount of substance of each; equating this to the value of U_{P_2} in [1] allows a value of a to be calculated.

Similarly, when T_2 is known a value of $\ln(K^\ominus)$ can be read from tables, and from [2] a value of a is then found.

Therefore, one convenient trial-and-error method is to choose a value of T_2, calculate a value of a from [1], and then find a value of $K^\ominus$ from [2]. Compare this value of $K^\ominus$ with that found from tables at T_2. When the two values of $K^\ominus$ are the same then the correct value of T_2 has been found.

For example, at $T_2 = 3000$ K, from tables:

$$\begin{aligned} U_{P_2} &= 127\,920a + 68\,598(1 - a) \\ &\quad + 73\,155(0.455 - 0.5a) + (67\,795 \times 1.709) \\ &= 217\,745 + 22\,744.5a \end{aligned}$$

i.e. in [1],

$$217\,745 + 22\,744.5a = 9487 + 282\,991a$$

therefore

$$a = 0.8$$

Substituting for a and T_2 in [2]

$$\begin{aligned} K^\ominus &= \frac{0.8}{0.2}\left\{\frac{212.08}{(0.455 - 0.5a) \times 3000}\right\}^{1/2} \\ &= 4.54 \end{aligned}$$

From tables at $T_2 = 3000$ K,

$$\ln(K^\ominus) = 1.110 \quad \text{therefore } K^\ominus = 3.03 \text{ (too low)}$$

By such a method the value of T_2 is found to be 2949 K to the nearest degree. This value should be compared with the value of 3280 K from Example 7.15 when dissociation was ignored.

7.9 Enthalpy of formation, $\Delta\tilde{h}_f$

The combustion reaction is a particular kind of chemical reaction in which products are formed from reactants with the release or absorption of energy as heat is transferred to or from the surroundings. As some substances, for instance hydrocarbon fuels, may be many in number and complex in structure the enthalpy of reaction may be calculated on the basis of known values of the molar enthalpy of formation, $\Delta\tilde{h}_f^\ominus$ of the constituents of the reactants and products at the reference temperature T_0.

The molar enthalpy of formation $\Delta\tilde{h}_f$ is the increase in enthalpy when a compound is formed from its constituent elements in their natural form and in a standard state. Something needs to be said about the standard form. The normal forms of oxygen (O_2) and hydrogen (H_2) are gaseous, so $\Delta\tilde{h}_f^\ominus$ for the can be put equal to zero. The normal form of carbon (C) is graphite, for solid carbon is put to zero. Carbon in another form, e.g. diamond is not 'normal' and $\Delta\tilde{h}_f^\ominus$ is quoted. The standard state is 25 °C, and 1 bar pressure, but it must be borne in mind that not all substances can exist in the natural form, e.g. H_2O cannot be a vapour at 1 bar and 25 °C.

For calculation purposes, for a particular reaction

$$\Delta\tilde{h}^\ominus = \sum_P n_i \Delta\tilde{h}_{f_i}^\ominus - \sum_R n_i \Delta\tilde{h}_{f_i}^\ominus \tag{7.33}$$

Typical values of $\Delta\tilde{h}_f^\ominus$ are quoted for different substances in Table 7.11.

Table 7.11 Typical heats of formation $\Delta\tilde{h}_f^\ominus$ of various species at 25 °C (298 K) and 1 bar

Substance	Formula	State	$\Delta\tilde{h}_f^\ominus$ (kJ/kmol)
	O	Gas	249 170
Oxygen	O_2	Gas	0
Water	H_2O	Liquid	−285 820
Water	H_2O	Vapour	−241 830
Carbon	C	Gas	714 990
Carbon	C	Diamond	1 900
Carbon	C	Graphite	0
Carbon monoxide	CO	Gas	−110 530
Carbon dioxide	CO_2	Gas	−393 520
Methane	CH_4	Gas	−74 870
Methyl alcohol	CH_3OH	Vapour	−240 532
Ethyl alcohol	C_2H_5OH	Vapour	−281 102
Ethane	C_2H_6	Gas	−83 870
Ethene	C_2H_4	Gas	52 470
Propane	C_3H_8	Gas	−102 900
Butane	C_4H_{10}	Gas	−125 000
Octane	C_8H_{18}	Liquid	−247 600

Example 7.17 Calculate the molar enthalpy of reaction at 25 °C of ethyl alcohol, C_2H_5OH, using the data of Table 7.11.

Solution Using equation (7.33)

$$\Delta\tilde{h}_f^\ominus = \sum_P n_i \Delta\tilde{h}_{f_i}^\ominus - \sum_R n_i \Delta\tilde{h}_{f_i}^\ominus$$

and the combustion equation

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$\sum_R n_i \Delta\tilde{h}_{f_i}^\ominus = 1 \times (-281\,102) + 3 \times 0 = -281\,102$$

$$\sum_P n_i \Delta\tilde{h}_{f_i}^\ominus = 2 \times (-393\,520) + 3 \times (-241\,830) = -1\,512\,530$$

therefore

$$\Delta\tilde{h}^\ominus = -1\,512\,530 - (-281\,102)$$

$$= -1\,231\,428 \text{ kJ/kmol}$$

7.10 Calorific value of fuels

The quantities $\Delta h^\ominus$ and $\Delta u^\ominus$ are approximated to in fuel specifications by quantities called *calorific values* which are obtained by the combustion of the fuels in suitable apparatus. This may be of the constant volume type (e.g. bomb calorimeter) or constant pressure, steady-flow type (e.g. Boys' calorimeter). Both of these are described in section 7.1. Definitions of calorific value are as follows:

(1) The energy transferred as heat to the surroundings (cooling water) per unit quantity of fuel when burned at constant volume with the H_2O product of combustion in the liquid phase is called the gross (or higher) calorific value (GCV) at constant volume $Q_{gr,v}$. This approximates to $-\Delta u^\ominus$ at a reference temperature of 25 °C with the H_2O in the liquid phase.

If the H_2O products are in the vapour phase the energy released per unit quantity is called the net (or lower) calorific value (NCV) at constant volume, $Q_{net,v}$. This approximates to $-\Delta u^\ominus$ at 25 °C with the H_2O in the vapour phase.

(2) The energy transferred as heat to the surroundings (cooling water) per unit quantity of fuel when burned at constant pressure with the H_2O products of combustion in the liquid phase is called the gross (or higher) calorific value (GCV) at constant pressure, $Q_{gr,p}$. This approximates to $-\Delta h^\ominus$ at a reference temperature of 25 °C with the H_2O in the liquid phase.

If the H_2O products are in the vapour phase the energy released is called the net (or lower) calorific value (NCV) at constant pressure, $Q_{net,p}$. This approximates to $-\Delta h^\ominus$ at 25 °C with the H_2O in the vapour phase.

Contrary to the definition of $\Delta u^\ominus$ and $\Delta h^\ominus$ it is usual to quote calorific values as positive quantities. If $Q_{gr,p}$ and the fuel composition is known, the other quantities can be calculated. The above quantities are related as follows. For the constant volume process

$$Q_{gr,v} = Q_{net,v} + m_c u_{fg} \tag{7.34}$$

For the constant pressure process

$$Q_{gr,p} = Q_{net,p} + m_c h_{fg} \tag{7.35}$$

where m_c is the mass of condensate per unit quantity of fuel.

$$u_{fg} = u_{fg} \text{ at } 25\,^\circ\text{C for } H_2O = 2304.4 \text{ kJ/kg}$$

$$h_{fg} = h_{fg} \text{ at } 25\,^\circ\text{C for } H_2O = 2441.8 \text{ kJ/kg}$$

The calorific values differ from $\Delta h^\ominus$ and $\Delta u^\ominus$ due to the departure of experimental conditions from ideal with regard to temperatures of products and reactants and also heat transfer conditions. This topic is discussed further in section 7.12.

7.11 Power plant thermal efficiency

The purpose of any power plant is the power output which should be obtained as economically as possible consistent with capital cost and running conditions.

It is necessary to assess the overall performance of a plant for comparison purposes and an important criterion is the *overall thermal efficiency* η_0. This is defined as

$$\eta_0 = \frac{\text{work output}}{\text{fuel energy supplied}}$$

It is necessary to decide on the denominator for this definition. It is desirable, if we consider a steady-flow process, to relate the plant conditions to those for the steady-flow calorimeter in which the products are cooled to atmospheric temperature giving $Q_{gr,p}$. However, it is not possible, or desirable, to cool the products of combustion in a real plant to atmospheric temperature so there is a substantial energy loss to atmosphere. Complete cooling of the products would require large heat transfer surfaces which are expensive and the condensate produced would form corrosive acids. As achieving these conditions is not even attempted it seems that the use of $Q_{gr,p}$ is unsatisfactory and $Q_{net,p}$ is more appropriate and this is often preferred. It does not matter for comparison purposes except that both values are in use making the definition of η_0 somewhat arbitrary as

$$\eta_0 = \frac{-W}{Q_{gr,p}} \quad \text{or} \quad \frac{-W}{Q_{net,p}} \tag{7.36}$$

It is necessary to state with the definition whether $Q_{gr,p}$ or $Q_{net,p}$ is being used.

In a plant it may be required to assess the boiler or steam generator performance only, in which case the *boiler efficiency*, given similarly in equation (8.16), is defined as

$$\text{Boiler efficiency} = \frac{\text{heat transferred to working fluid}}{\text{fuel energy supplied}}$$

therefore

$$\eta_B = \frac{\text{heat transferred to working fluid}}{Q_{gr,p} \text{ or } Q_{net,p}} \tag{7.37}$$

It is again necessary to state whether $Q_{gr,p}$ or $Q_{net,p}$ is being used when boiler efficiency is quoted.

Example 7.18 A medium-size steam boiler required to supply a generator of output 25 000 kW has a performance specification as follows: steam output 31.6 kg/s; steam pressure 60 bar; steam temperature 500 °C; feed water temperature 100 °C; fuel, natural gas (96.5% CH_4, 0.5% C_2H_6, remainder incombustible); gross calorific value 38 700 kJ/m^3 at 1.013 bar and 15 °C; fuel consumption 2.85 m^3/s.

Calculate the boiler efficiency and the overall thermal efficiency based on the net calorific value of the fuel.

Solution 1 kmol of CH_4 burns to give 2 kmol H_2O, therefore 0.965 kmol of CH_4 burns to give $2 \times 0.965 \times 18 = 34.74$ kg H_2O.

1 kmol of C_2H_6 burns to give 3 kmol H_2O, therefore 0.005 kmol of C_2H_6 burns to give $3 \times 0.005 \times 18 = 0.27$ kg H_2O. Therefore 1 kmol of gas produces $34.74 + 0.27 = 35.01$ kg H_2O, and 1 kmol of gas occupies a volumeof $(\tilde{R}T/p) = (8314.5 \times 288/1.013 \times 10^5) = 23.64\ \mathrm{m^3}$ at 1.013 bar and 15 °C, therefore

$$\text{Steam formed per m}^3 \text{ of gas} = \frac{35.01}{23.64} = 1.481 \text{ kg}$$

Using equation (7.35)

$$Q_{gr,p} = Q_{net,p} + m_c h_{fg}$$

therefore

$$Q_{net,p} = 38\,700 - (1.481 \times 2441.8) = 35\,084 \text{ kJ/m}^3$$

$$\text{Heat to working fluid} = h_{\text{supply steam}} - h_{\text{feedwater}}$$

$$= 3421 - 419.1 = 3001.9 \text{ kJ/kg}$$

Using equation (7.37), therefore

$$\eta_B = \frac{3001.9 \times 31.6}{2.85 \times 35\,084} = 0.95(95\%)$$

and using equation (7.36)

$$\eta_O = \frac{\text{work output}}{Q_{net,p}} = \frac{25\,000}{2.85 \times 35\,084} = 0.25(25\%)$$

7.12 Practical determination of calorific values

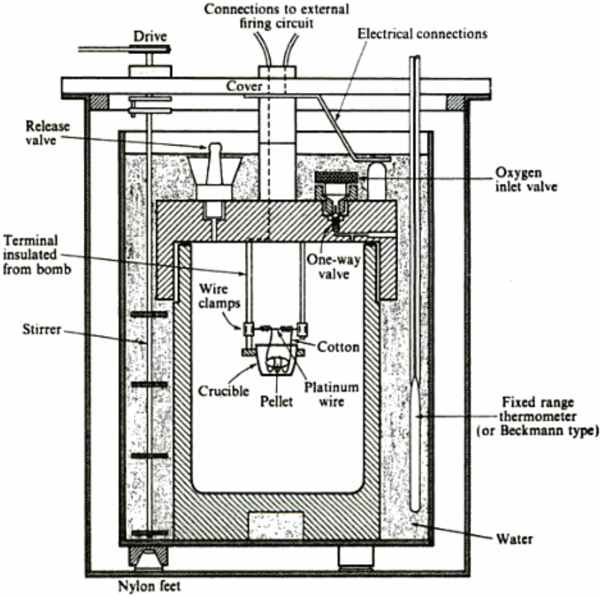
The methods for determining calorific value depend on the type of fuel; solid and liquid fuels are usually tested in a bomb calorimeter, and gaseous fuels in a continuous-flow apparatus such as Boys' calorimeter. The apparatus in every case is required to meet with a standard specification and the procedure to be adopted is also laid down.

Solid and liquid fuel

In the bomb calorimeter combustion occurs at constant volume and is a non-flow process; in Boys' calorimeter the gas is burnt continuously under steady-flow conditions.

The bomb is a small stainless steel vessel in which a small mass of the fuel is held in a crucible (see Fig. 7.14). If the fuel is solid, it is usually crushed, passed through a sieve, and then pressed into the form of a pellet in a special press. The size of pellet is estimated from the expected heat release, and is such that the temperature rise to be measured does not exceed 2–3 K. The pellet is ignited

Fig. 7.14 Bomb calorimeter



by fusing a piece of platinum or nichrome wire which is in contact with it. The wire forms part of an electric circuit which can be completed by a firing button, which is situated in a position remote from the bomb. With a special form of press the pellet can be formed with the fuse wire passing through it. This facilitates the firing, particularly with some of the more difficult fuels. The crucible carrying the pellet is located in the bomb, a small quantity of distilled water is put into the bomb to absorb the vapours formed by combustion and to ensure that the water vapour produced is condensed, and the top of the bomb is screwed down. Oxygen is then admitted slowly until the pressure is above 23 atm. The bomb is located in the calorimeter and a measured quantity of water is poured into the calorimeter. The calorimeter is closed, the external connections to the circuit are made, and an accurate thermometer of the fixed range or Beckman type is immersed to the proper depth in the water. The water is stirred in a regular manner by a motor-driven stirrer, and temperature observations are taken every minute. At the end of the fifth minute the charge is fired and temperature readings are taken every 10 s during this period. When the temperature readings begin to fall the frequency of readings can be reduced to every minute.

The measured temperature rise is corrected for various losses. The cooling loss is the largest, but corrections are also necessary for the heat released by the combustion of the wire itself, and for the formation of acids on combustion. The cooling correction can be determined graphically or by use of a formula developed by Regnault and Pfaundler. The allowance for the combustion of the wire is determined from its weight and known calorific value. The allowance for acids present is determined by a chemical titration. For most purposes only the correction for cooling need be applied.

If a liquid fuel is being tested, it is contained in a gelatine capsule and the firing may be assisted by including in the crucible a little paraffin of known calorific value.

The water equivalent of the calorimeter is determined by burning a fuel of known calorific value (e.g. benzoic acid) in the bomb. The calculation for the test is then as follows:

Mass of fuel × calorific value
= (mass of water + water equivalent of bomb)
× corrected temperature rise × specific heat capacity of water

From this equation the calorific value of the fuel tested can be found.

Example 7.19 Table 7.12 gives the results of a bomb calorimeter test on a sample of coal. The mass of coal burned was 0.825 g and the total water equivalent of the apparatus was determined as 2500 g. Calculate the calorific value of the coal in kilojoules per kilogram. The temperature rise is to be corrected according to the formula by Regnault and Pfaundler, but no correction need be made for the acids formed.

Table 7.12 Results for a bomb calorimeter test

Pre-firing period time (min.)	Temp. (°C)	Heating time (min.)	Temp. (°C)	Cooling period time (min.)	Temp. (°C)
0	25.730	t_1 6	27.340	t_n 10	27.880
1	25.732	t_2 7	27.880	11	27.878
2	25.734	t_3 8	27.883	12	27.876
3	25.736	t_4 9	27.885	13	27.874
4	25.738			14	27.872
t_0 5	25.740			15	27.870

Solution The Regnault and Pfaundler cooling correction is as follows:

$$\text{Correction} = nv + \left(\frac{v_1 - v}{t_1 - t}\right)\left\{\sum_{1}^{(n-1)}(t) + \tfrac{1}{2}(t_0 + t_n) - nt\right\}$$

where n is the number of minutes between the time of firing and the first reading after the temperature begins to fall from the maximum, v the rate of fall of temperature per minute during the pre-firing period, v_1 the rate of fall of temperature per minute after the maximum temperature, t and t_1 the average temperatures during the pre-firing and final periods respectively, $\Sigma_1^{(n-1)}(t)$ the sum of the readings during the period between firing and the start of cooling, and $\frac{1}{2}(t_0 + t_n)$ the mean of the temperature at the moment of firing and the first temperature after the rate of change of temperature becomes constant. The pre-firing and final periods are of the same duration.

In this example

$$n = 10 - 5 = 5 \text{ min}$$

$$v = -\left(\frac{25.740 - 25.730}{5}\right) = -0.002 \text{ K/min}$$

the negative sign indicates that the temperature was rising in the pre-firing period.

$$v_1 = \frac{27.880 - 27.870}{5} = 0.002 \text{ K/min}$$

$$t = 25.735\,^\circ\text{C} \quad \text{and} \quad t_1 = 27.875\,^\circ\text{C}$$

$$\sum_1^{(n-1)}(t) = 110.988\,^\circ\text{C} \quad \text{and}$$

$$\tfrac{1}{2}(t_0 + t_n) = \frac{25.740 + 27.880}{2} = 26.81\,^\circ\text{C}$$

Substituting the values in the equation gives

$$\text{Correction} = -5 \times 0.002 + \left(\frac{0.002 + 0.002}{27.875 - 25.735}\right) \times (110.988 + 26.81 - 5 \times 25.735)$$

i.e. $\text{Correction} = 0.00705 \text{ K}$

$$\text{Uncorrected temperature rise} = -t_n - t_0 = 27.880 - 25.740 = 2.14 \text{ K}$$

therefore

$$\text{Correct temperature rise} = 2.14 + 0.00705 = 2.147 \text{ K}$$

Then $\text{Heat released from 0.825 g coal} = 2.147 \times 2500 \times 4.187 \times 10^{-3} = 22.5 \text{ kJ}$

i.e. $\text{Calorific value} = \dfrac{22.5}{0.825 \times 10^{-3}} = 27\,250 \text{ kJ/kg}$

i.e. Calorific value of fuel = 27 250 kJ/kg

Gaseous fuels

For a gaseous fuel a continuous supply of the gas is metered and passed at constant pressure into the calorimeter, where it is burned in an ample supply of air (see Fig. 7.15). The products of combustion are cooled as nearly as possible to the initial temperature of the reactants by a continuously circulating supply of cooling water. The gas pressure and temperature are measured and the amount of gas burned is referred to 1.013 bar and 15 °C. The temperature rise of the circulating water is measured, and the condensate from the products of combustion is collected. A test is carried out over a fixed time period. The water flow rate is measured and the condensate is weighed. Then we have

(Volume of fuel at 1.013 bar and 15 °C) × (calorific value)
= (mass of water circulated) × specific heat capacity
× (temperature rise of water)

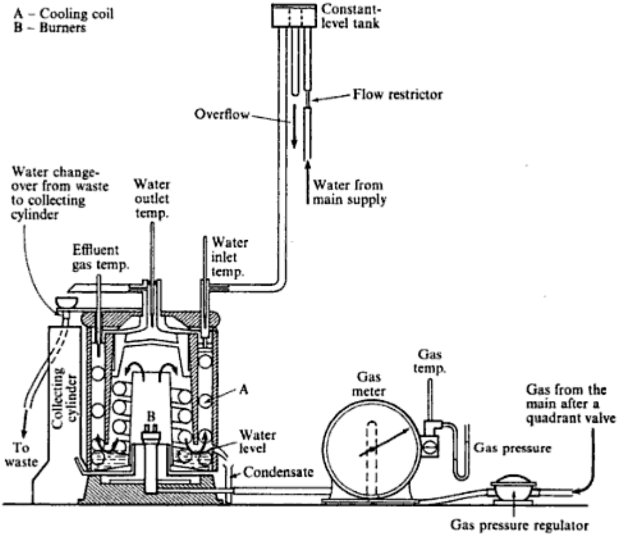


Fig. 7.15 Boys' gas calorimeter

The calorific value of the fuel is obtained in megajoules per cubic metre of gas. The correct procedure for this determination is given in ref. 7.7.

In both the bomb calorimeter test and Boys' calorimeter test the steam formed on combustion is condensed, and so the heat released by the steam on condensing is transferred to the cooling water.

Example 7.20 In a bomb calorimeter test on petrol the GCV was determined and found to be 46 900 kJ/kg. If the fuel contains 14.4% H by mass, calculate the NCV.

Solution From equation (7.1),

$$2H_2 + O_2 \rightarrow 2H_2O$$

therefore

$$4 \text{ kg H} + 32 \text{ kg } O_2 \rightarrow 36 \text{ kg } H_2O$$

or 1 kg H gives 9 kg H_2O, therefore

$$0.144 \text{ kg H gives } 0.144 \times 9 = 1.296 \text{ kg } H_2O$$

Then using equation (7.34)

$$Q_{net,v} = Q_{gr,v} - m_c u_{fg}$$

therefore

$$Q_{net,v} = 46\,900 - (1.296 \times 2304.4) = 43\,910 \text{ kJ/kg}$$

Table 7.13 gives some typical calorific values of solid, liquid, and gaseous fuels.

7.13 Air and fuel–vapour mixtures

The mixture supplied to an engine fitted with a carburettor is one of air and fuel vapour, and the quality of the mixture is controlled by the carburettor. If the mixture is saturated with fuel vapour then the relative proportions of fuel to air can be determined from a knowledge of the temperature-pressure relationship for the saturated fuel. Such values are given for ethyl alcohol in Table 7.14.

Example 7.21 In Example 7.3 the stoichiometric A/F ratio for ethyl alcohol, C_2H_6O, was found to be 8.957/1. If the NCV of ethyl alcohol is 27 800 kJ/kg, calculate the calorific value of the combustion mixture per cubic metre at 1.013 bar and 15 °C.

Solution The molar mass of ethyl alcohol is 46 kg/kmol, therefore we have

$$\text{amount of substance of fuel per kilogram of fuel} = \frac{1}{46}$$

$$= 0.021\,74 \text{ kmol/kg}$$

The molar mass of air is 28.96 kg/kmol, therefore

$$\text{amount of substance of air per kg of fuel} = \frac{8.957}{28.96} = 0.3093 \text{ kmol/kg}$$

i.e.

$$\text{Total amount of substance of mixture} = 0.021\,74 + 0.3093$$

$$= 0.3310 \text{ kmol/kg}$$

Table 7.13 Typical calorific values of some fuels

Fuel	Calorific value at 15 °C (kJ/kg) Gross	Net
Solid		
Anthracite	34 600	33 900
Bituminous coal	33 500	32 450
Coke	30 750	30 500
Lignite	21 650	20 400
Peat	15 900	14 500
Liquid		
100-octane petrol	47 300	44 000
Motor petrol	46 800	43 700
Benzole	42 000	40 200
Kerosene	46 250	43 250
Diesel oil	46 000	43 250
Light fuel oil	44 800	42 100
Heavy fuel oil	44 000	41 300
Residual fuel oil	42 100	40 000

Gas	Calorific value at 15 °C and 1 bar (MJ/m^3) Gross	Net
Butane	122.00	113.00
Propane	96.00	86.00
Natural gas	38.20	35.20
Coal gas	20.00	17.85
Hydrogen	11.85	10.00
Producer gas	6.04	6.00
Blast-furnace gas	3.41	3.37

Table 7.14 Approximate saturation temperatures and pressures for ethyl alcohol (C_2H_6O)

Temp./(°C)	0	10	20	30	40	50	60
Pressure/(bar)	0.0162	0.0314	0.0584	0.1049	0.1800	0.2960	0.4690

From equation (2.8)

$$pV = n\tilde{R}T$$

therefore

$$V = \frac{0.331 \times 8314.5 \times 288}{1.013 \times 10^5} = 7.824 \text{ m}^3 \text{ per kg of fuel}$$

Now NCV of fuel $= Q_{net,v} = 27.8$ MJ/kg

therefore

$$\text{NCV of mixture} = \frac{27.8}{7.824} = 3.55 \text{ MJ/m}^3 \text{ of mixture}$$

Example 7.22 For a stoichiometric mixture of ethyl alcohol and air calculate the temperature above which there will be no liquid fuel in the mixture. The pressure of the mixture is 1.013 bar.

Solution Using the results of Example 7.21, we have

amount of substance of ethyl alcohol = 0.021 74 kmol/kg

and Total amount of substance = 0.331 kmol

Then using equation (6.14), $p_i = (n_i/n)p$, we have

$$\text{Partial pressure of ethyl alcohol vapour} = \frac{0.021\,74}{0.331} \times 1.013$$

$$= 0.0665 \text{ bar}$$

From Table 7.14, the saturation temperature corresponding to this pressure lies between 20 and 30 °C. Therefore interpolating

$$t = 20 + \left(\frac{0.0665 - 0.0584}{0.1049 - 0.0584}\right) \times (30 - 20) = 21.74\,°\text{C}$$

Hence the minimum temperature of the mixture is 21.74 °C for complete evaporation of the liquid fuel.

Problems

7.1 A sample of bituminous coal gave the following ultimate analysis by mass: C 81.9%; H 4.9%; O 6%; N 2.3%; ash 4.9%. Calculate:
(i) the stoichiometric A/F ratio;
(ii) the analysis by volume of the wet and dry products of combustion when the air supplied is 25% in excess of that required for complete combustion.
(10.8/1; CO_2 14.14%; H_2O 5.07%; O_2 4.08%; N_2 76.71%; CO_2 14.89%; O_2 4.30%; N_2 80.81%)

7.2 An analysis of natural gas gave the following values: CH_4 93%; C_2H_6 4%; N_2 3%. Calculate the stoichiometric A/F ratio and the analysis of the wet and dry products of combustion when the A/F ratio is 12/1.
(9.524/1; CO_2 7.76%; H_2O 15.21%; O_2 3.99%; N_2 73.04%; CO_2 9.15%; O_2 4.71%; N_2 86.14%)

7.3 Calculate the stoichiometric A/F ratio for benzene (C_6H_6), and the wet and dry analysis of the combustion products.
(13.2/1; CO_2 16.13%; H_2O 8.06%; N_2 75.81%; CO_2 17.54%; N_2 82.46%)

7.4 In the actual combustion of benzene in an engine the A/F ratio was 12/1. Calculate the analysis of the wet products of combustion.

(CO_2 13.38%; CO 3.94%; H_2O 8.66%; N_2 74.03%)

7.5 The ultimate analysis of a sample of petrol was 85.5% C and 14.5% H. Calculate:

(i) the stoichiometric A/F ratio;
(ii) the A/F ratio when the mixture strength is 90%;
(iii) the A/F ratio when the mixture strength is 120%;
(iv) the analyses of the dry products for (ii) and (iii);
(v) the volume flow rate of the products through the engine exhaust per unit rate of fuel consumption for (iii) when the pressure is 1.013 bar and the temperature is 110 °C.

(14.76/1; 16.4/1; 12.3/1; CO_2 13.38%; O_2 2.24%; N_2 84.38%; CO_2 8.67%; CO 8.79%; N_2 82.54%; 15.11 m^3/s per kg/s)

7.6 The ultimate analysis of a sample of petrol was C 85.5% and H 14.5%. The analysis of the dry products gave 14% CO_2 and some O_2. Calculate the A/F ratio supplied to the engine, and the mixture strength.

(15.72/1; 94%)

7.7 In an engine test the dry product analysis was CO_2 15.5%; O_2 2.3% and the remainder N_2. Assuming that the fuel burned was a pure hydrocarbon, calculate the ratio of carbon to hydrogen in the fuel, the A/F ratio used, and the mixture strength.

(11.5; 14.84/1; 89.5%)

7.8 The ultimate analysis of a sample of petrol was 85% C and 15% H. The analysis of the dry products showed 13.5% CO_2, some CO and the remainder N_2. Calculate:

(i) the actual A/F ratio;
(ii) the mixture strength;
(iii) the mass of H_2O vapour carried by the exhaust gas per kilogram of total exhaust gas;
(iv) the temperature to which the gas must be cooled before condensation of the H_2O vapour begins, if the pressure in the exhaust pipe is 1.013 bar.

(14.31/1; 104%; 0.088 kg/kg; 52.7 °C)

7.9 A quantity of coal used in a boiler had the following analysis: 82% C; 5% H; 6% O; 2% N; 5% ash. The dry flue gas analysis showed 14% CO_2 and some oxygen. Calculate:

(i) the oxygen content of the dry flue gas;
(ii) the A/F ratio and the excess air supplied.

(5.52%; 14.29/1; 31.8%)

7.10 For the mixture of Problem 7.4 calculate the calorific value per cubic metre of mixture at 1.013 bar and 38 °C. The calorific value of benzene is 40 700 kJ/kg.

(3.73 MJ/m^3)

7.11 The lower explosive limit of ethyl alcohol in air is 3.56% by volume at a pressure of 1013 mbar. If the pressure in a room is 1013 mbar calculate the lowest temperature at which the explosive mixture would be formed. What quantity of ethyl alcohol in litres would be needed in a room of volume 115 m^3 to produce this mixture. The specific gravity of liquid ethyl alcohol is 0.794. Use the data of Table 7.14 for this problem.

(11.73 °C; 10.15/1)

7.12 The products of combustion of a hydrocarbon fuel, of carbon to hydrogen ratio 0.85:0.15, are found to be CO_2 8%, CO 1%, O_2 8.5%. Calculate the A/F ratio for the process by two methods and hence check the consistency of the data.

(23.70, 23.53)

7.13 A stoichiometric mixture of CO and air was burned adiabatically at constant volume and at the peak pressure of 7.2 bar the temperature was 2469 °C; analysis showed the volume of CO present in the products to be 0.192 of the volume of CO supplied. Show by calculating the equilibrium constant for $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$ that the data are consistent. The value of ln $K^{\ominus}$ for this reaction at 2600 K is 2.800 and at 2800 K it is 1.893.

7.14 The products of a fuel when measured at a high temperature gave the following analysis: 9.27% CO_2; 4.00% CO; 14.20% H_2O; 0.90% H_2; 71.03% N_2. Using appropriate values of equilibrium constants from tables such as those of ref. 7.3, estimate the temperature and pressure of the products.

(2800 K; 20.31 bar)

7.15 A stoichiometric mixture of benzene (C_6H_6) and air is induced into an engine of volumetric compression ratio 5 to 1. The pressure and temperature at the beginning of compression are 1 bar and 100 °C. The estimated maximum temperature reached, allowing for dissociation, after adiabatic combustion at constant volume is 2727 °C and at this temperature the standard equilibrium constants are

$$\frac{p_{CO_2}(p^{\ominus})^{1/2}}{p_{CO}(p_{O_2})^{1/2}} = 3.034 \qquad \frac{p_{H_2O}p_{CO}}{p_{H_2}p_{CO_2}} = 7.214$$

Show that about 74.4% of the carbon in the fuel is burned to CO_2 and calculate the maximum pressure reached.

(41.7 bar)

7.16 The enthalpy of combustion of propane gas, C_3H_8, at 25 °C with the H_2O in the products in the liquid phase is −50 360 kJ/kg. Calculate the enthalpy of combustion with the H_2O in the vapour phase per unit mass of fuel and per unit amount of substance of fuel.

(−46 364 kJ/kg; −2 040 030 kJ/kmol)

7.17 Calculate, for propane liquid, C_3H_8, at 25 °C the enthalpy of combustion with the H_2O in the products in the vapour phase. Use the data of Problem 7.16 and take h_{fg} at 25 °C for propane as 372 kJ/kg.

(−45 992 kJ/kg)

7.18 Calculate the internal energy of combustion per unit mass of propane vapour, C_3H_8, at 25 °C with the H_2O in the vapour phase from the corresponding value of $\Delta h^{\ominus} = -46\,364$ kJ/kg.

(−46 420 kJ/kg)

7.19 Calculate the internal energy of combustion per unit mass for gaseous propane, C_3H_8, at 25 °C with the H_2O of combustion in the liquid phase from the corresponding value of $\Delta h^{\ominus} = -50\,360$ kJ/kg.

(−50 191 kJ/kg)

7.20 Calculate the internal energy of combustion per unit mass for liquid propane, C_3H_8, at 25 °C with the H_2O of combustion in the vapour phase from the corresponding value of $\Delta h^{\ominus} = -45\,992$ kJ/kg.

(−46 105 kJ/kg)

7.21 $\Delta \tilde{h}^{\ominus}$ for hydrogen at 60 °C is given as −242 400 kJ/kmol. Calculate $\Delta \tilde{h}^{\ominus}$ at 1950 °C given that the molar enthalpies of the gases concerned are as in Table 7.15.

(−252 087 kJ/kmol)

7.22 A stoichiometric mixture of hydrogen and air at 25 °C is ignited and combustion takes place adiabatically at a constant pressure of 1 bar. $\Delta \tilde{h}^{\ominus}$ for hydrogen at 25 °C with the

Table 7.15 Molar enthalpies of gases for problem 7.21

	Molar enthalpy/(kJ/kmol)	
Gas	60 °C	1950 °C
H_2	9 492	69 250
O_2	9 697	76 500
H_2O	11 147	94 620

H_2O in the liquid phase is −286 000 kJ/kmol. Calculate, neglecting changes in kinetic energy, and using the tables of ref. 7.6:

(i) the temperature reached if the process is assumed to be adiabatic and dissociation is neglected;

(ii) the temperature reached after adiabatic combustion if the constituents are H_2, O_2, H_2O, and N_2.
At 25 °C h_{fg} for H_2O is 2441.8 kJ/kg

(2254 °C; 2200 °C)

7.23 Octane vapour, C_8H_{18}, is to be burned in air in a steady-flow process. Both the fuel and air are supplied at 25 °C and the product temperature is to be 760 °C. Dissociation is negligible and the heat loss is to be taken as 10% of the increase in enthalpy of the products above the reference temperature.

$\Delta\tilde{h}^{\ominus}$ for octane vapour is −5 510 294 kJ/kmol with the products in the liquid phase. Calculate the A/F ratio by mass required; h_{fg} at 25 °C for H_2O is 2441.8 kJ/kg. Use the molar enthalpies in ref. 7.6.

(49.2)

7.24 Calculate the molar enthalpy of reaction of methane CH_4, at 25 °C and 1 bar pressure. Use Table 7.11 (p. 220) and assume the H_2O of combustion to be in the liquid phase.

(−890 290 kJ/kmol)

7.25 Calculate the molar enthalpy of combustion at 25 °C and 1 bar pressure of a gas of volumetric analysis 12% H_2, 29% CO, 2.6% CH_4, 0.4% C_2H_4, 4% CO_2 and 52% N_2 for the H_2O in the vapour phase and in the liquid phase.

(−137 240 kJ/kmol; −145 158 kJ/kmol)

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8

Steam Cycles

The heat engine cycle is discussed in Chapter 5, and it is shown that the most efficient cycle is the Carnot cycle for given temperatures of source and sink. This applies to both gases and vapours, and the cycle for a wet vapour is shown in Fig. 8.1. A brief summary of the essential features is as follows:

4 to 1: heat is supplied at constant temperature and pressure.

1 to 2: the vapour expands isentropically from the high pressure and temperature to the low pressure. In doing so it does work on the surroundings, which is the purpose of the cycle.

2 to 3: the vapour, which is wet at 2, has to be cooled to state point 3 such that isentropic compression from 3 will return the vapour to its original state at 4. From 4 the cycle is repeated.

The cycle described shows the different types of processes involved in the complete cycle and the changes in the thermodynamic properties of the vapour as it passes through the cycle. The four processes are physically very different from each other and thus they each require particular equipment. The heat supply, 4–1, can be made in a boiler. The work output, 1–2, can be obtained by expanding the vapour through a turbine. The vapour is condensed, 2–3, in a condenser, and to raise the pressure of the wet vapour, 3–4, requires a pump or compressor.

Thus the components of the plant are defined, but before these are discussed

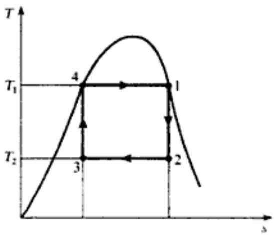


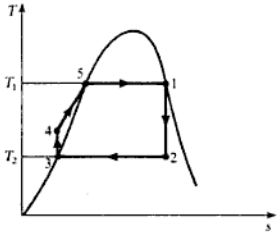
Fig. 8.1 Carnot cycle for a wet vapour on a T–s diagram

further, the deficiencies of the Carnot cycle as the ideal cycle for a vapour must be considered.

8.1 The Rankine cycle

It is stated in section 5.3 that, although the Carnot cycle is the most efficient cycle, its work ratio is low. Further, there are practical difficulties in following it. Consider the Carnot cycle for steam as shown in Fig. 8.1: at state 3 the steam is wet at T_2 but it is difficult to stop condensation at the point 3 and then compress it just to state 4. It is more convenient to allow the condensation process to proceed to completion, as in Fig. 8.2. The working fluid is water at the new state point 3 in Fig. 8.2, and this can be conveniently pumped to boiler pressure as shown at state point 4. The pump has much smaller dimensions than it would have if it had to pump a wet vapour, the compression process is carried out more efficiently, and the equipment required is simpler and less expensive. One of the features of the Carnot cycle has thus been departed from by the modification to the condensation process. At state 4 the water is not at the saturation temperature corresponding to the boiler pressure. Thus heat must be supplied to change the state from water at 4 to saturated water at 5; this is a constant pressure process, but is not at constant temperature. Hence the efficiency of this modified cycle is not as high as that of the Carnot cycle. This ideal cycle, which is more suitable as a criterion for actual steam cycles than the Carnot cycle, is called the *Rankine cycle.*

Fig. 8.2 Rankine cycle using wet steam on a T–s diagram



The plant required for the Rankine cycle is shown in Fig. 8.3, and the numbers refer to the state points of Fig. 8.2. The steam at inlet to the turbine may be wet, dry saturated, or superheated, but only the dry saturated condition is shown in Fig. 8.2. The steam flows round the cycle and each process may be analysed using the steady-flow energy equation; changes in kinetic energy and potential energy may be neglected, then for unit mass flow rate

$$Q + W = dh$$

Each process in the cycle can be considered in turn as follows. Boiler:

$$Q_{451} + W = h_1 - h_4$$

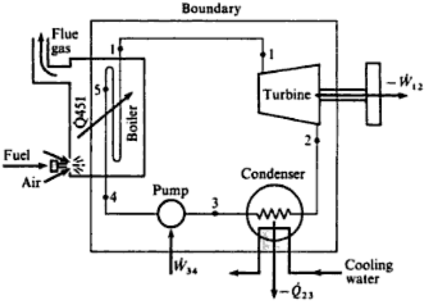


Fig. 8.3 Basic steam plant

Therefore, since $W = 0$,

$$Q_{451} = h_1 - h_4 \quad (8.1)$$

Turbine: the expansion is adiabatic (i.e. $Q = 0$), and isentropic (i.e. $s_1 = s_2$), and h_2 can be calculated using this latter fact. Then

$$Q_{12} + W_{12} = h_2 - h_1$$

therefore

$$W_{12} = h_2 - h_1$$

or Work output, $-W_{12} = h_1 - h_2$ (8.2)

Condenser:

$$Q_{23} + W = h_3 - h_2$$

Therefore, since $W = 0$

$$Q_{23} = h_3 - h_2$$

therefore

Heat rejected in condenser, $-Q_{23} = h_2 - h_3$ (8.3)

Pump:

$$Q_{34} + W_{34} = h_4 - h_3$$

The compression is isentropic (i.e. $s_3 = s_4$), and adiabatic (i.e. $Q = 0$). Therefore

$$W_{34} = (h_4 - h_3)$$

i.e. Work input to pump, $W_{34} = h_4 - h_3$ (8.4)

This is the feed-pump term, and as it is a small quantity in comparison with the turbine work output, $-W_{12}$, it is usually neglected, especially when boiler pressures are low.

Net work input for the cycle $\sum W = W_{12} + W_{34}$

i.e. $\sum W = (h_2 - h_1) + (h_4 - h_3)$

or Net work output, $-\sum W = (h_1 - h_2) - (h_4 - h_3)$ (8.5)

Or, if the feed-pump work is neglected,

$$\text{Net work output}, \; -\sum W = h_1 - h_2 \tag{8.6}$$

The heat supplied in the boiler, $Q_{451} = h_1 - h_4$. Then we have

$$\text{Rankine efficiency}, \; \eta_R = \frac{\text{net work output}}{\text{heat supplied in the boiler}} \tag{8.7}$$

i.e.
$$\eta_R = \frac{(h_1 - h_2) - (h_4 - h_3)}{h_1 - h_4}$$

or
$$\eta_R = \frac{(h_1 - h_2) - (h_4 - h_3)}{(h_1 - h_3) - (h_4 - h_3)} \tag{8.8}$$

If the feed-pump term, $h_4 - h_3$, is neglected equation (8.8) becomes

$$\eta_R = \frac{h_1 - h_2}{h_1 - h_3} \tag{8.9}$$

When the feed-pump term is to be included it is necessary to evaluate the quantity, W_{34}.

From equation (8.4)

$$\text{Pump work} = W_{34} = h_4 - h_3$$

It can be shown that for a liquid, which is assumed to be incompressible (i.e. v = constant), the increase in enthalpy for isentropic compression is given by

$$(h_4 - h_3) = v(p_4 - p_3)$$

The proof is as follows. For a reversible adiabatic process, from equation (3.15),

$$dQ = dh - v\,dp = 0$$

therefore

$$dh = v\,dp$$

i.e.
$$\int_3^4 dh = \int_3^4 v\,dp$$

For a liquid, since v is approximately constant, we have

$$h_4 - h_3 = v\int_3^4 dp = v(p_4 - p_3)$$

i.e.
$$h_4 - h_3 = v(p_4 - p_3)$$

therefore

$$\text{Pump work input} = h_4 - h_3 = v(p_4 - p_3) \tag{8.10}$$

where v can be taken from tables for water at the pressure p_3.

The *efficiency ratio* of a cycle is the ratio of the actual efficiency to the ideal efficiency. In vapour cycles the efficiency ratio compares the actual cycle efficiency to the Rankine cycle efficiency,

$$\text{i.e.} \qquad \text{Efficiency ratio} = \frac{\text{cycle efficiency}}{\text{Rankine efficiency}} \qquad (8.11)$$

The actual expansion process is irreversible, as shown by line 1–2 in Fig. 8.4. Similarly the actual compression of the water is irreversible, as indicated by line 3–4. The *isentropic efficiency* of a process is defined by

$$\text{Isentropic efficiency} = \frac{\text{actual work}}{\text{isentropic work}} \quad \text{for an expansion process}$$

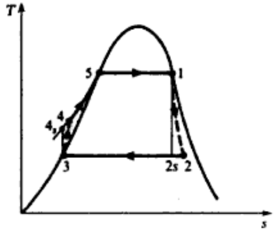


Fig. 8.4 Rankine cycle showing real processes on a T–s diagram

and

$$\text{Isentropic efficiency} = \frac{\text{isentropic work}}{\text{actual work}} \quad \text{for a compression process}$$

Hence

$$\text{Turbine isentropic efficiency} = \frac{-W_{12}}{-W_{12s}} = \frac{h_1 - h_2}{h_1 - h_{2s}} \qquad (8.12)$$

It has been stated that the efficiency of the Carnot cycle is the maximum possible, but that the cycle has a low work ratio. Both efficiency and work ratio are criteria of performance. By the definition of work ratio in section 5.3,

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} \qquad (8.13)$$

Another criterion of performance in steam plant is the *specific steam consumption* (ssc). It relates the power output to the steam flow necessary to produce it. The steam flow indicates the size of plant and its component parts, and the ssc is a means whereby the relative sizes of different plants can be compared.

The ssc is the steam flow required to develop unit power output. The power output is $-\dot{m}\sum W$, therefore

$$\text{ssc} = \frac{\dot{m}}{-\dot{m}\sum W} = \frac{1}{-\sum W} \tag{8.14}$$

Neglecting the feed pump work we have

$$-\sum W = h_1 - h_2$$

therefore

$$\text{ssc} = \frac{1}{(h_1 - h_2)}$$

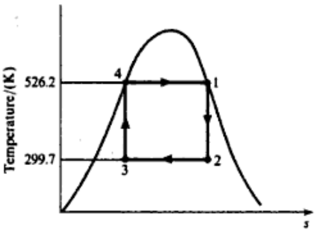
Note that when h_1 and h_2 are expressed in kilojoules per kilogram then the units of ssc are kg/kJ or kg/kW h.

Example 8.1 A steam power plant operates between a boiler pressure of 42 bar and a condenser pressure of 0.035 bar. Calculate for these limits the cycle efficiency, the work ratio, and the specific steam consumption:

(i) for a Carnot cycle using wet steam;
(ii) for a Rankine cycle with dry saturated steam at entry to the turbine;
(iii) for the Rankine cycle of (ii), when the expansion process has an isentropic efficiency of 80%.

Solution (i) A Carnot cycle is shown in Fig. 8.5.

Fig. 8.5 Carnot cycle for Example 8.1(a)



$$T_1 = \text{saturation temperature at 42 bar}$$
$$= 253.2 + 273 = 526.2 \text{ K}$$
$$T_2 = \text{saturation temperature at 0.035 bar}$$
$$= 26.7 + 273 = 299.7 \text{ K}$$

Then from equation (5.1)

$$\eta_{\text{Carnot}} = \frac{T_1 - T_2}{T_1} = \frac{526.2 - 299.7}{526.2} = 0.432 \quad \text{or} \quad 43.2\%$$

Also Heat supplied $= h_1 - h_4 = h_{fg}$ at 42 bar $= 1698$ kJ/kg

Then $$\eta_{Carnot} = \frac{\text{Net work output, } -\sum W}{\text{Gross heat supplied}} = 0.432$$

Therefore $-\sum W = 0.432 \times 1698$,

i.e. Net work output, $-\sum W = 734$ kJ/kg

To find the gross work of the expansion process it is necessary to calculate h_2, using the fact that $s_1 = s_2$.

From tables

$$h_1 = 2800 \text{ kJ/kg} \quad \text{and} \quad s_1 = s_2 = 6.049 \text{ kJ/kg K}$$

Using equation (4.10)

$$s_2 = 6.049 = s_{f_2} + x_2 s_{fg_2} = 0.391 + x_2 8.13$$

therefore

$$x_2 = \frac{6.049 - 0.391}{8.13} = 0.696$$

Then using equation (2.2)

$$h_2 = h_{f_2} + x_2 h_{fg_2} = 112 + (0.696 \times 2438) = 1808 \text{ kJ/kg}$$

Hence, from equation (8.2)

$$-W_{12} = h_1 - h_2 = 2800 - 1808 = 992 \text{ kJ/kg}$$

Therefore we have, using equation (8.13),

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{734}{992} = 0.739$$

Using equation (8.14)

$$\text{ssc} = \frac{1}{734}$$

i.e. $$\text{ssc} = 0.001\,36 \text{ kg/kW s}$$

$$= 4.91 \text{ kg/kW h}$$

(ii) The Rankine cycle is shown in Fig. 8.6.

As in part (i)

$$h_1 = 2800 \text{ kJ/kg} \quad \text{and} \quad h_2 = 1808 \text{ kJ/kg}$$

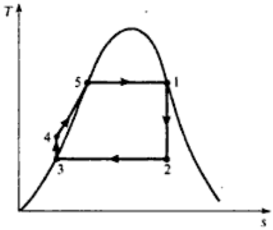
Also, $h_3 = h_f$ at 0.035 bar $= 112$ kJ/kg

Using equation (8.10), with $v = v_f$ at 0.035 bar

$$\text{Pump work} = v_f(p_4 - p_3) = 0.001 \times (42 - 0.035) \times \frac{10^5}{10^3}$$

$$= 4.2 \text{ kJ/kg}$$

Fig. 8.6 T–s diagram for Example 8.1(b)



Using equation (8.2)

$$-W_{12} = h_1 - h_2 = 2800 - 1808 = 992 \text{ kJ/kg}$$

Then using equation (8.8)

$$\eta_R = \frac{(h_1 - h_2) - (h_4 - h_3)}{(h_1 - h_3) - (h_4 - h_3)} = \frac{992 - 4.2}{(2800 - 112) - 4.2} = 0.368$$

i.e. $\eta_R = 36.8\%$

Using equation (8.13)

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{992 - 4.2}{992} = 0.996$$

Using equation (8.14)

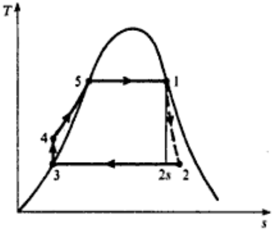
$$\text{ssc} = \frac{1}{-\sum W}$$

i.e. $\text{ssc} = \dfrac{1}{(992 - 4.2)} = 0.001\,01 \text{ kg/kW s} = 3.64 \text{ kg/kW h}$

(iii) The cycle with an irreversible expansion process is shown in Fig. 8.7. Using equation (8.12)

$$\text{Isentropic efficiency} = \frac{h_1 - h_2}{h_1 - h_{2s}} = \frac{-W_{12}}{-W_{12s}}$$

Fig. 8.7 T–s diagram for Example 8.1(c)



therefore

$$0.8 = \frac{-W_{12}}{992}$$

i.e. $-W_{12} = 0.8 \times 992 = 793.6\ \text{kJ/kg}$

Then the cycle efficiency is given by

$$\text{Cycle efficiency} = \frac{(h_1 - h_2) - (h_4 - h_3)}{\text{gross heat supplied}}$$

$$= \frac{793.6 - 4.2}{(2800 - 112) - 4.2} = 0.294$$

i.e. Cycle efficiency = 29.4%

$$\text{Work ratio} = \frac{-W_{12} - \text{pump work}}{-W_{12}} = \frac{793.6 - 4.2}{793.6} = 0.995$$

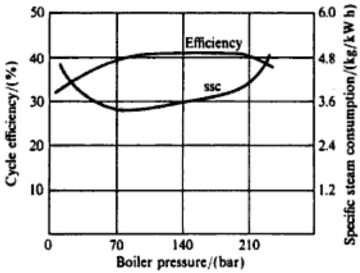
Also

$$\text{ssc} = \frac{1}{793.6 - 4.2} = 0.001\,267\ \text{kg/kW s} = 4.56\ \text{kg/kW h}$$

The feed-pump term has been included in the above calculations, but an inspection of the comparative values shows that it could have been neglected without having a noticeable effect on the results.

It is instructive to carry out these calculations for different boiler pressures and to represent the results graphically against boiler pressure, as in Fig. 8.8. As the boiler pressure increases the specific enthalpy of vaporization decreases, thus less heat is transferred at the maximum cycle temperature. Although the efficiency increases with boiler pressure over the first part of the range, due to the maximum cycle temperature being raised, it is affected by the lowering of the mean temperature at which heat is transferred. Therefore the graph for this efficiency rises, reaches a maximum, and then falls.

Fig. 8.8 Steam cycle efficiency and specific steam consumption against boiler pressure

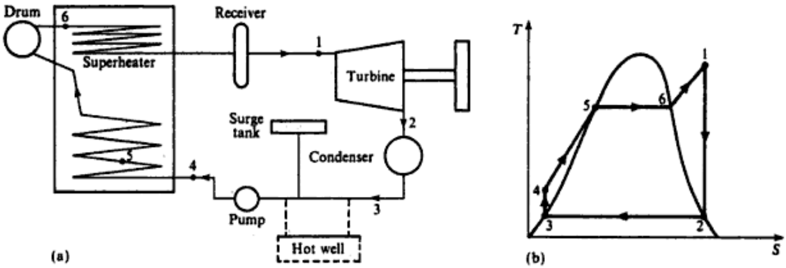


8.2 Rankine cycle with superheat

The average temperature at which heat is supplied in the boiler can be increased by superheating the steam. Usually the dry saturated steam from the boiler drum is passed through a second bank of smaller bore tubes within the boiler. This bank is situated such that it is heated by the hot gases from the furnace until the steam reaches the required temperature.

The Rankine cycle with superheat is shown in Fig. 8.9(a) and 8.9(b). Figure 8.9(a) includes a *steam receiver* which can receive steam from other boilers. In modern plant a receiver is used with one boiler and is placed between the boiler and the turbine. Since the quantity of feedwater varies with the different demands on the boiler, it is necessary to provide a storage of condensate between the condensate and boiler feed pumps. This storage may be either a *surge tank* or *hot well*. A hot well is shown dotted in Fig. 8.9(a).

Fig. 8.9 Steam plant with a superheater (a) and the cycle on a T–s diagram (b)



Example 8.2 Compare the Rankine cycle performance of Example 8.1 with that obtained when the steam is superheated to 500 °C. Neglect the feed-pump work.

Solution From tables, by interpolation, at 42 bar:

$$h_1 = 3442.6 \text{ kJ/kg} \quad \text{and} \quad s_1 = s_2 = 7.066 \text{ kJ/kg K}$$

Using equation (4.10)

$$s_2 = s_{f_2} + x_2 s_{fg_2} \quad \text{therefore } 0.391 + x_2 8.13 = 7.066$$

i.e. $x_2 = 0.821$

Using equation (2.2)

$$h_2 = h_{f_2} + x_2 h_{fg_2} = 112 + (0.821 \times 2438) = 2113 \text{ kJ/kg}$$

From tables:

$$h_3 = 112 \text{ kJ/kg}$$

Then, using equation (8.2)

$$-W_{12} = h_1 - h_2 = 3442.6 - 2113 = 1329.6 \text{ kJ/kg}$$

Neglecting the feed-pump term, we have

$$\text{Heat supplied} = h_1 - h_3 = 3442.6 - 112 = 3330.6\ \text{kJ/kg}$$

Using equation (8.9)

$$\text{Cycle efficiency} = \frac{h_1 - h_2}{h_1 - h_3} = \frac{1329.6}{3330.6} = 0.399 \text{ or } 39.9\%$$

Also, using equation (8.14)

$$\text{ssc} = \frac{1}{h_1 - h_2} = \frac{1}{1329.6} = 0.000\,752\ \text{kg/kW s} = 2.71\ \text{kg/kW h}$$

The cycle efficiency has increased due to superheating and the improvement in specific steam consumption is even more marked. This indicates that for a given power output the plant using superheated steam will be of smaller proportions than that using dry saturated steam.

The condenser heat loads for different plants can be compared by calculating the rate of heat removal in the condenser, per unit power output. This is given by the product, ssc × $(h_2 - h_3)$, where $(h_2 - h_3)$ is the heat removed in the condenser by the cooling water, per unit mass of steam. Comparing the condenser heat loads for the Rankine cycles of Examples 8.1 and 8.2, we have with dry saturated steam at entry to turbine, using the results from Example 8.1(ii):

$$\text{Condenser heat load} = 0.001\,01(1808 - 112)$$
$$= 1.713\ \text{kW per kW power output}$$

With superheated steam at entry to the turbine, using the results from Example 8.2:

$$\text{Condenser heat load} = 0.000\,752(2113 - 112)$$
$$= 1.505\ \text{kW per kW power output}$$

For given boiler and condenser pressures, as the superheat temperature increases, the Rankine cycle efficiency increases, and the specific steam consumption decreases, as shown in Fig. 8.10.

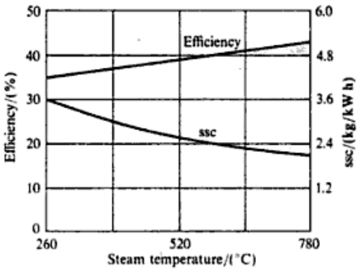
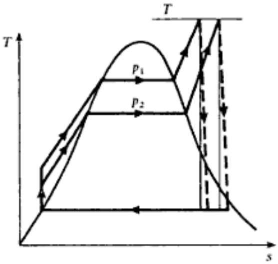


Fig. 8.10 Steam cycle efficiency and specific steam consumption against steam temperature at turbine entry

There is also a practical advantage in using superheated steam. For the data of the Rankine cycle of Examples 8.1 and 8.2, the steam leaves the turbine with dryness fractions of 0.696 and 0.821 respectively. The presence of water during the expansion is undesirable, since the droplets are denser than the remainder of the working fluid and therefore have different flow characteristics. The result is the physical erosion of the turbine blades, and a reduction in isentropic efficiency.

The modern tendency is to use higher boiler pressures, and a comparison of cycles on the T–s diagram shows that for a given steam temperature at turbine inlet, the higher pressure plant will have the wetter steam at turbine exhaust (see Fig. 8.11 in which $p_1 > p_2$). It is usual to design for a dryness fraction of not less than 0.9 at the turbine exhaust.

Fig. 8.11 T–s diagram showing the effect of a higher boiler pressure on the steam condition in the turbine



8.3 The enthalpy–entropy chart

In this chapter, and in later ones, we are concerned with changes in enthalpy. It is convenient to have a chart on which enthalpy is plotted against entropy. The h–s chart recommended is that of ref. 8.1, which covers a pressure range of 0.01–1000 bar, and temperatures up to 800 °C. Lines of constant dryness fraction are drawn in the wet region to values less than 0.5, and lines of constant temperature are drawn in the superheat region. In general h–s charts do not show values of specific volume, nor do they show the enthalpies of saturated water at pressures which are of the order of those experienced in steam condensers. Hence the chart is useful only for the enthalpy change in the expansion process of the steam cycle; the methods used in Examples 8.1 and 8.2 are recommended for problems on the Rankine cycle.

A sketch for the h–s chart is shown in Fig. 8.12. Lines of constant pressure are indicated by p_1, p_2, etc.; lines of constant temperature by T_1, T_2, etc. Any two independent properties which appear on the chart are sufficient to define the state (e.g. p_1 and x_1 define state A, and h_A can be read off the vertical axis). In the superheat region, pressure and temperature can define the state (e.g. p_3 and T_4 define the state B, and h_B can be read off). A line of constant entropy between two state points B and C defines the properties at all points during an isentropic process between the two states.

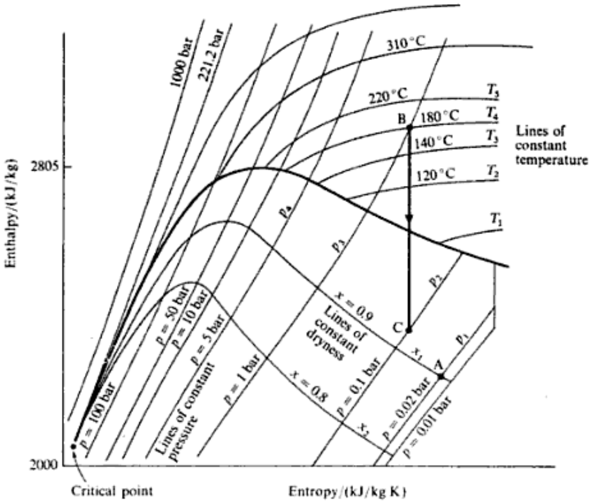


Fig. 8.12 Sketch of an enthalpy–entropy chart for steam

8.4 The reheat cycle

It is desirable to increase the average temperature at which heat is supplied to the steam, and also to keep the steam as dry as possible in the lower pressure stages of the turbine. The wetness at exhaust should be no greater than 10%. The considerations of section 8.2 show that high boiler pressures are required for high efficiency, but that expansion in one stage can result in exhaust steam which is wet. This is a condition which is improved by superheating the steam. The exhaust steam condition can be improved most effectively by reheating the steam, the expansions being carried out in two stages. Referring to Fig. 8.13, 1–2 represents isentropic expansion in the high-pressure turbine, and 6–7 represents isentropic expansion in the low-pressure turbine. The steam is reheated at constant pressure in process 2–6. The reheat can be carried out by returning the steam to the boiler, and passing it through a special bank of tubes, the reheat bank of tubes being situated in the proximity of the superheat tubes. Alternatively, the reheat may take place in a separate reheater situated near the turbine; this arrangement reduces the amount of pipe work required. The use of reheat cycles has encouraged the development of higher pressure, forced circulation boilers, since the specific steam consumption is improved, and the dryness fraction of the exhaust steam is increased.

The analysis is as follows:

$$\text{Heat supplied} = Q_{451} + Q_{26}$$

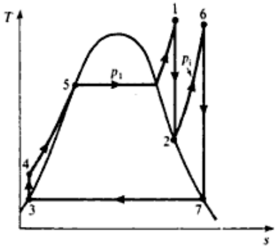


Fig. 8.13 T–s diagram showing a reheat steam cycle

Neglecting the feed-pump work

$$Q_{451} = h_1 - h_3$$

Also, for the reheat process

$$Q_{26} = h_6 - h_2$$

$$\text{Work output} = -W_{12} - W_{67}$$

and $\quad -W_{12} = h_1 - h_2 \quad \text{and} \quad -W_{67} = h_6 - h_7$

$$\text{Cycle efficiency} = \frac{-W_{12} - W_{67}}{Q_{451} + Q_{26}}$$

$$= \frac{(h_1 - h_2) + (h_6 - h_7)}{(h_1 - h_3) + (h_6 - h_2)}$$

Example 8.3 Calculate the new cycle efficiency and specific steam consumption if reheat is included in the plant of Example 8.2. The steam conditions at inlet to the turbine are 42 bar and 500 °C, and the condenser pressure is 0.035 bar as before. Assume that the steam is just dry saturated on leaving the first turbine, and is reheated to its initial temperature. Neglect the feed-pump term.

Solution The cycle is shown on a T–s diagram in Fig. 8.14.

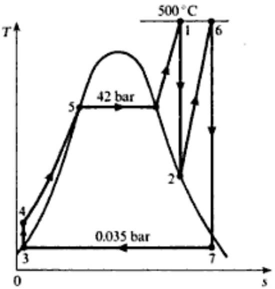


Fig. 8.14 T–s diagram for Example 8.3

It is convenient to read off the values of enthalpy from the h–s chart, i.e. $h_1 = 3442.6$ kJ/kg; $h_2 = 2713$ kJ/kg (at 2.3 bar); $h_6 = 3487$ kJ/kg (at 2.3 bar and 500 °C); $h_7 = 2535$ kJ/kg.

From tables

$$h_3 = 112 \text{ kJ/kg}$$

Then $\quad$ Turbine work $= (h_1 - h_2) + (h_6 - h_7)$

$$= (3443 - 2713) + (3487 - 2535)$$

i.e. $\quad$ Turbine work $= 1682$ kJ/kg

Heat supplied $= (h_1 - h_3) + (h_6 - h_2)$

$$= (3443 - 112) + (3487 - 2713)$$

i.e. $\quad$ Heat supplied $= 4105$ kJ/kg

therefore

$$\text{Cycle efficiency} = \frac{1682}{4105} = 0.41 \text{ or } 41\%$$

Also $\quad$ $\text{ssc} = \dfrac{1}{1682} = 0.000\,595 \text{ kg/kJ}$

i.e. $\quad$ ssc $= 2.14$ kg/kW h

Comparing these answers with the results of Example 8.2 it can be seen that the specific steam consumption has been improved considerably by reheating (i.e. reduced from 2.71 kg/kW h to 2.14 kg/kW h). The efficiency is greater (i.e. increased from 39.9 to 41%). The cycle efficiency will be increased by reheating only if the mean temperature of the heat supply is increased; this will not be the case if the reheat pressure is too low.

8.5 The regenerative cycle

In order to achieve the Carnot efficiency it is necessary to supply and reject heat at single fixed temperatures. One method of doing this, and at the same time having a work ratio comparable to the Rankine cycle, is by raising the feedwater to the saturation temperature corresponding to the boiler pressure before it enters the boiler. This method is not a practical proposition, but is of academic interest. The feedwater is passed from the pump through the turbine in counter-flow to the steam, as shown in Fig. 8.15(a). The feedwater enters the turbine at t_3 and is heated to the steam temperature at inlet to the turbine. If at all points the temperature difference between the steam and the water is negligibly small, then the heat transfer takes place in an ideal reversible manner. Assuming dry saturated steam at turbine inlet, the expansion process is represented by line 1–2–2′ in Fig. 8.15(b). The heat rejected by the steam, area 12561, is equal to the heat supplied to the water, area 34783. The heat supplied in the boiler is given by area 41674, and the heat rejected in the condenser is

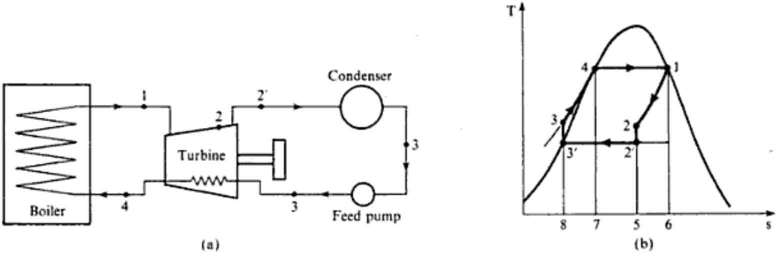


Fig. 8.15 Steam plant operating (a) on a regenerative cycle and (b) the cycle on a T–s diagram

given by area 3′2′583′. This *regenerative* cycle has an efficiency equal to the Carnot cycle, since the heat supplied and rejected externally is done at constant temperature.

This cycle is clearly not a practical proposition, and in addition it can be seen that the turbine operates with wet steam which is to be avoided if possible. However, the Rankine efficiency can be improved upon in practice by bleeding off some of the steam at an intermediate pressure during the expansion, and mixing this steam with feedwater which has been pumped to the same pressure. The mixing process is carried out in a *feed heater*, and the arrangement is represented in Figs 8.16(a) and (b). Only one feed heater is shown but several could be used.

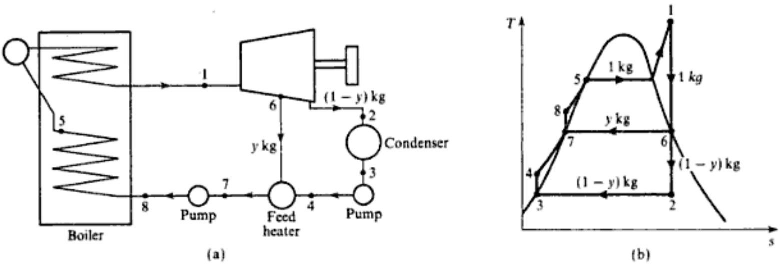


Fig. 8.16 Steam plant with (a) one open feed heater and (b) the cycle on a T–s diagram

The steam expands from condition 1 through the turbine. At the pressure corresponding to point 6, a quantity of steam, say y kg per kilogram of steam supplied from the boiler, is bled off for feed heating purposes. The rest of the steam, $(1 - y)$ kg, completes the expansion and is exhausted at state 2. This amount of steam is then condensed and pumped to the same pressure as the bleed steam. The bleed steam and the feedwater are mixed in the feed heater, and the quantity of bleed steam, y kg, is such that, after mixing and being pumped in a second feed pump, the condition is as defined by state 8. The heat to be supplied in the boiler is then given by $(h_1 - h_8)$ kJ/kg of steam; this heat is supplied between the temperatures T_8 and T_1.

If this procedure could be repeated an infinite number of times, then the ideal regenerative cycle would be approached.

It is necessary to determine the bleed pressure when one or more feed heaters are used, and this can be based on the assumption that the bleed temperature to obtain maximum efficiency for such a cycle is approximately the arithmetic mean of the temperatures at 5 and 2 (see Fig. 8.16(b)),

i.e. $$t_{\text{bleed}} = \frac{t_5 + t_2}{2} \qquad (8.15)$$

Example 8.4 If the Rankine cycle of Example 8.1 is modified to include one feed heater, calculate the cycle efficiency and the specific steam consumption.

Solution The steam enters the turbine at 42 bar, dry saturated, and the condenser pressure is 0.035 bar.

At 42 bar, $t_1 = 253.2\,°\text{C}$; and at 0.035 bar, $t_2 = 26.7\,°\text{C}$.

Therefore by equation (8.15)

$$t_6 = \frac{253.2 + 26.7}{2} = 140\,°\text{C}$$

Selecting the nearest saturation pressure from the tables gives the bleed pressure as 3.5 bar (i.e. $t_6 = 138.9\,°\text{C}$).

To determine the fraction y, consider the adiabatic mixing process at the feed heater, in which y kg of steam of enthalpy h_6, mix with $(1 - y)$ kg of water of enthalpy h_3, to give 1 kg of water of enthalpy h_7. The feed pump can be neglected (i.e. $h_4 = h_3$). Therefore

$$yh_6 + (1 - y)h_4 = h_7$$

i.e. $$y = \frac{h_7 - h_4}{h_6 - h_4} = \frac{h_7 - h_3}{h_6 - h_3}$$

Now, $h_7 = 584$ kJ/kg; $h_3 = 112$ kJ/kg; and $s_1 = s_6 = s_2 = 6.049$ kJ/kg K. Therefore

$$x_6 = \frac{6.049 - 1.727}{5.214} = 0.829$$

and $$x_2 = \frac{6.049 - 0.391}{8.130} = 0.696$$

Hence

$$h_6 = h_{f_6} + x_6 h_{fg_6} = 584 + (0.829 \times 2148) = 2364 \text{ kJ/kg}$$

and $$h_2 = h_{f_2} + x_2 h_{fg_2} = 112 + (0.696 \times 2438) = 1808 \text{ kJ/kg}$$

therefore

$$y = \frac{584 - 112}{2364 - 112} = 0.21 \text{ kg}$$

Neglecting the second feed-pump term (i.e. $h_7 = h_8$), we have

$$\text{Heat supplied in boiler} = (h_1 - h_7) = 2800 - 584 = 2216 \text{ kJ/kg}$$

$$\text{Total work output, } -W = -W_{16} - W_{62} = (h_1 - h_6) + (1 - y)(h_6 - h_2)$$

i.e. $\text{Work output} = (2800 - 2364) + (1 - 0.21)(2364 - 1808)$
$= 876$ kJ per kilogram of steam delivered by the boiler

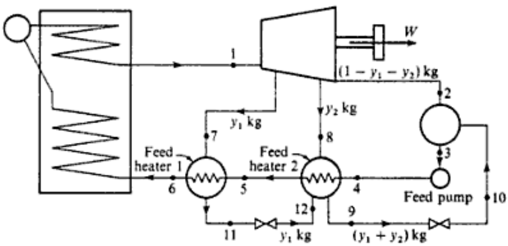
Therefore

$$\text{Cycle efficiency} = \frac{-W}{Q} = \frac{876}{2216} = 0.396 \text{ or } 39.6\%$$

i.e. $\text{ssc} = \frac{1}{876} = 0.001\,142 \text{ kg/kJ} = 4.11 \text{ kg/kW h}$

Comparing these results with those of Example 8.1, it can be seen that the addition of one feed heater has increased the cycle efficiency from 36.8 to 39.6%, but the specific steam consumption has increased from 3.64 kg/kW h to 4.11 kg/kW h. The cycle efficiency continues to be increased with the addition of further heaters, but the capital expenditure is also increased considerably. Because of the number of feed pumps required, the heating of the feed water by mixing is dispensed with and *closed heaters* are used. The method is indicated in Fig. 8.17 for two feed heaters, but the number used could be as high as eight. Referring to Fig. 8.17, the feedwater is passed at boiler pressure through the feed heaters 2 and 1 in series. An amount of bleed steam, y_1, is passed to feed heater 1, and the feedwater receives heat from it by the transfer of heat through the separating tubes. The condensed steam is then throttled to the next feed heater which is also supplied with a second quantity of bleed steam, y_2, and a lower temperature heating of the feedwater is carried out. After passing through the various feed heaters the condensed steam is then fed to the condenser. The temperature differences between successive heaters

Fig. 8.17 Steam plant with two closed feed heaters



are constant, and in the ideal case the heating process at each is considered to be complete (i.e. the feedwater leaves the feed heater at the temperature of the bleed steam supplied to it).

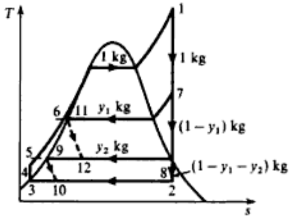
Example 8.5 In a regenerative steam cycle employing two closed-feed heaters the steam is supplied to the turbine at 40 bar and 500 °C and is exhausted to the condenser at 0.035 bar. The intermediate bleed pressures are obtained such that the saturation temperature intervals are approximately equal, giving pressures of 10 and 1.1 bar.

Calculate the amount of steam bled at each stage, the work output of the plant per kilogram of boiler steam and the cycle efficiency of the plant. Assume ideal processes where required.

Solution Referring to Fig. 8.17 and the T–s diagram of Fig. 8.18, from tables:

$$h_1 = 3445.8 \text{ kJ/kg} \quad \text{and} \quad s_1 = 7.089 \text{ kJ/kg K} = s_2$$

Fig. 8.18 T–s diagram for Example 8.5



At state 2,

$$0.391 + (x_2 \times 8.13) = 7.089$$

therefore

$$x_2 = \frac{6.698}{8.13} = 0.824$$

i.e. $h_2 = 112 + (0.824 \times 2348) = 2117 \text{ kJ/kg}$

Also $h_3 = h_f \text{ at } 0.035 \text{ bar} = 112 \text{ kJ/kg}$

For the first stage of expansion, 1–7, $s_7 = s_1 = 7.089$ kJ/kg K, and from tables at 10 bar $s_g < 7.089$, hence the steam is superheated at state 7. By interpolation between 250 and 300 °C at 10 bar we have

$$h_7 = 2944 + \left(\frac{7.089 - 6.926}{7.124 - 6.926}\right)(3052 - 2944) = 2944 + \frac{0.163}{0.198} \times 108$$

i.e. $h_7 = 3032.9 \text{ kJ/kg}$

For the throttling process, 11–12, we have

$$h_6 = h_{11} = h_{12} = 763 \text{ kJ/kg}$$

For the second stage of expansion, 7–8, $s_7 = s_8 = s_1 = 7.089$ kJ/kg K, and from tables at 1.1 bar $s_g > 7.089$ kJ/kg K, hence the steam is wet at state 8. Therefore,

$$1.333 + (x_8 \times 5.994) = 7.089$$

therefore

$$x_8 = 0.961$$

i.e. $$h_8 = 429 + (0.961 \times 2251) = 2591 \text{ kJ/kg}$$

For the throttling process, 9–10:

$$h_5 = h_9 = h_{10} = 429 \text{ kJ/kg}$$

Applying an energy balance to the first feed heater, remembering that there is no work or heat transfer:

$$y_1 h_7 + h_5 = y_1 h_{11} + h_6$$

i.e. $$y_1 = \frac{h_6 - h_5}{h_7 - h_{11}} = \frac{763 - 429}{3032.9 - 763} = 0.147$$

Similarly for the second heater, taking $h_4 = h_3$:

$$y_2 h_8 + y_1 h_{12} + h_4 = h_5 + (y_1 + y_2) h_9$$

i.e. $$y_2(h_8 - h_9) + y_1 h_{12} + h_4 = h_5 + y_1 h_9$$

$$y_2(2591 - 429) + (0.147 \times 763) + 112 = 429 + (0.147 \times 429)$$

therefore

$$y_2 = \frac{267.8}{2162} = 0.124$$

The heat supplied to the boiler, Q_1, per kilogram of boiler steam is given by

$$Q_1 = h_1 - h_6 = 3445 - 763 = 2682 \text{ kJ/kg}$$

The work output, neglecting pump work, is given by

$$\begin{aligned} -W &= (h_1 - h_7) + (1 - y_1)(h_7 - h_8) + (1 - y_1 - y_2)(h_8 - h_2) \\ &= (3445 - 3032.9) + (1 - 0.147)(3032.9 - 2591) \\ &\quad + (1 - 0.147 - 0.124)(2591 - 2117) \\ &= 412.1 + 376.9 + 345.5 = 1134.5 \text{ kJ/kg} \end{aligned}$$

Then $$\text{Cycle efficiency} = \frac{-W}{Q_1} = \frac{1134.5}{2682} = 0.423 \text{ or } 42.3\%$$

8.6 Further considerations of plant efficiency

Up to now the considerations of efficiency have been based on the heat which is actually supplied to the steam, and not the heat which has been produced by the combustion of fuel in the boiler. The heat is transferred to the steam from gases which are at a higher temperature than the steam, and the exhaust gases pass to the atmosphere at a high temperature.

To utilize some of the energy in the flue gas an *economizer* can be fitted. This consists of a coil situated in the flue gas stream. The cold feedwater enters at the top of the coil, and as it descends it is heated, and continues to meet higher temperature gas. For the Carnot, the ideal regenerative, and complete feed heating cycles, no use can be made of an economizer since the feedwater enters the boiler at the saturation temperature corresponding to the boiler pressure.

To cool the flue gas even further and improve the plant efficiency, the air which is required for the combustion of the fuel can be pre-heated. For a given temperature of combustion gases, the higher the initial temperature of the air then the less will be the energy input required, and hence less fuel will be used.

Plants which have both economizer and pre-heater coils in the boiler usually require a forced draught for the flue gas, and the power input to the fan, which is a comparatively small quantity, must be taken into account in the energy balance for the plant. Figure 8.19 represents diagrammatically a plant with economizer, pre-heater, and a re-heater.

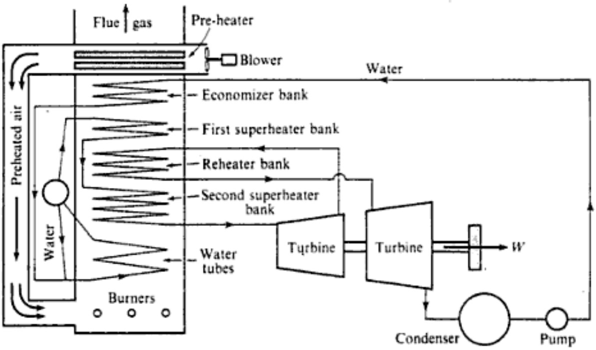
The boiler efficiency is the heat supplied to the steam in the boiler expressed as a percentage of the chemical energy of the fuel which is available on combustion,

i.e. $$\text{Boiler efficiency} = \frac{h_1 - (\text{enthalpy of the feedwater})}{m_f \times (\text{GCV or NCV})} \qquad (8.16)$$

where h_1 is the enthalpy of the steam entering the turbine and m_f the mass of fuel burned per kilogram of steam delivered from the boiler.

The GCV and NCV are the higher and lower calorific values of the fuel, and the determination of these quantities was considered in Chapter 7.

Fig. 8.19 Steam plant with economizer and air pre-heater



The size of the boiler, or its *capacity*, is quoted as the rate in kilogram per hour at which the steam is generated. A comparison is sometimes made by an *equivalent evaporation*, which is defined as the quantity of steam produced per unit quantity of fuel burned when the evaporation process takes place from and at 100 °C.

8.7 Steam for heating and process use

When steam is required for heating or for a process it may be raised in a boiler and used directly, or passed to a calorifier to heat water which is then circulated. In factory complexes where power and process steam are both required it is usually more efficient to use a plant combining both requirements. In reaching the compromise between power and process demands two main possibilities are available as discussed below.

Back pressure turbine

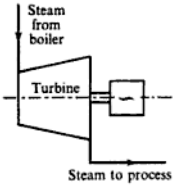


Fig. 8.20 Back-pressure turbine for process steam

The turbine works with an exhaust pressure which is appropriate to the process steam requirements; the steam leaving the turbine is not condensed but is passed to the process. A typical example is shown in Fig. 8.20.

One of the disadvantages of the back pressure turbine is that if the demand for process steam falls off but the power requirement is unchanged then some steam must be blown off to waste at the process steam pressure. If the power requirement increases with the process demand unchanged then excess power requirements can be bought from the grid. If the power requirements falls off with the process demand unchanged the best solution is to arrange to sell excess power to the grid.

A back pressure turbine used for process steam is suitable for high values of the ratio of process energy to power, say 10 or above.

Pass-out turbine

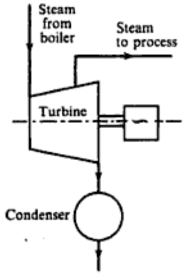


Fig. 8.21 Pass-out turbine for process steam

Steam is bled from the turbine at some point or points between inlet and exhaust and is passed to process work. A typical example is shown in Fig. 8.21.

In this system the boiler supply conditions and the condenser pressure can be fixed and the process steam load varied by varying the mass flow rate of process steam bled off the turbine. If the rate of process steam flow is much less than the design value then the excess power generated by the second stage expansion can be solid to the grid; alternatively process steam can be blown off or the boiler operated at part load, but both of these alternatives are wasteful of energy. If the power requirement falls off with the process demand unchanged, the best solution is to sell the excess power to the grid; a more wasteful solution is to blow off excess steam at the bleed point to reduce the power from the second stage of expansion. If the rate of process steam demand increases above the design value the best solution is to use a stand-by boiler to raise the excess steam direct. The pass-out turbine system for satisfying process and power requirements is most suitable for low process energy to power ratios, say in the range from 4 to 10.

When the process steam energy to power ratio falls below about 4 it becomes more efficient to generate power and steam for process use separately. Heat–power ratios using various prime movers are discussed in more detail in ref. 7.2.

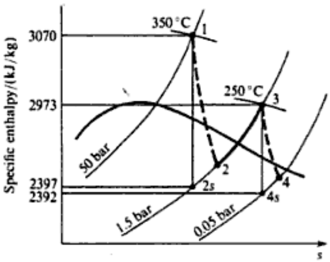
Example 8.6 A pass-out two-stage turbine receives steam at 50 bar and 350 °C. At 1.5 bar the high-pressure stage exhausts and 12 000 kg of steam per hour are taken at this stage for process purposes. The remainder is reheated at 1.5 bar to 250 °C and then expanded through the low-pressure turbine to a condenser pressure of 0.05 bar. The power output from the turbine unit is to be 3750 kW. The relevant values should be taken from an h–s chart. Take the isentropic efficiency of the high-pressure stage as 0.84, and that of the low-pressure stage as 0.81. Calculate the boiler capacity.

Solution The processes are shown on an h–s chart in Fig. 8.22. High-pressure stage:

$$\text{Actual work output} = \eta_{\text{isentropic}} \times (h_1 - h_{2s})$$

i.e. $$(h_1 - h_2) = 0.84 \times (3070 - 2397) = 565.3 \text{ kJ/kg}$$

Fig. 8.22 Processes on the h–s chart for Example 8.6



Low-pressure stage:

$$(h_3 - h_4) = \eta_{\text{isentropic}} \times (h_3 - h_{4s})$$
$$= 0.81 \times (2973 - 2392) = 470.6 \text{ kJ/kg}$$

$$\text{Process steam flow} = \frac{12\,000}{3600} = 3.33 \text{ kg/s}$$

$$\text{Steam flow through the boiler} = \dot{m} \text{ kg/s}$$

$$\text{Steam flow through low-pressure stage} = (\dot{m} - 3.33) \text{ kg/s}$$

$$\text{Turbine power output} = 3750 \text{ kW}$$

therefore

$$\dot{m}(h_1 - h_2) + (\dot{m} - 3.33)(h_3 - h_4) = 3750$$

i.e. $$(\dot{m} \times 565.3) + (\dot{m} - 3.33) \times 470.6 = 3750$$

therefore

$$\dot{m} = 5.14 \text{ kg/s}$$

i.e. Boiler capacity = 18 500 kg of steam per hour

Problems

8.1 (a) Steam is supplied, dry saturated at 40 bar to a turbine and the condenser pressure is 0.035 bar. If the plant operates on the Rankine cycle, calculate, per kilogram of steam:

(i) the work output neglecting the feed-pump work;
(ii) the work required for the feed pump;
(iii) the heat transferred to the condenser cooling water, and the amount of cooling water required through the condenser if the temperature rise of the water is assumed to be 5.5 K;
(iv) the heat supplied;
(v) the Rankine efficiency;
(vi) the specific steam consumption.

(b) For the same steam conditions calculate the efficiency and the specific steam consumption for a Carnot cycle operating with wet steam.

(986 kJ; 4 kJ; 1703 kJ; 74 kg; 2685 kJ; 36.6%; 3.67 kg/kW h; 42.7%; 4.92 kg/kW h)

8.2 Repeat Problem 8.1(a) for a steam supply condition of 40 bar and 350 °C and the same condenser pressure of 0.035 bar.

(1125 kJ; 4 kJ; 1857 kJ; 80.7 kg; 2978 kJ; 37.6%; 3.21 kg/kW h)

8.3 Steam is supplied to a two-stage turbine at 40 bar and 350 °C. It expands in the first turbine until it is just dry saturated, then it is re-heated to 350 °C and expanded through the second-stage turbine. The condenser pressure is 0.035 bar. Calculate the work output and the heat supplied per kilogram of steam for the plant, assuming ideal processes and neglecting the feed-pump term. Calculate also the specific steam consumption and the cycle efficiency.

(1290 kJ; 3362 kJ; 2.79 kg/kW h; 38.4%)

8.4 If the expansion processes in the turbines of Problem 8.3 have isentropic efficiencies of 84% and 78% respectively, in the first and second stages, calculate the work output and the heat supplied per kilogram of steam, the cycle efficiency, and the specific steam consumption.

Compare the efficiencies and specific steam consumptions obtained from Problems 8.1, 8.2, 8.3, and 8.4. Compare also the wetness of the steam leaving the turbines in each case.

(1028 kJ; 3311 kJ; 31.1%; 3.5 kg/kW h)
(Dryness fractions at condenser in each case: 0.699, 0.762, 0.85, and 0.94.)

8.5 A generating station is to give a power output of 200 MW. The superheat outlet pressure of the boiler is to be 170 bar and the temperature 600 °C. After expansion through the first-stage turbine to a pressure of 40 bar, 15% of the steam is extracted for feed heating. The remainder is reheated at 600 °C and is then expanded through the second turbine stage to a condenser pressure of 0.035 bar. For preliminary calculations it is assumed that the actual cycle will have an efficiency ratio of 70% and that the generator mechanical and electrical efficiency is 95%. Calculate the maximum continuous rating of the boiler in kilograms per hour.

(632 000 kg/h)

8.6 A steam turbine is to operate on a simple regenerative cycle. Steam is supplied dry saturated at 40 bar, and is exhausted to a condenser at 0.07 bar. The condensate is pumped to a pressure of 3.5 bar at which it is mixed with bleed steam from the turbine at 3.5 bar. The resulting water which is at saturation temperature is then pumped to the boiler. For the ideal cycle calculate, neglecting feed-pump work,

(i) the amount of bleed steam required per kilogram of supply steam;
(ii) the cycle efficiency of the plant;
(iii) the specific steam consumption.

(0.1906; 37%; 4.39 kg/kW h)

8.7 Steam is supplied to a two-stage turbine at 40 bar and 500 °C. In the first stage the steam expands isentropically to 3.0 bar at which pressure 2500 kg/h of steam is extracted for process work. The remainder is reheated to 500 °C and then expanded isentropically to 0.06 bar. The by-product power from the plant is required to be 6000 kW. Calculate the amount of steam required from the boiler, and the heat supplied. Neglect feed-pump terms, and assume that the process condensate returns at the saturation temperature to mix adiabatically with the condensate from the condenser.

(14 950 kg/h; 15 880 kW)

8.8 For the plant of Problem 8.7 it is required to improve the efficiency by employing regenerative feed heating by taking off the necessary bleed steam at the same point as the process steam. The process steam is not returned to the boiler, but make-up water at 15 °C is supplied. The bleed steam is mixed with the condensate and make-up water at 3.0 bar such that the resultant water is at the saturation temperature corresponding to 3.0 bar. Calculate:

(i) the steam supply necessary to meet the same power and process requirements;
(ii) the amount of bleed steam;
(iii) the heat supplied in kW.

Neglect feed-pump terms.

(16 480 kg/h; 2660 kg/h; 15 460 kW)

8.9 In a regenerative steam cycle employing three closed feed heaters the steam is supplied to the turbine at 42 bar and 500 °C and is exhausted to the condenser at 0.035 bar. The bleed steam for feed heating is taken at pressures of 15, 4, and 0.5 bar. Assuming ideal processes and neglecting pump work, calculate:

(i) the fraction of the boiler steam bled at each stage;
(ii) the power output of the plant per unit mass flow rate of boiler steam;
(iii) the cycle efficiency.

(0.0952, 0.0969, 0.0902; 1133.6 kW per kg/s; 43.6%)

8.10 A boiler plant, see Fig. 8.19 (p. 254), incorporates an economizer and an air pre-heater, and generates steam at 40 bar and 300 °C with fuel of calorific value 33 000 kJ/kg burned at a rate of 500 kg/h. The temperature of the feedwater is raised from 40 to 125 °C in the economizer, and the flue gases are cooled at the same time from 395 to 225 °C. The flue gases then enter the air pre-heater in which the temperature of the combustion air is raised by 75 K. A forced-draught fan delivers the air to the pre-heater at a pressure of 1.02 bar and a temperature of 16 °C with a pressure rise across the fan of 180 mm of water. The power input to the fan is 5 kW and it has a mechanical efficiency of 78%. Neglecting heat losses, and taking c_p as 1.01 kJ/kg K for the flue gases, calculate:

(i) the mass flow rate of air;
(ii) the temperature of the flue gases leaving the plant;
(iii) the mass flow rate of steam;
(iv) the efficiency of the boiler.

The power required to drive the fan is given by

$$\dot{W} = \frac{h\rho_w g\dot{V}}{\eta_M}$$

where h is the pressure rise across the fan expressed as a head of water, ρ_w the density of water, g the acceleration due to gravity, $\dot{V}$ the volume flow rate of air, and η_M is the mechanical efficiency of the fan.

(2.72 kg/s; 154 °C; 1.37 kg/s; 83.6%)

References

8.1 HICKSON D C and TAYLOR F R 1980 *Enthalpy–Entropy Diagram for Steam* Basil Blackwell

8.2 EASTOP T D and WATSON W E 1992 *Mechanical Services for Buildings* Longman

9

Gas Turbine Cycles

The simple constant pressure cycle and the open- and closed-cycle gas turbine units have been considered briefly in Chapter 5. In this chapter the various parts of the cycle will be considered in more detail and the practical limitations and modifications to the ideal cycle will be discussed.

The main use for the gas turbine at the present day is in the aircraft field, although gas turbine units for electric power generation are being used increasingly, usually using natural gas as fuel. Gas turbines are used in marine propulsion, but the oil engine and steam turbine are more frequently used, particularly for larger ships. The gas turbine is also used in conjunction with the oil engine, and as part of total energy schemes in combination with steam plant; this is discussed more fully in Chapter 17.

The inefficiencies in the compression and expansion processes become greater for smaller stand-alone gas turbine units and a heat exchanger is frequently used in order to improve the cycle efficiency. A compact effective heat exchanger is necessary before the small gas turbine can compete for economy with the small oil engine or petrol engine.

The use of constant pressure combustion with a rotary compressor driven by a rotary turbine, mounted on a common shaft, gives a combination which is ideal for conditions of steady mass flow over a wide operating range.

9.1 The practical gas turbine cycle

The most basic gas turbine unit is one operating on the open cycle in which a rotary compressor and a turbine are mounted on a common shaft, as shown diagrammatically in Fig. 9.1. Air is drawn into the compressor, C, and after compression passes to a combustion chamber, CC. Energy is supplied in the combustion chamber by spraying fuel into the airstream, and the resulting hot gases expand through the turbine, T, to the atmosphere. In order to achieve net work output from the unit, the turbine must develop more gross work output than is required to drive the compressor and to overcome mechanical losses in the drive.

The compressor used is either a centrifugal or an axial flow compressor and

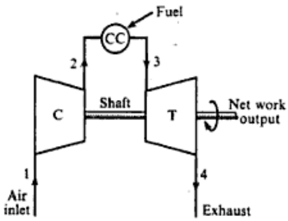


Fig. 9.1 Open-cycle gas turbine unit

the compression process is therefore irreversible but approximately adiabatic. Similarly the expansion process in the turbine is irreversible but adiabatic. Due to these irreversibilities, more work is required in the compression processes for a given pressure ratio, and less work is developed in the expansion process. It is possible that the compressor and turbine may be so inefficient that the unit is not self-sustaining, and in fact it was the difficulties in improving the compressor and turbine design to cut down irreversibilities that retarded the development of the gas turbine unit.

As stated in section 5.5 the open-cycle gas turbine cannot be compared directly with the ideal constant pressure cycle. The actual cycle involves a chemical reaction in the combustion chamber which results in high-temperature products which are chemically different from the reactants (see section 7.8). During combustion there is no energy exchange with the surroundings, the effect being a gradual decrease in chemical energy with a corresponding increase in enthalpy of the working fluid. The combustion reaction will not be considered in detail here, and a simplification will be made by assuming that the chemical energy released on a combustion is equivalent to a transfer of heat at constant pressure to a working fluid of constant mean specific heat. This simplified approach allows the actual process to be compared with the ideal and to be represented on a T–s diagram.

Neglecting the pressure loss in the combustion chamber the cycle may be drawn on a T–s diagram as shown in Fig. 9.2. Line 1–2 represents irreversible adiabatic compression; line 2–3 represents constant pressure heat supply in the

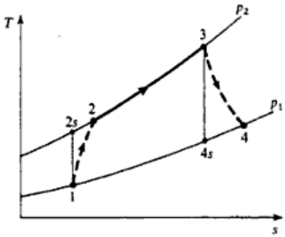


Fig. 9.2 Gas turbine cycle on a T–s diagram

combustion chamber; line 3–4 represents irreversible adiabatic expansion. The process 1–2s represents the ideal isentropic process between the same pressures p_1 and p_2. Similarly the process 3–4s represents the ideal isentropic expansion process between the pressures p_2 and p_1. For the moment it will be assumed that the change in kinetic energy between the various points in the cycle is negligibly small compared with the enthalpy changes. Then applying the flow equation to each part of the cycle, we have the following for unit mass. For the compressor:

$$\text{Work input} = c_p(T_2 - T_1)$$

For the combustion chamber:

$$\text{Heat supplied} = c_p(T_3 - T_2)$$

For the turbine:

$$\text{Work output} = c_p(T_3 - T_4)$$

Then $\quad \text{Net work output} = c_p(T_3 - T_4) - c_p(T_2 - T_1)$

and $\quad \text{Thermal efficiency} = \dfrac{\text{net work output}}{\text{heat supplied}}$

$$= \frac{c_p(T_3 - T_4) - c_p(T_2 - T_1)}{c_p(T_3 - T_2)}$$

The value of the specific heat capacity of a real gas varies with temperature; also, in the open cycle, the specific heat capacity of the gases in the combustion chamber and in the turbine is different from that in the compressor because fuel has been added and a chemical change has taken place. Curves showing the variation of c_p with temperature and air–fuel ratio can be used, and a suitable mean value of c_p and hence γ can be found. It is usual in the gas turbine practice to assume fixed mean values of c_p and γ for the expansion process, and fixed mean values of c_p and γ for the compression process. For the combustion process, curves as shown in Fig. 9.18 (p.282) are used; for simple calculations a mean value of c_p can be assumed. In an open-cycle gas turbine unit the mass flow of gases in the turbine is greater than that in the compressor due to the mass of fuel burned, but it is possible to neglect the mass of fuel, since the air–fuel ratios used are large. Also, in many cases, air is bled from the compressor for cooling purposes, or in the case of aircraft at high altitude, bleed air is used for de-icing and cabin air-conditioning. This amount of air bleed is approximately the same as the mass of fuel injected.

The isentropic efficiency of the compressor is defined as the ratio of the work input required in isentropic compression between p_1 and p_2 to the actual work required.

Neglecting changes in kinetic energy, we have

$$\text{Compressor isentropic efficiency, } \eta_C = \frac{c_p(T_{2s} - T_1)}{c_p(T_2 - T_1)}$$

$$= \frac{T_{2s} - T_1}{T_2 - T_1} \qquad (9.1)$$

Similarly the isentropic efficiency of the turbine is defined as the ratio of the actual work output to the isentropic work output between the same pressures.

Neglecting kinetic energy changes

$$\text{Turbine isentropic efficiency, } \eta_T = \frac{c_p(T_3 - T_4)}{c_p(T_3 - T_{4s})}$$

$$= \frac{T_3 - T_4}{T_3 - T_{4s}} \quad (9.2)$$

Example 9.1 A gas turbine unit has a pressure ratio of 10/1 and a maximum cycle temperature of 700 °C. The isentropic efficiencies of the compressor and turbine are 0.82 and 0.85 respectively. Calculate the power output of an electric generator geared to the turbine when the air enters the compressor at 15 °C at the rate of 15 kg/s. Take $c_p = 1.005$ kJ/kg K and $\gamma = 1.4$ for the compression process, and take $c_p = 1.11$ kJ/kg K and $\gamma = 1.333$ for the expansion process.

Solution A line diagram of the unit is shown in Fig. 9.3(a), and the cycle is shown on a T–s diagram in Fig. 9.3(b). In order to evaluate the net work output it is necessary to calculate the temperatures T_2 and T_4. To calculate T_2 we must first calculate T_{2s} and then use the isentropic efficiency.

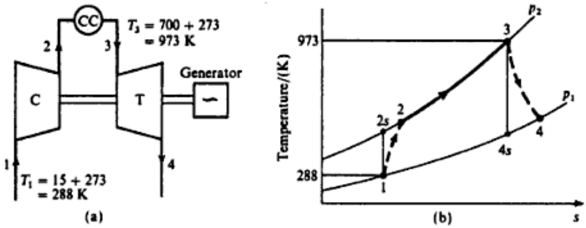


Fig. 9.3 Gas turbine unit (a) and T–s diagram (b) for Example 9.1

From equation (3.21) for an isentropic process

$$\frac{T_{2s}}{T_1} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$$

therefore

$$T_{2s} = 288 \times (10)^{0.4/1.4} = 288 \times 1.931 = 556 \text{ K}$$

Then using equation (9.1)

$$\eta_C = \frac{T_{2s} - T_1}{T_2 - T_1} = \frac{556 - 288}{T_2 - 288} = 0.82$$

i.e. $$(T_2 - 288) = \frac{268}{0.82} = 326.8 \text{ K}$$

therefore

$$T_2 = 288 + 326.8 = 614.8 \text{ K}$$

Similarly for the turbine

$$\frac{T_3}{T_{4s}} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$$

therefore

$$T_{4s} = \frac{973}{(10)^{0.333/1.333}} = \frac{973}{1.778} = 547.4 \text{ K}$$

Then from equation (9.2)

$$\eta_T = \frac{T_3 - T_4}{T_3 - T_{4s}} = \frac{973 - T_4}{973 - 547.4} = 0.85$$

i.e. $(973 - T_4) = 425.6 \times 0.85 = 361.8$ K

therefore

$$T_4 = 973 - 361.8 = 611.2 \text{ K}$$

Hence Compressor work input $= c_p(T_2 - T_1) = 1.005 \times 326.8$

$$= 328.4 \text{ kJ/kg}$$

Turbine work output $= c_p(T_3 - T_4) = 1.11 \times 361.8$

$$= 401.6 \text{ kJ/kg}$$

therefore

Net work output = (401.6 − 328.4) = 73.2 kJ/kg

i.e. Power output = 73.2 × 15 = 1098 kW

Example 9.2 Calculate the cycle efficiency and the work ratio of the plant in Example 9.1, assuming that c_p for the combustion process is 1.11 kJ/kg K

Solution Heat supplied $= c_p(T_3 - T_2)$

$$= 1.11(973 - 614.8) = 1.11 \times 358.2 \text{ kJ/kg}$$

i.e. Heat supplied = 397.6 kJ/kg

Therefore

$$\text{Cycle efficiency} = \frac{\text{net work output}}{\text{heat supplied}} = \frac{73.2}{397.6}$$

i.e. Cycle efficiency = 0.184 or 18.4%

From the definition of work ratio given in section 5.3, we have

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{73.2}{401.6} = 0.182$$

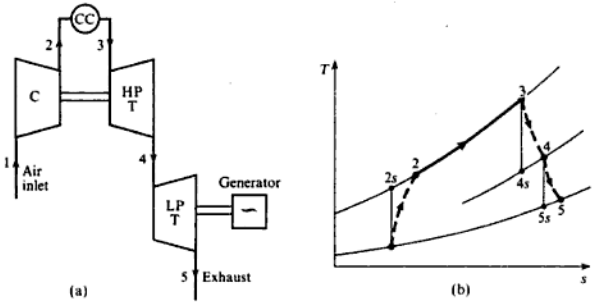
Use of a power turbine

In Examples 9.1 and 9.2 the turbine is arranged to drive the compressor and to develop net work. It is sometimes more convenient to have two separate turbines, one of which drives the compressor while the other provides the power output. The first, or high-pressure (HP) turbine, is then known as the compressor turbine, and the second, or low-pressure (LP) turbine, is called the power turbine. The arrangement is shown in Fig. 9.4(a). Assuming that each turbine has its own isentropic efficiency, the cycle is as shown on a T–s diagram in Fig. 9.4(b). The numbers on Fig. 9.4(b) correspond to those of Fig. 9.4(a). Neglecting kinetic energy changes, we have

work from HP turbine = work input to compressor

i.e. $c_{p_g}(T_3 - T_4) = c_{p_a}(T_2 - T_1)$

Fig. 9.4 Gas turbine unit with separate power turbine (a) and the cycle on a T–s diagram (b)



where c_{p_g} and c_{p_a} are the specific heat capacities at constant pressure of the gases in the turbine and the air in the compressor respectively. The net work output is then given by the LP turbine,

i.e. Net work output $= c_{p_g}(T_4 - T_5)$

Example 9.3 A gas turbine unit takes in air at 17 °C and 1.01 bar and the pressure ratio is 8/1. The compressor is driven by the HP turbine and the LP turbine drives a separate power shaft. The isentropic efficiencies of the compressor, and the HP and LP turbines are 0.8, 0.85, and 0.83 respectively. Calculate the pressure and temperature of the gases entering the power turbine, the net power developed by the unit per kg/s mass flow rate, the work ratio and the cycle efficiency of the unit. The maximum cycle temperature is 650 °C. For the compression process take $c_p = 1.005$ kJ/kg K and $\gamma = 1.4$; for the combustion process, and for the expansion process take $c_p = 1.15$ kJ/kg K and $\gamma = 1.333$. Neglect the mass of fuel.

Solution The unit is as shown in Figs 9.4(a) and 9.4(b).

From equation (3.21), for an isentropic process,

$$\frac{T_{2s}}{T_1} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$$

i.e. $T_{2s} = 290 \times 8^{0.4/1.4} = 290 \times 1.811 = 525$ K

Then, using equation (9.1)

$$\eta_C = \frac{T_{2s} - T_1}{T_2 - T_1} = \frac{525 - 290}{T_2 - 290} = 0.8$$

therefore

$$T_2 - 290 = \frac{235}{0.8}$$

i.e. $T_2 = 290 + 294 = 584$ K

Then Work input to the compressor $= c_{p_a}(T_2 - T_1)$

$$= 1.005 \times 294 = 295.5 \text{ kJ/kg}$$

Now the work output from the HP turbine must be sufficient to drive the compressor,

i.e. Work output from HP turbine $= c_{p_g}(T_3 - T_4) = 295.5$ kJ/kg

therefore

$$T_3 - T_4 = \frac{295.5}{1.15} = 257 \text{ K}$$

therefore

$$T_4 = T_3 - 257 = 923 - 257 = 666 \text{ K}$$

Then, using equation (9.2),

$$\eta_T \text{ for HP turbine} = \frac{T_3 - T_4}{T_3 - T_{4s}} = \frac{923 - 666}{923 - T_{4s}} = 0.85$$

i.e. $923 - T_{4s} = \dfrac{257}{0.85} = 302.5$ K

therefore

$$T_{4s} = 923 - 302.5 = 620.5 \text{ K}$$

Then from equation (3.21) for an isentropic process,

$$\frac{T_3}{T_{4s}} = \left(\frac{p_3}{p_4}\right)^{(\gamma-1)/\gamma}$$

or $$\frac{p_3}{p_4} = \left(\frac{T_3}{T_{4s}}\right)^{\gamma/(\gamma-1)} = \left(\frac{923}{620.5}\right)^{1.333/0.333} = 4.9$$

i.e. $$p_4 = \frac{p_3}{4.9} = \frac{8 \times 1.01}{4.9} = 1.65 \text{ bar}$$

Hence the pressure and temperature at entry to the LP turbine are 1.65 bar and 393 °C, where $t_4 = 666 - 273 = 393\,°\text{C}$.

To find the power output it is now necessary to evaluate T_5. The pressure ratio, p_4/p_5, is given by $(p_4/p_3) \times (p_3/p_5)$,

i.e. $$\frac{p_4}{p_5} = \frac{p_4}{p_3} \times \frac{p_2}{p_1} \quad \text{(since } p_2 = p_3 \text{ and } p_5 = p_1\text{)}$$

therefore

$$\frac{p_4}{p_5} = \frac{8}{4.9} = 1.63$$

Then $$\frac{T_4}{T_{5s}} = \left(\frac{p_4}{p_5}\right)^{(\gamma-1)/\gamma} = 1.63^{0.333/1.333} = 1.131$$

therefore

$$T_{5s} = \frac{666}{1.131} = 588 \text{ K}$$

Then, using equation (9.2)

$$\eta_T \text{ for the LP turbine} = \frac{T_4 - T_5}{T_4 - T_{5s}}$$

i.e. $$T_4 - T_5 = 0.83(666 - 588) = 0.83 \times 78 = 64.8 \text{ K}$$

Then $$\text{Work output from LP turbine} = c_{p_g}(T_4 - T_5)$$
$$= 1.15 \times 64.8 = 74.5 \text{ kJ/kg}$$

i.e. $$\text{Net power output} = 74.5 \times 1 = 74.5 \text{ kW}$$

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{74.5}{74.5 + 295.5} = \frac{74.5}{370} = 0.201$$

$$\text{Heat supplied} = c_{p_g}(T_3 - T_2) = 1.15(923 - 584)$$

i.e. $$\text{Heat supplied} = 1.15 \times 339 = 390 \text{ kJ/kg}$$

Then $$\text{Cycle efficiency} = \frac{\text{net work output}}{\text{heat supplied}} = \frac{74.5}{390}$$
$$= 0.191 \text{ or } 19.1\%$$

Aircraft engines

In a *jet engine* the propulsion nozzle takes the place of the LP stage turbine, as shown diagrammatically in Fig. 9.5(a). The cycle is shown on a T–s diagram in Fig. 9.5(b), and it can be seen to be identical with Fig. 9.4(b). The aircraft is powered by the reactive thrust of the jet of gases leaving the nozzle, and this high-velocity jet is obtained at the expense of the enthalpy drop from 4 to 5. The turbine develops just enough work to drive the compressor and overcome mechanical losses.

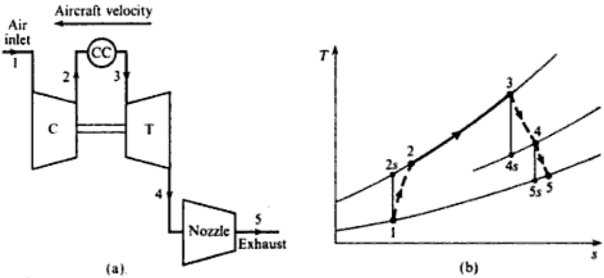


Fig. 9.5 Simple jet engine (a) with the cycle on a T–s diagram (b)

In a *turbo-prop* engine the turbine drives the compressor and also the airscrew, or propeller, as shown in Figs 9.6(a) and 9.6(b). The net work output available to drive the propeller is given by

$$\text{Net work output} = c_{p_g}(T_3 - T_4) - c_{p_a}(T_2 - T_1)$$

(neglecting mechanical losses).

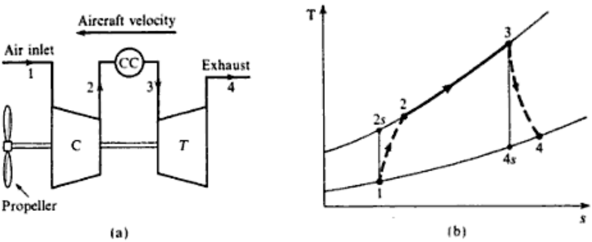


Fig. 9.6 Turboprop engine (a) with the cycle on a T–s diagram (b)

In practice there is also a small jet thrust developed in a turbo-prop aircraft. Jet engines and turbo-prop engines are considered again in Section 10.9.

Parallel flow units

In some industrial and marine gas turbine units, the air flow is split into two streams after the compression process is completed. Some air is then passed to a combustion chamber which supplies hot gases to the turbine driving the compressor, while the rest of the air is passed to a second combustion chamber and from thence to the power turbine. The system is shown diagrammatically in Fig. 9.7, and is called a *parallel flow* unit. In this system each turbine expands the gases received by it through the full pressure ratio. The advantage of this system is that the net power output can be varied using the second combustion chamber, and the power turbine operates independently of the compressor turbine.

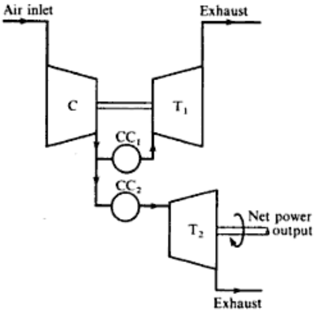


Fig. 9.7 Parallel-flow gas turbine unit

9.2 Modifications to the basic cycle

It can be seen from Examples 9.1, 9.2, and 9.3 that the work ratio and the cycle efficiency of the basic gas turbine cycle are low. These can be improved by increasing the isentropic efficiencies of the compressor and turbine, and this is a matter of blade design and manufacture.

In a practical cycle with irreversibilities in the compression and expansion processes the cycle efficiency depends on the maximum cycle temperatures as well as on the pressure ratio. For fixed values of the isentropic efficiencies of the compressor and turbine, the cycle efficiency can be plotted against pressure ratio for various values of maximum temperature. This is illustrated in Fig. 9.8, for a cycle in which the compressor isentropic efficiency is 0.89, the turbine isentropic efficiency is 0.92, and the air inlet temperature is 20 °C. The ideal air standard cycle thermal efficiency is shown chain-dotted. In section 5.4 it is shown that the ideal constant pressure cycle efficiency is given by

$$\eta = 1 - \left(\frac{1}{r_p}\right)^{(\gamma-1)/\gamma}$$

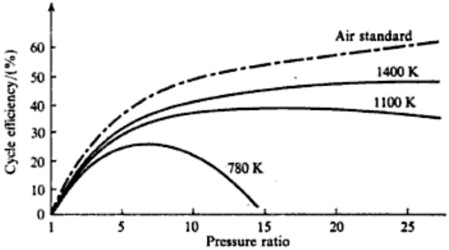


Fig. 9.8 Gas turbine cycle efficiency against pressure ratio for different maximum cycle temperatures

where r_p is the pressure ratio and is independent of the maximum cycle temperature.

It can be seen from Fig. 9.8 that at any one fixed maximum cycle temperature there is a value of pressure ratio which will give maximum cycle efficiency.

The net work output also depends on the pressure ratio and on the maximum cycle temperature, and curves of specific power output against pressure ratio for various maximum temperatures are shown in Fig. 9.9. The isentropic efficiencies of the compressor and turbine, and the air inlet temperature are the same as those used in deriving the curves of Fig. 9.8. It can be seen that the cycle efficiency reaches a maximum at a different value of pressure ratio than the work output. The choice of pressure ratio is therefore a compromise.

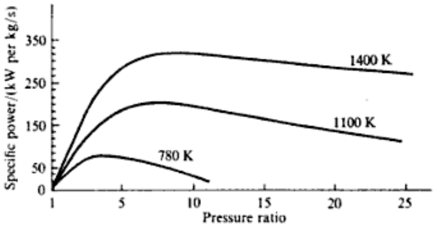


Fig. 9.9 Specific power against pressure ratio for different maximum cycle temperatures

The maximum cycle temperature is limited by metallurgical considerations. The blades of the turbine are under great mechanical stress and the temperature of the blade material must be kept to a safe working value. The temperature of the gases entering the turbine can be raised, provided a means of blade cooling is available. Various methods of blade cooling have been investigated and a discussion of these will be found in ref. 9.1. In aircraft practice where the life expectancy of the engine is shorter, the maximum temperatures used are usually higher than those used in industrial and marine gas turbine units; more expensive alloys and blade cooling allow maximum temperatures of above 1600 K.

It is important to have as high a work ratio as possible, and methods of increasing the work ratio, such as intercooling between compressor stages, and reheating between turbine stages, will be considered in this section. Intercooling and reheating, while increasing the work ratio, can cause a decrease in the cycle efficiency, but when they are used in conjunction with a heat exchanger then intercooling and reheating increase both the work ratio and the cycle efficiency.

Intercooling

When the compression is performed in two stages with an intercooler between the stages, then the work input for a given pressure ratio and mass flow is reduced. Consider a system as shown in Fig. 9.10(a); the T–s diagram for the unit is shown in Fig. 9.10(b). The actual cycle processes are 1–2 in the LP compressor, 2–3 in the intercooler, 3–4 in the HP compressor, 4–5 in the combustion chamber, and 5–6 in the turbine. The ideal cycle for this arrangement is 1–2s–3–4s–5–6s; the compression process without intercooling is shown as 1–A in the actual case, and 1–As in the ideal isentropic case.

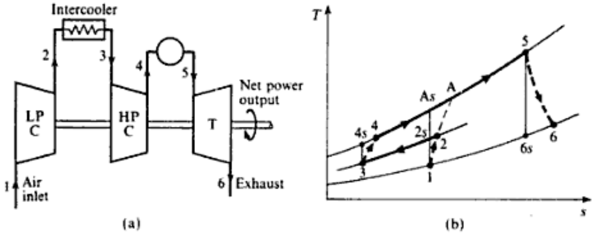


Fig. 9.10 Gas turbine unit with intercooling (a) and the cycle on the T–s diagram (b)

The work input with intercooling is given by

$$\text{Work input (with intercooling)} = c_p(T_2 - T_1) + c_p(T_4 - T_3) \quad (9.3)$$

The work input with no intercooling is given by

$$\text{Work input (no intercooling)} = c_p(T_A - T_1)$$
$$= c_p(T_2 - T_1) + c_p(T_A - T_2)$$

Comparing this equation with equation (9.3), it can be seen that the work input with intercooling is less than the work input with no intercooling, when $c_p(T_4 - T_3)$ is less than $c_p(T_A - T_2)$. This is so if it is assumed that the isentropic efficiencies of the two compressors, operating separately, are each equal to the isentropic efficiency of the single compressor which would be required if no intercooling were used. Then $(T_4 - T_3) < (T_A - T_2)$ since the pressure lines diverge from left to right on the T–s diagram.

It can be shown that the best interstage pressure is the one which gives equal pressure ratios in each stage of compression; referring to Fig. 9.10(b) this means that $p_2/p_1 = p_4/p_3$. The work input required is a minimum when the pressure ratio in each stage is the same, and when the temperature of the air is cooled in the intercooler, back to the value at inlet to the unit (i.e. referring to Fig. 9.10(b), $T_3 = T_1$).

Now

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}}$$

$$= \frac{\text{work of expansion} - \text{work of compression}}{\text{work of expansion}}$$

It follows, therefore, that when the compressor work input is reduced then the work ratio is increased. However, referring to Fig. 9.10(b), the heat supplied in the combustion chamber when intercooling is used in the cycle is given by

$$\text{Heat supplied (with intercooling)} = c_p(T_5 - T_4)$$

whereas the heat supplied when intercooling is not used, with the same maximum cycle temperature T_5, is given by

$$\text{Heat supplied (no intercooling)} = c_p(T_5 - T_A)$$

Hence the heat supplied when intercooling is used is greater than with no intercooling. Although the net work output is increased by intercooling it is found in general that the increase in the heat to be supplied causes the cycle efficiency to decrease. It will be shown later that this disadvantage is offset when a heat exchanger is also used.

When intercooling is used a supply of cooling water must be readily available. The additional bulk of the unit may offset the advantage to be gained by increasing the work ratio.

Reheat

As stated earlier, the expansion process is very frequently performed in two separate turbine stages, the HP turbine driving the compressor and the LP turbine providing the useful power output. The work output of the LP turbine can be increased by raising the temperature at inlet to this stage. This can be done by placing a second combustion chamber between the two turbine stages in order to heat the gases leaving the HP turbine. The system is shown diagrammatically in Fig. 9.11(a), and the cycle is represented on a T–s diagram in Fig. 9.11(b). The line 4–A represents the expansion in the LP turbine if reheating is not used.

As before, the work output of the HP turbine must be exactly equal to the work input required for the compressor (neglecting mechanical losses),

i.e. $\quad c_{p_a}(T_2 - T_1) = c_{p_g}(T_3 - T_4)$

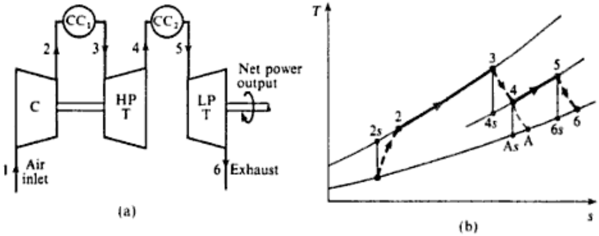


Fig. 9.11 Gas turbine unit with reheating (a) and the cycle on a T–s diagram (b)

The net work output, which is the work output of the LP turbine, is given by

$$\text{Net work output} = c_{p_g}(T_5 - T_6)$$

If reheating is not used, then the work of the LP turbine is given by

$$\text{Net work output (no reheat)} = c_{p_g}(T_4 - T_A)$$

Since pressure lines diverge to the right on the T–s diagram, it can be seen that the temperature difference $(T_5 - T_6)$ is always greater than $(T_4 - T_A)$, so that reheating increases the net work output. Also

$$\text{Work ratio} = \frac{\text{work of expansion} - \text{work of compression}}{\text{work of expansion}}$$

i.e.
$$\text{Work ratio} = 1 - \frac{\text{work of compression}}{\text{work of expansion}}$$

Therefore, when the work of expansion is increased and the work of compression is unchanged, then the work ratio is increased.

Although the net work is increased by reheating, the heat to be supplied is also increased, and the net effect can be to reduce the thermal efficiency,

i.e.
$$\text{Heat supplied} = c_{p_g}(T_3 - T_2) + c_{p_g}(T_5 - T_4)$$

However, the exhaust temperature of the gases leaving the LP turbine is much higher when reheating is used (i.e. T_6 as compared with T_A), and a heat exchanger can be used to enable some of the energy of the exhaust gases to be used.

Heat exchanger

The exhaust gases leaving the turbine at the end of expansion are still at a high temperature, and therefore a high enthalpy (e.g. in Example 9.3, $t_5 = 328.2\,^\circ\text{C}$). If these gases are allowed to pass into the atmosphere, then this represents a loss of available energy. Some of this energy can be recovered by passing the gases from the turbine through a heat exchanger, where the heat transferred from the gases is used to heat the air leaving the compressor. The simple unit

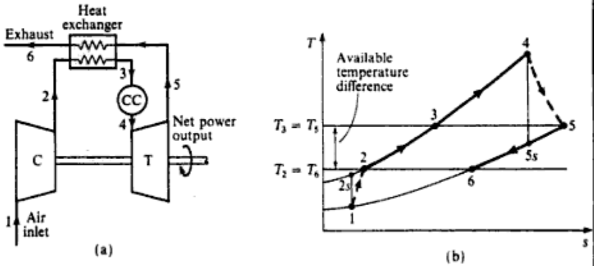


Fig. 9.12 Gas turbine unit with heat exchanger (a) and the cycle on a T–s diagram (b)

with a heat exchanger added is shown diagrammatically in Fig. 9.12(a), and the cycle is represented on a T–s diagram in Fig. 9.12(b). In the ideal heat exchanger the air would be heated from T_2 to $T_3 = T_5$ and the gases would be cooled from T_5 to $T_6 = T_2$. This ideal case is shown in Fig. 9.12(b). In practice this is impossible, since a finite temperature difference is required at all points in the heat exchanger in order to overcome the resistance to the heat transfer. Referring to Fig. 9.13, the required temperature difference between the gases and the air entering the heat exchanger is $(T_6 - T_2)$, and the required temperature difference between the gases and the air leaving the heat exchanger is $(T_5 - T_3)$.

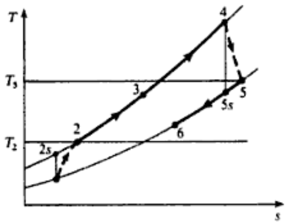


Fig. 9.13 T–s diagram for a gas turbine unit with a heat exchanger showing temperature differences for heat transfer

If no heat is lost from the heat exchanger to the atmosphere, then the heat given up by the gases must be exactly equal to the heat taken up by the air,

i.e. $$\dot{m}_a c_{p_a}(T_3 - T_2) = \dot{m}_g c_{p_g}(T_5 - T_6) \quad (9.4)$$

The assumption that no heat is lost from the heat exchanger is sufficiently accurate in most practical cases. Equation (9.4) is therefore true whatever the temperatures T_3 and T_6 may be.

A heat exchanger *effectiveness* is defined to allow for the temperature difference necessary for the transfer of heat,

i.e. $$\text{Effectiveness} = \frac{\text{heat received by the air}}{\text{maximum possible heat which could be transferred from the gases in the heat exchanger}}$$

therefore

$$\text{Effectiveness} = \frac{\dot{m}_a c_{p_a}(T_3 - T_2)}{\dot{m}_g c_{p_g}(T_5 - T_2)} \tag{9.5}$$

A more convenient way of assessing the performance of the heat exchanger is to use a *thermal ratio*, defined as

$$\text{Thermal ratio} = \frac{\text{temperature rise of the air}}{\text{maximum temperature difference available}}$$

i.e.

$$\text{Thermal ratio} = \frac{T_3 - T_2}{T_5 - T_2} \tag{9.6}$$

Comparing equations (9.5) and (9.6) it can be seen that the thermal ratio is equal to the effectiveness when the product, $\dot{m}_a c_{p_a}$, is equal to the product, $\dot{m}_g c_{p_g}$.

When a heat exchanger is used then the heat to be supplied in the combustion chamber is reduced, assuming that the maximum cycle temperature is unchanged. The net work output is unchanged and hence the cycle efficiency is increased.

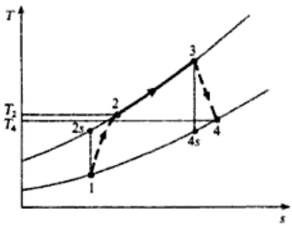
Referring to Fig. 9.13

$$\text{Heat supplied by the fuel (without heat exchanger)} = c_{p_g}(T_4 - T_2)$$

$$\text{Heat supplied by the fuel (with heat exchanger)} = c_{p_g}(T_4 - T_3)$$

A heat exchanger can be used only if there is a sufficiently large temperature difference between the gases leaving the turbine and the air leaving the compressor. For example, in the cycle shown in Fig. 9.14 a heat exchanger could not possibly be used because the temperature of the exhaust gases, T_4, is lower than the temperature of the air leaving the compressor, T_2. In practice, although the gas temperature may be higher than the temperature of the air leaving the compressor, the difference in temperature may not be sufficiently large to warrant the additional capital cost and subsequent maintenance required for a heat exchanger. Also, when the temperature difference is small in a heat exchanger, then the surface areas for the heat transfer must be made large in order to achieve a reasonably high value of the thermal ratio. For small gas turbine units (e.g. for pumping sets or for motor cars) a compact heat exchanger must be designed before such units can hope to become competitive for economy

Fig. 9.14 Example of a cycle where a heat exchanger is not feasible



with conventional internal combustion engines of equivalent power. In large gas turbine units for marine propulsion or industrial power, a heat exchanger may be used, although the trend now is towards combined cycles using the turbine exhaust to generate steam or heat water (see Chapter 17).

Example 9.4 A 5000 kW gas turbine generating set operates with two compressor stages with intercooling between stages; the overall pressure ratio is 9/1. A HP turbine is used to drive the compressors, and a LP turbine drives the generator. The temperature of the gases at entry to the HP turbine is 650 °C and the gases are reheated to 650 °C after expansion in the first turbine. The exhaust gases leaving the LP turbine are passed through a heat exchanger to heat the air leaving the HP stage compressor. The compressors have equal pressure ratios and intercooling is complete between stages. The air inlet temperature to the unit is 15 °C. The isentropic efficiency of each compressor stage is 0.8 and the isentropic efficiency of each turbine stage is 0.85; the heat exchanger thermal ratio is 0.75. A mechanical efficiency of 98% can be assumed for both the power shaft and the compressor turbine shaft. Neglecting all pressure losses and changes in kinetic energy, calculate:

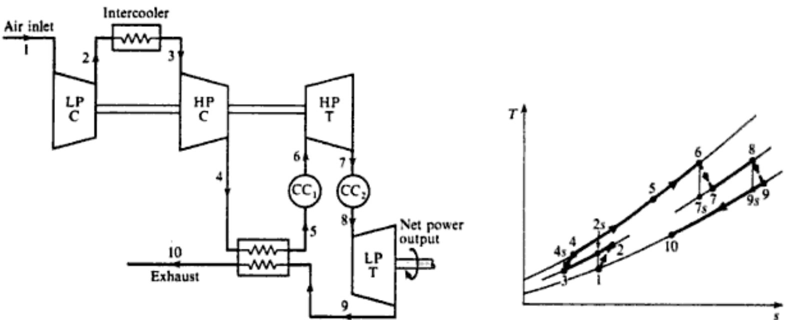
(i) the cycle efficiency;
(ii) the work ratio;
(iii) the mass flow rate.

For air take $c_p = 1.005$ kJ/kg K and $\gamma = 1.4$, and for the gases in the combustion chamber and in the turbines and heat exchanger take $c_p = 1.15$ kJ/kg K and $\gamma = 1.333$. Neglect the mass of fuel.

Solution (i) The plant is shown diagrammatically in Fig. 9.15(a), and the cycle is represented on a T–s diagram in Fig. 9.15(b).

Since the pressure ratio and the isentropic efficiency of each compressor is the same, then the work input required for each compressor is the same since both compressors have the same air inlet temperature, i.e. $T_1 = T_3$ and $T_2 = T_4$.

Fig. 9.15 Gas turbine plant (a) and T–s diagram (b) for Example 9.4



(a) (b)

From equation (3.21)

$$\frac{T_{2s}}{T_1} = \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma} \quad \text{and} \quad \frac{p_2}{p_1} = \sqrt{9} = 3$$

therefore

$$T_{2s} = 288 \times 3^{0.4/1.4} = 394 \text{ K}$$

Then from equation (9.1),

$$\eta_C, \text{ LP compressor} = \frac{T_{2s} - T_1}{T_2 - T_1} = 0.8$$

therefore

$$T_2 - T_1 = \frac{394 - 288}{0.8} = \frac{106}{0.8} = 132.5 \text{ K}$$

i.e. $T_2 = 288 + 132.5 = 420.5$ K

Also Work input per compressor stage $= c_{p_a}(T_2 - T_1)$

$$= 1.005 \times 132.5 = 133.1 \text{ kJ/kg}$$

The HP turbine is required to drive both compressors and to overcome mechanical friction,

i.e. Work output of HP turbine $= \dfrac{2 \times 133.1}{0.98} = 272$ kJ/kg

therefore

$$c_{p_g}(T_6 - T_7) = 272$$

i.e. $1.15(923 - T_7) = 272$

therefore

$$923 - T_7 = \frac{272}{1.15} = 236.5 \text{ K}$$

i.e. $T_7 = 923 - 236.5 = 686.5$ K

From equation (9.2)

$$\eta_T, \text{ HP turbine} = \frac{T_6 - T_7}{T_6 - T_{7s}} = 0.85$$

therefore

$$T_6 - T_{7s} = \frac{236.5}{0.85} = 278 \text{ K}$$

i.e. $T_{7s} = 923 - 278 = 645$ K

Then using equation (3.21)

$$\frac{p_6}{p_7} = \left(\frac{T_6}{T_{7s}}\right)^{\gamma/(\gamma-1)} = \left(\frac{923}{645}\right)^{1.333/0.333} = 4.19$$

Then $\dfrac{p_8}{p_9} = \dfrac{9}{4.19} = 2.147$

Using equation (3.21)

$$\frac{T_8}{T_{9s}} = \left(\frac{p_8}{p_9}\right)^{(\gamma-1)/\gamma} = 2.147^{0.333/1.333} = 1.211$$

therefore

$$T_{9s} = \frac{923}{1.211} = 762.6 \text{ K}$$

Then using equation (9.2)

$$\eta_T, \text{ LP turbine} = \frac{T_8 - T_9}{T_8 - T_{9s}} = 0.85$$

therefore

$$T_8 - T_9 = 0.85 \times (923 - 762.6) = 136.3 \text{ K}$$

i.e. $T_9 = 923 - 136.3 = 786.7$ K

Therefore

$$\text{Net work output} = c_{p_g}(T_8 - T_9) \times 0.98$$
$$= 1.15 \times 136.3 \times 0.98 = 153.7 \text{ kJ/kg}$$

From equation (9.6)

$$\text{Thermal ratio of heat exchanger} = \frac{T_5 - T_4}{T_9 - T_4} = 0.75$$

i.e.

$$T_5 - 420.5 = 0.75(786.7 - 420.5) = 274.7 \text{ K}$$

therefore

$$T_5 = 420.5 + 274.7 = 695.2 \text{ K}$$

Now $\quad \text{Heat supplied} = c_{p_g}(T_6 - T_5) + c_{p_g}(T_8 - T_7)$

$$= 1.15\{(923 - 695.2) + (923 - 686.5)\} = 534 \text{ kJ/kg}$$

Then, from equation (5.2)

$$\text{Cycle efficiency} = \frac{-\dot{W}}{\dot{Q}} = \frac{153.7}{534} = 0.288 \text{ or } 28.8\%$$

(ii) Gross work output

= work output of HP turbine + work output of LP turbine i.e. Gross work output $= 272 + \dfrac{153.7}{0.98} = 429$ kJ/kg

Therefore

$$\text{Work ratio} = \frac{\text{net work output}}{\text{gross work output}} = \frac{153.7}{429} = 0.358$$

(iii) The electrical output is 5000 kW. Let the mass flow rate be $\dot{m}$ kg/s, then

$$5000 = \dot{m} \times 153.7$$

$$\dot{m} = \frac{5000}{153.7} = 32.6 \text{ kg/s}$$

i.e. Rate of flow of air = 32.6 kg/s

Effect of pressure loss

In Example 9.4 all pressure losses were neglected. In an actual gas turbine unit there are pressure losses due to friction and turbulence in the intercooler, in the air side of the heat exchanger, in both combustion chambers, and in the gas side of the heat exchanger, and in the exhaust duct. The high heat transfer rate in a combustion chamber leading to an appreciable velocity increase in a duct of approximately constant cross-sectional area causes a further pressure loss in addition to that due to friction and turbulence.

Example 9.5 For the gas turbine generating set of Example 9.4 recalculate the cycle efficiency and work ratio, taking the following pressure losses into account, but assuming all other assumptions still apply: air side of heat exchanger, 0.3 bar; gas side of heat exchanger and exhaust duct, 0.05 bar; intercooler, 0.15 bar; each combustion chamber, 0.2 bar.

Take an ambient pressure of 1.01 bar, a pressure ratio for each compressor of 3:1 as previously calculated, and find a new overall pressure ratio for the compression. All other data are unchanged.

Solution Referring to the T–s diagram shown in Fig. 9.16, as before:

$$T_{2s} = 288(3)^{0.286} = 394 \text{ K}$$

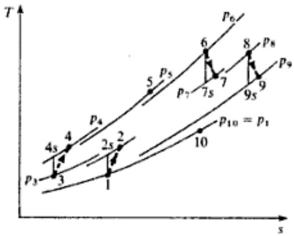


Fig. 9.16 T–s diagram showing pressure losses for Example 9.5

and using the isentropic efficiency

$$T_2 = 420.5 \text{ K} = T_4$$

Also as before

Work output per compressor stage = 133.1 kJ/kg

The pressure at inlet to the HP compressor, p_3, is now given by $(3 \times 1.01) - 0.15 = 2.88$ bar, and at outlet from the HP compressor, p_4, is $3 \times 2.88 = 8.64$ bar. The new overall pressure ratio is therefore $8.64/1.01 = 8.555$, compared with 9 previously. The pressure at entry to the HP turbine, p_6, is now $8.64 - 0.3 - 0.2 = 8.14$ bar.

The work output of the HP turbine is given as before by $(2 \times 133.1/0.98) = 272$ kJ/kg, and hence the temperatures T_7 and T_{7_s} are the same as before and hence the ratio $p_6/p_7 = 4.19$ is also the same as before,

i.e. $\quad p_7 = p_6/4.19 = 8.14/4.19 = 1.943$ bar

Therefore

$$p_8 = (p_7 - 0.2) = 1.743 \text{ bar}$$

Now $p_{10} = p_1 = 1.01$ bar and therefore

$$p_9 = 1.01 + 0.05 = 1.06 \text{ bar}$$

$$p_8/p_9 = 1.743/1.06 = 1.644$$

Then $\quad T_{9_s} = T_8/(1.644)^{0.333/1.333} = 923/1.132 = 815.4$ K

and $\quad T_9 = 923 - (923 - 815.4) \times 0.85 = 831.5$ K

Therefore

$$\text{Net work output} = c_{p_g}(T_8 - T_9) = 1.15(923 - 831.5)$$
$$= 105.2 \text{ kJ/kg}$$

Then using equation (9.6) for the thermal ratio of the heat exchanger as before, we have

$$T_5 = 420.5 + 0.75(831.5 - 420.5)$$
$$= 728.8 \text{ K}$$

Then $\quad$ Heat supplied $= c_{p_g}(T_6 - T_5) + c_{p_g}(T_8 - T_7)$

$$= 1.15(923 - 728.8) + 1.15(923 - 686.5) = 495.3 \text{ kJ/kg}$$

Hence $\quad$ Cycle efficiency = 105.2/495.3 = 21.2%

This compares with the previous value of 28.8% when pressure losses are neglected.

The gross work of the plant is (105.2/0.98) + 277 = 384.3 kJ/kg. Therefore,

Work ratio = 105.2/384.3 = 0.274

This compares with the previous value of 0.358 when pressure losses were neglected.

9.3 Combustion

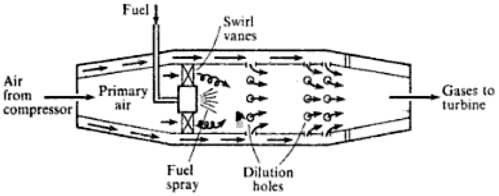
In the closed-cycle gas turbine unit heat is transferred to the air in a heat exchanger, but in the open-cycle unit the fuel must be sprayed into the air continuously, and combustion is a continuous process unlike the cyclic combustion of the IC engine.

There are two main combustion systems for open cycles: one in which the air leaving the compressor is split into several streams and each stream is supplied to a separate cylindrical 'can'-type combustion chamber, and the other in which the air flows from the compressor through an annular combustion chamber. The annular type would appear to be more suitable for a unit using an axial flow compressor, but it is difficult to obtain good fuel–air distribution and research and development work on this type is harder than with the simpler can type. The annular type can be modified by having a series of interconnected cans placed in a ring; this is known as the cannular type. In aircraft practice at present the majority of engines use either the cannular or the can type of combustion chamber.

In industrial plants where space is not important the combustion may be arranged to take place in one or two large cylindrical combustion chambers with ducting to convey the hot gases to the turbine; this system gives better control over the combustion process.

In all types of combustion chamber, combustion is initiated by electrical ignition, and once the fuel starts burning, a flame is stabilized in the chamber. In the can type it is usual to have interconnecting pipes between cans, to stabilize the pressure and to allow combustion to be initiated by a spark in one chamber on starting up. A typical can-type chamber is shown diagrammatically in Fig. 9.17. Some of the air from the compressor is introduced directly to the fuel burner; this is called primary air, and represents about 25% of the total airflow. The remaining air enters the annulus round the flame tube, thus cooling the upper portion of the flame tube, and then enters the combustion zone through dilution holes as shown in Fig. 9.17. The primary air forms a comparatively rich mixture and the temperature is high in this zone. The air entering the dilution holes completes the combustion and helps to stabilize the flame in the high-temperature region of the chamber. In some combustion chambers the fuel is injected upstream into the airflow, and a sheet metal cone and perforated baffle plate ensure the necessary mixing of the fuel and air.

Fig. 9.17 Gas turbine can-type combustion chamber



The air–fuel ratio overall is of the order of 60/1 to 120/1, and the air velocity at entry to the combustion chamber is usually not more than 75 m/s. There is a rich and a weak limit for flame stability, and the limit is usually taken at flame blow-out. Instability of the flame results in rough running with consequent effect on the life of the combustion chamber.

It should be noted that because of the high air–fuel ratios used, the gases entering the HP turbine contain a high percentage of oxygen, and therefore if reheating is performed between turbine stages, the additional fuel can be burned satisfactorily in the exhaust gas from the HP turbine.

A combustion efficiency may be defined as follows:

$$\text{Combustion efficiency} = \frac{\text{theoretical fuel–air ratio for actual temperature rise}}{\text{actual fuel–air ratio for actual temperature rise}} \quad (9.7)$$

The theoretical temperature rise is a function of the calorific value of the fuel used, the fuel–air ratio, and the initial temperature of the air. The theoretical temperature rise for any one fuel of known calorific value can be plotted against the fuel–air ratio for various values of air inlet temperature to the chamber, and curves of the form shown in Fig. 9.18 obtained. The combustion efficiency can be evaluated by testing the chamber; sections are traversed to obtain true mean readings of the inlet and outlet temperatures, and the fuel and air mass flow rates are also measured. The fuel used in aircraft gas turbine practice is a light petroleum distillate known as kerosene with a gross calorific value of about 46 400 kJ/kg; for turbines used in power production or as part of a combined heat and power unit the fuel used can also be natural gas; for some process plants a gas turbine unit is used for power production using waste gases as fuel. In cases where kerosene or gas is to be burned a dual-fuel burner is used.

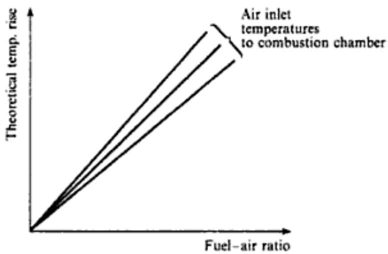


Fig. 9.18 Theoretical temperature rise against fuel–air ratio

In order to give a comparison of combustion chambers of different size operating under different ambient conditions, a *combustion intensity* is defined as follows:

$$\text{Combustion intensity} = \frac{\text{heat release rate}}{(\text{volume of chamber} \times \text{inlet pressure})} \quad (9.8)$$

The lower the combustion intensity the better the design. In aircraft practice a figure of about 2 kW/m^3 atm would be normal, whereas in the larger industrial plant a figure of about 0.2 kW/m^3 atm is usually achievable.

The pressure loss in the combustion chamber is mainly due to friction and turbulence. There is also a small drop in pressure due to non-adiabatic flow in a duct of approximately constant cross-sectional area. The loss due to friction can be found experimentally by blowing air through the combustion chamber without initiating combustion and measuring the change in pressure. This friction loss in pressure is therefore called the *cold loss*. The loss due to the heating process alone is called the *fundamental loss*. For a more extensive treatment of the combustion process ref. 9.1 should be consulted.

9.4 Additional factors

In considering aircraft propulsion it is necessary first to study the theory of flow in nozzles, and to introduce the concept of total head, or stagnation, pressures and temperatures. Gas turbine cycles for aircraft propulsion are therefore considered again in section 10.9. Another useful concept is small stage, or polytropic, efficiency; this is considered, and cycles analysed using polytropic efficiency in section 11.8 after blading design and the concept of a stage have been introduced.

Problems

(For all problems c_p and γ may be taken as 1.005 kJ/kg K and 1.4 for air, and as 1.15 kJ/kg K and 1.333 for combustion and expansion processes.)

9.1 A gas turbine has an overall pressure ratio of 5 and a maximum cycle temperature of 550 °C. The turbine drives the compressor and an electric generator, the mechanical efficiency of the drive being 97%. The ambient temperature is 20 °C and air enters the compressor at a rate of 15 kg/s; the isentropic efficiencies of the compressor and turbine are 80 and 83%. Neglecting changes in kinetic energy, the mass flow rate of fuel, and all pressure losses, calculate:
(i) the power output;
(ii) the cycle efficiency;
(iii) the work ratio.

(660.3 kW; 12.1%; 0.169)

9.2 In a marine gas turbine unit a HP stage turbine drives the compressor, and a LP stage turbine drives the propeller through suitable gearing. The overall pressure ratio is 4/1, the mass flow rate is 60 kg/s, the maximum temperature is 650 °C, and the air intake conditions are 1.01 bar and 25 °C. The isentropic efficiencies of the compressor, HP turbine, and LP turbine, are 0.8, 0.83, and 0.85 respectively, and the mechanical efficiency of both shafts is 98%. Neglecting kinetic energy changes, and the pressure loss in combustion, calculate:
(i) the pressure between turbine stages;
(ii) the cycle efficiency;
(iii) the shaft power.

(1.57 bar; 14.9%; 4560 kW)

9.3 For the unit of Problem 9.2, calculate the cycle efficiency obtainable when a he exchanger is fitted. Assume a thermal ratio of 0.75.

(23.4%

9.4 In a gas turbine generating set two stages of compression are used with an intercool between stages. The HP turbine drives the HP compressor, and the LP turbine driv the LP compressor and the generator. The exhaust from the LP turbine passes throu a heat exchanger which transfers heat to the air leaving the HP compressor. There is reheat combustion chamber between turbine stages which raises the gas temperature 600 °C, which is also the gas temperature at entry to the HP turbine. The overall pressu ratio is 10/1, each compressor having the same pressure ratio, and the air temperatu at entry to the unit is 20 °C. The heat exchanger thermal ratio may be taken as 0.7, a intercooling is complete between compressor stages. Assume isentropic efficiencies 0.8 for both compressor stages, and 0.85 for both turbine stages, and that 2% of t work of each turbine is used in overcoming friction. Neglecting all losses in pressu and assuming that velocity changes are negligibly small, calculate:

(i) the power output in kilowatts for a mass flow of 115 kg/s;
(ii) the overall cycle efficiency of the plant

(14 460 kW; 25.7%

9.5 A motor car gas turbine unit has two centrifugal compressors in series giving an over pressure ratio of 6/1. The air leaving the HP compressor passes through a heat exchang before entering the combustion chamber. The expansion is in two turbine stages, t first stage driving the compressors and the second stage driving the car through geari The gases leaving the LP turbine pass through the heat exchanger before exhausting atmosphere. The HP turbine inlet temperature is 800 °C and the air inlet temperatu to the unit is 15 °C. The isentropic efficiency of the compression is 0.8, and that of ea turbine is 0.85; the mechanical efficiency of each shaft is 98%. The heat exchang thermal ration may be assumed to be 0.65. Neglecting pressure losses and changes kinetic energy, calculate:

(i) the overall cycle efficiency;
(ii) the power developed when the air mass flow is 0.7 kg/s;
(iii) the specific fuel consumption when the calorific value of the fuel used is 42 600 kJ/k and the combustion efficiency is 97%.

(29.4%; 94.7 kW; 0.302 kg/kW

9.6 In a gas turbine generating station the overall compression ratio is 12/1, performed three stages with pressure ratios of 2.5/1, 2.4/1, and 2/1 respectively. The air in temperature to the plant is 25 °C and intercooling between stages reduces the temperatu to 40 °C. The HP turbine drives the HP and intermediate-pressure compressor stag the LP turbine drives the LP compressor and the generator. The gases leaving the L turbine are passed through a heat exchanger which heats the air leaving the H compressor. The temperature at inlet to the HP turbine is 650 °C, and reheating betwe turbine stages raises the temperature to 650 °C. The gases leave the heat exchanger a temperature of 200 °C. The isentropic efficiency of each compressor stage is 0.83, a the isentropic efficiencies of the HP and LP turbines are 0.85 and 0.88 respectively. Ta the mechanical efficiency of each shaft as 98%. The air mass flow is 140 kg/s. Neglecti pressure losses and changes in kinetic energy, and taking the specific heat of water 4.19 kJ/kg K, calculate:

(i) the power output in kilowatts;
(ii) the cycle efficiency;
(iii) the flow of cooling water required for the intercoolers when the rise in wat temperature must not exceed 30 K;
(iv) the heat exchanger thermal ratio.

(25 540 kW; 33.4%; 224 kg/s; 0.8

9.7 In a gas turbine plant air enters a compressor at atmospheric conditions of 15°C, 1.0133 bar and is compressed through a pressure ratio of 10. The air leaving the compressor passes through a heat exchanger before entering the combustion chamber. The hot gases leave the combustion chamber at 800°C and expand through an HP turbine which drives the compressor. On leaving the HP turbine the gases pass through a reheat combustion chamber which raises the temperature of the gases to 800°C before they expand through the power turbine, and thence to the heat exchanger where they flow in counter-flow to the air leaving the compressor. Using the data below, neglecting the mass flow rate of fuel and changes of velocity throughout, calculate:

(i) the airflow rate required for a net power output of 10 MW;
(ii) the work ratio of the cycle;
(iii) the temperature of the air entering the first combustion chamber;
(iv) the overall cycle efficiency.

Data Isentropic efficiency of compressor, 80%; isentropic efficiencies of HP and power turbine, 87 and 85%; mechanical efficiency of HP turbine-compressor drive, 92%; mechanical efficiency of power turbine drive, 94%; thermal ratio of heat exchanger, 0.75; pressure drop on air side of heat exchanger, 0.125 bar; pressure drop in first combustion chamber, 0.100 bar; pressure drop in reheat combustion chamber, 0.080 bar; pressure drop on gas side of heat exchanger, 0.100 bar.

(91.0 kg/s; 0.25; 611°C; 18.9%)

9.8 An open-cycle gas turbine plant is used to generate power in an oil refinery. The gas turbine unit drives a generator which supplies electric motors of 2400 kW; the overall mechanical and electrical efficiency is 92%. Some of the exhaust gas from the turbine at 530°C is supplied to a furnace in the refinery at a rate of 2 kg/s; the remainder of the exhaust gas is passed in counter-flow through a heat exchanger where it heats the air leaving the compressor, and then passes to exhaust at 400°C. The compressor has a pressure ratio of 8 and the air at entry is at 1.013 bar and 20°C. The pressure loss in the air side of the heat exchanger is 0.16 bar, the pressure loss in the combustion chamber is 0.12 bar, and the pressure loss in the gas side of the heat exchanger is 0.05 bar. The isentropic efficiencies of the compressor and turbine are 0.85 and 0.92 respectively. Neglecting heat losses in the heat exchanger, and the mass flow rate of fuel, calculate:

(i) the mass flow rate of air entering the compressor;
(ii) the temperature of the air entering the combustion chamber;
(iii) the overall cycle efficiency.

(10.82 kg/s; 421.0°C; 34.2%)

9.9 A closed-cycle gas turbine plant using helium as the working fluid is proposed for an experimental nuclear reactor. The helium is compressed in two stages with an intercooler between stages. Before passing through a heater where it is heated externally by the reactor coolant, the helium is pre-heated in a heat exchanger where it is in counter-flow with the helium leaving the turbine. The helium leaving the turbine is cooled in the heat exchanger before passing through a cooler where it is cooled by cooling water to the required inlet temperature to the compressor, and the cycle is complete. Using the data below, calculate the overall cycle efficiency.

Data Pressure and temperature at entry to the first compressor, 18 bar and 30°C; pressure ratio for each compressor, 2; temperature of helium leaving the intercooler, 30°C; temperature of helium, entering the turbine, 800°C; isentropic efficiency of each compressor, 0.83; isentropic efficiency of the turbine, 0.86; effectiveness of the heat