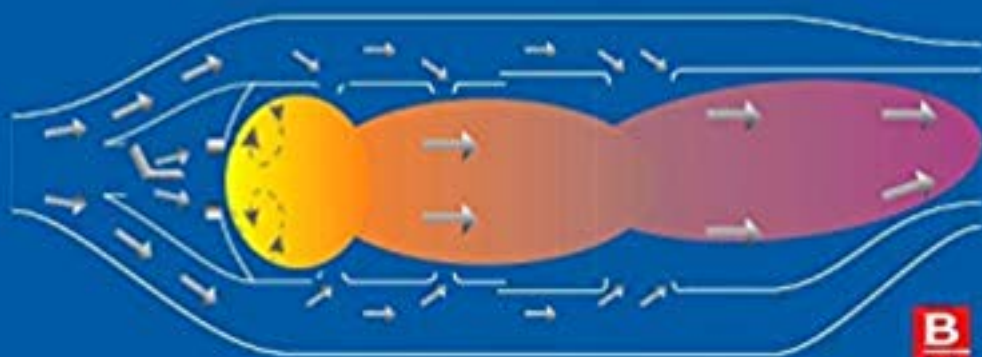


SECOND EDITION



ADVANCED THERMODYNAMICS FOR ENGINEERS

D.E. WINTERBONE and A. TURAN



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Advanced Thermodynamics for Engineers

Second Edition

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Second Edition

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Preface – First Edition

When reviewing, or contemplating writing, a text-book on engineering thermodynamics, it is necessary to ask what does this book offer that is not already available? The author has taught thermodynamics to mechanical engineering students, at both undergraduate and postgraduate level, for 25 years, and has found that the existing texts cover very adequately the basic theories of the subject. However, by the final years of a course, and at postgraduate level, the material which is presented is very much influenced by the lecturer, and here it is less easy to find one book which covers all the syllabus in the required manner. This book attempts to answer this need, for the author at least.

The engineer is essentially concerned with manufacturing devices to enable tasks to be performed cost-effectively and efficiently. Engineering has produced a new generation of automatic ‘slaves’ which enable those in the developed countries to maintain their lifestyle by the consumption of fuels rather than by manual labour. The developing countries still rely to a large extent on ‘manpower’, but the pace of development is such that the whole world wishes to have the machines and quality of life which we, in the developed countries, take for granted: this is a major challenge to the engineer, and particularly the thermodynamicist. The reason why the thermodynamicist plays a key role in this scenario is because the methods of converting any form of energy into power are the domain of thermodynamics: all of these processes obey the four laws of thermodynamics, and their efficiency is controlled by the second law. The emphasis of the early years of an undergraduate course is on the first law of thermodynamics, which is simply the conservation of energy; the first law does not give any information on the *quality* of the energy. It is the hope of the author that this text will introduce the concept of the quality of energy and help future engineers use our resources more efficiently. Ironically, some of the largest demands for energy may come from cooling (e.g. refrigeration and air-conditioning) as the developing countries in the tropical regions become wealthier – this might require a more basic way of considering energy utilisation than that emphasised in current thermodynamic texts. This book attempts to introduce basic concepts which should apply over the whole range of new technologies covered by engineering thermodynamics. It considers new approaches to cycles, which enable their irreversibility to be taken into account; a detailed study of combustion to show how the chemical energy in a fuel is converted into thermal energy and emissions; an analysis of fuel cells to give an understanding of the direct conversion of chemical energy to electrical power; a detailed study of property relationships to enable more sophisticated analyses to be made of both high and low temperature plant; and irreversible thermodynamics, whose principles might hold a key to new ways of efficiently converting energy to power (e.g. solar energy, fuel cells).

The great advances in the understanding and teaching of thermodynamics came rapidly towards the end of the nineteenth century, and it was not until the 1940s that these were embodied in thermodynamics textbooks for mechanical engineers. Some of the approaches used in teaching thermodynamics still contain the assumptions embodied in the theories of heat engines without explicitly recognising the limitations they impose. It was the desire to remove some of these shortcomings, together with an increasing interest in what limits the efficiency of thermodynamic devices, that led the author down the path which has culminated in this text.

I am still a strong believer in the pedagogical necessity of introducing thermodynamics through the traditional route of the zeroth, first, second and third laws, rather than attempting to use the Single-Axiom Theorem of Hatsopoulos and Keenan, or The Law of Stable Equilibrium of Haywood. While

both of these approaches enable thermodynamics to be developed in a logical manner, and limit the reliance on cyclic processes, their understanding benefits from years of experience – the one thing students are lacking. I have structured this book on the conventional method of developing the subject. The other dilemma in developing an advanced level text is whether to introduce a significant amount of *statistical thermodynamics*; since this subject is related to the particulate nature of matter, and most engineers deal with systems far from regions where molecular motion dominates the processes, the majority of the book is based on *equilibrium thermodynamics*; which concentrates on the macroscopic nature of systems. A few examples of statistical thermodynamics are introduced to demonstrate certain forms of behaviour, but a full understanding of the subject is not a requirement of the text.

The book contains XX chapters and while this might seem an excessive number, these are of a size where they can be readily incorporated into a degree course with a modular structure. Many such courses will be based on 2 h lecturing per week, and this means that most of the chapters can be presented in a single week. Worked examples are included in most of the chapters to illustrate the concepts being propounded, and the chapters are followed by exercises. Some of these have been developed from texts which are now not available (e.g. Benson, Haywood) and others are based on examination questions. Solutions are provided for all the questions. The properties of gases have been derived from polynomial coefficients published by Benson: All the parameters quoted have been evaluated by the author using these coefficients, and equations published in the text: this means that all the values are self-consistent, which is not the case in all texts. Some of the combustion questions have been solved using computer programs developed at UMIST, and these are all based on these gas property polynomials. If the reader uses other data, e.g. JANAF tables, the solutions obtained might differ slightly from those quoted.

Engineering thermodynamics is basically *equilibrium thermodynamics* although for the first two years of the conventional undergraduate course these words are used but not often defined. Much of the thermodynamics done in the early years of a course also relies heavily on *reversibility*, without explicit consideration of the effects of irreversibility. Yet, if the performance of thermodynamic devices is to be improved, it is the irreversibility which must be tackled. This book introduces the effects of irreversibility through considerations of availability (exergy), and the concept of the endoreversible engine. The thermal efficiency is related to that of an ideal cycle by the rational efficiency – to demonstrate how closely the performance of an engine approaches that of a reversible one. It is also shown that the Carnot efficiency is a very artificial yardstick against which to compare real engines: the internal and external reversibilities imposed by the cycle mean that it produces zero power at the maximum achievable efficiency. The approach by Curzon and Ahlborn to define the efficiency of an endoreversible engine producing maximum power output is introduced: this shows the effect of *external irreversibility*. This analysis also introduces the concept of *entropy generation* in a manner readily understandable by the engineer; this concept is the cornerstone of the theories of *irreversible thermodynamics* which are at the end of the text.

Whilst the laws of thermodynamics can be developed in isolation from consideration of the property relationships of the system under consideration, it is these relationships which enable the equations to be *closed*. Most undergraduate texts are based on the evaluation of the fluid properties from the simple perfect gas law, or from tables and charts. While this approach enables typical engineering problems to be solved, it does not give much insight into some of the phenomena which can happen under certain circumstances. For example, is the specific heat at constant volume a function of temperature alone for gases in certain regions of the state diagram? Also, why is the assumption of

constant stagnation, or even static, temperature valid for flow of a perfect gas through a throttle, but never for steam? An understanding of these effects can be obtained by examination of the more complex equations of state. This immediately enables methods of gas liquefaction to be introduced.

An important area of engineering thermodynamics is the combustion of hydrocarbon fuels. These have formed the driving force for the improvement of living standards which has been seen over the last century, but they are presumably finite, and are producing levels of pollution that are a constant challenge to engineers. At present, there is the threat of global warming due to the build-up of carbon dioxide in the atmosphere: this requires more efficient engines to be produced, or for the carbon/hydrogen ratio in fuels to be reduced. Both of these are major challenges, and while California can legislate for the zero emissions vehicle (ZEV) this might not be a worldwide solution. It is said that the ZEV is an electric car running in Los Angeles on power produced in Arizona! – obviously a case of exporting pollution rather than reducing it. The real challenge is not what is happening in the West, although the energy consumption of the United States is prodigious, but how can the aspirations of the East be met. The combustion technologies developed today will be necessary to enable the newly industrialised countries (NICs) to approach the level of energy consumption which we enjoy. The section on combustion goes further than many general textbooks in an attempt to show the underlying general principles which affect combustion, and it introduces the interaction between thermodynamics and fluid mechanics which is so important to achieving clean and efficient combustion. The final chapter introduces the thermodynamic principles of fuel cells, which enable the direct conversion of the Gibbs energy in the fuel to electrical power. Obviously the fuel cell could be a major contributor to the production of ‘clean’ energy and is a goal for which it is worth aiming.

Finally, a section is included on irreversible thermodynamics. This is there partly as an intellectual challenge to the reader, but also because it introduces concepts that might gain more importance in assessing the performance of advanced forms of energy conversion. For example, although the fuel cell is basically a device for converting the Gibbs free energy of the reactants into electrical energy, is its efficiency compromised by the thermodynamics of the steady state that are taking place in the cell? Also, will photovoltaic devices be limited by phenomena considered by irreversible thermodynamics?

I have taken the generous advice of Dr Joe Lee, a colleague in the Department of Chemistry, UMIST, and modified some of the wording of the original text to bring it in line with more modern chemical phraseology. I have replaced the titles Gibbs free energy and Helmholtz free energy by Gibbs and Helmholtz energy respectively: this should not cause any problems and is more logical than including the word ‘free’. I have bowed, with some reservations, to using the internationally agreed spelling sulfur, which again should not cause problems. Perhaps the most difficult concept for engineers will be the replacement of the terms ‘mol’ and ‘kmol’ by the term ‘amount of substance’. This has been common practice in chemistry for many years, and separates the general concept of a quantity of matter from the units of that quantity. For example, it is common to talk of a mass of substance without defining whether it is in grams, kilograms, pounds, or whatever system of units is appropriate. The use of the phrase ‘amount of substance’ has the same generalising effect when dealing with quantities based on molecular equivalences. The term mol will still be retained as the adjective and hence molal enthalpy is the enthalpy per unit amount of substance in the appropriate units (e.g. kJ/mol, kJ/kmol, Btu/lb-mol, etc.).

The author would like to acknowledge all those who have helped and encouraged the writing of this text. First, I would like to acknowledge the influence of all those who attempted to teach me

thermodynamics; and then those who encouraged me to teach the subject, in particular Jim Picken, Frank Wallace and Rowland Benson. Second, I would like to thank those who have helped in the production of this book by reading the text or preparing some of the material. Amongst these are Ed Moses, Marcus Davies, Loh, Joe Lee, Richard Pearson and John Horlock; whilst they have read parts of the text and provided their comments, the responsibility for the accuracy of the book lies entirely in my hands. I would also like to acknowledge my secretary, Mrs P Shepherd, who did some of the typing of the original notes. Finally, I must thank my wife, Veronica, for putting up with lack of maintenance in the house and garden, and many evenings spent alone while I concentrated on this work.

Desmond E. Winterbone

Preface – Second Edition

It is almost 20 years since I wrote the first edition of this book, and I asked myself a number of questions when Elsevier invited me to consider writing a second edition. What is the status of thermodynamics in engineering education? Would a new edition basically be a minor update of the original one? Should I invite a 'colleague' to join me as a co-author? The answer to the last question is that Professor Ali Turan, who was appointed to my Chair in UMIST when I retired, agreed to join me in this venture. Professor Turan was extremely enthusiastic about the place of the book in engineering education, and this buoyed up my spirits during the long period of preparing the manuscript.

The first question we tackled was the status of thermodynamics in engineering syllabuses: we both agreed that it should be an integral part of any course, and that its influence and concepts were central to understanding a wide range of subjects. The need for an understanding of thermodynamic principles has increased over the last 20 years as the use of energy has expanded. The increase in the global demand for energy is shown in Figure 1, where it can be seen that a growth of around 3% per annum is occurring, but this is happening mainly in non-OECD countries where more than 5% is happening.

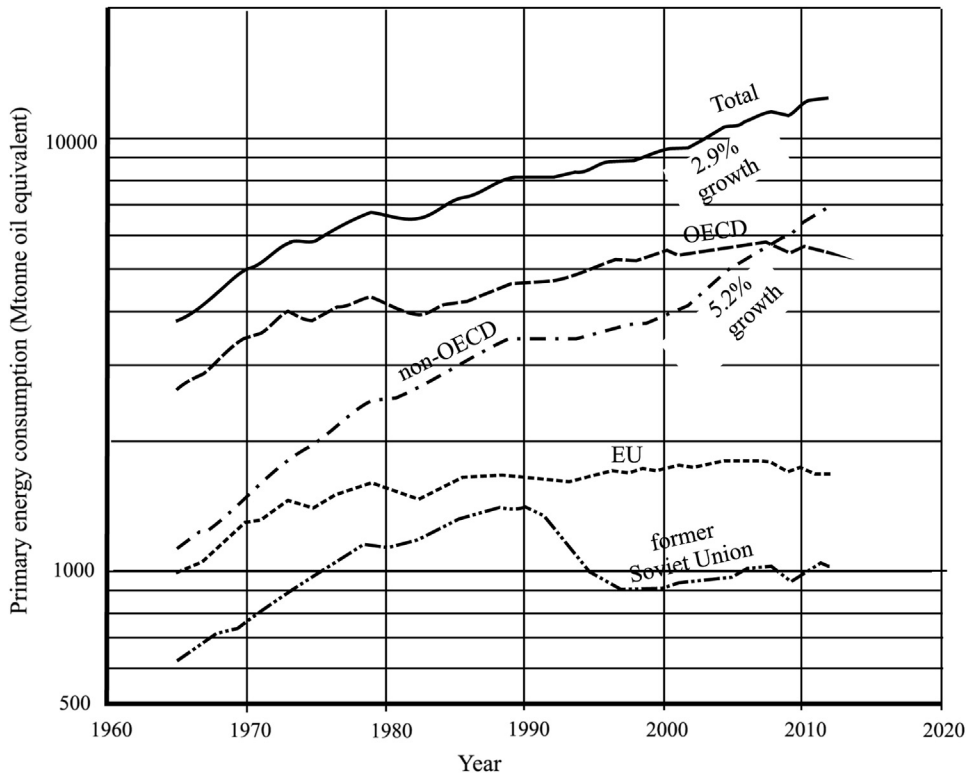


FIGURE 1

Increase in energy use since 1965.

Obviously it would be beneficial if the developed (OECD) countries could reduce their energy consumption, but it is essential that the developing countries are encouraged to employ the most efficient technology to contain their legitimate demands.

We then considered the development of the new edition, and were helped by comments on the first edition obtained by the publishers. We both agreed that the underlying approach, centred on equilibrium thermodynamics, should be maintained, but it was apparent that the original text, written by me to support the final year undergraduate course, and the postgraduate Masters course, relied too heavily on the structure of those courses and the assumed background of the reader. We hope we have remedied this by adding material at the beginning of the book that revises basic thermodynamics – this removes the rapid immersion of the reader in the concepts of equilibrium in the first chapter. We have also added some more ‘practical’ material on ‘heat engine’ cycles early in the text to help the reader get a feel for the applications of the more esoteric material later. Finally, Chapters 16 and 17 discuss how the basic concepts of engineering thermodynamics affect the operation of reciprocating internal combustion engines and gas turbines. Professor Turan provided many ideas about the structure of the book, and these are evident if the first and second editions are compared: we hope that the development of the material is now more logical than in the first edition. He was also able to bring in new material in a number of chapters, particularly on finite time thermodynamics, and fuel cells, which has enhanced this edition.

All of these modifications have resulted in a book that now has 21 chapters. Many of the chapters are based on the original 17 of the first edition. In some cases the changes are minor, resulting in the removal of spelling or minor arithmetic errors. In others, new material has been added, or some material has been moved to other more appropriate chapters. All of the original diagrams have received minor modifications, if only to the typeface, and some have been redrawn. The four new chapters cover a range of material. Chapter 1 is basically a revision of early thermodynamics, concentrating mainly on the concepts of systems and the first law: the material should be familiar to most readers. Chapter 2 has been modified to introduce the second law and the concept of the heat engine, before subsuming Chapter 1 of the first edition. Chapter 3 discusses heat engine cycles and shows that all heat engines have an efficiency dominated by a temperature ratio – the definition of this varies with the cycle. This has an important bearing on deciding how to improve the efficiency of a power plant. Realistic reciprocating engine cycles are introduced in the new Chapter 16, and it is shown why such engines do not achieve the efficiency of ideal heat engine cycles. In addition two computer programs are made available, in Chapters 12 and 16, to allow teachers and students to more fully develop the concepts in those chapters. Gas turbine cycles are discussed in some detail in Chapter 17, and these are related to the basic principles introduced in Chapter 2. Almost 90 completely new diagrams are included in this text, and it is hoped these help in the understanding of the principles involved.

I would like to acknowledge the work done by John Nichols and Richard Pearson in developing the two programs available for use with this book. They developed comprehensive programs that I have emasculated to make more amenable for the purposes of this book: I hope these prove useful. I must also thank Philip Kosky who sent me some corrections for the first edition. The authors would also like to acknowledge the contributions made by Khurram Kafeel, Dr Mario Ferrari, Dr Kate Smith, Xiaochuan Yang in preparing this edition. It is thanks to them that many of the errors in the original manuscript have been removed. Any shortcomings that remain in the text must be laid at the authors’ oversight, and for these we apologise. We would also like to acknowledge the patience of Chelsea Johnston at Elsevier who has coped with our many e-mails, our late response to requests, and our requirements to achieve the product we all desire.

Finally, I must thank my wife, Veronica, for allowing me to spend much more time on this project than I told her it would take. She has put up with my lack of domestic effort for almost a year, but I am sure there will be much to do now this task is finished.

Desmond E. Winterbone

Marple Bridge, UK

October 2014

When Professor Winterbone asked me to join him in putting together the second edition of *Advanced Thermodynamics for Engineers*, I was a bit apprehensive initially, because thermodynamics is regarded as a somewhat “stagnant topic” for an engineering curriculum. However, as the exercise developed and the contents were moulded into what I thought were self-consistent and fairly comprehensive format, I came to appreciate the all unifying power of the subject in terms providing a core competency for an engineer to possess regardless of his/her chosen field of endeavour. In this respect, I was guided tremendously by the long years I had spent in an industrial setting worrying about very down to earth design and development, and hardware issues for a variety of applications. These covered issues ranging from power generation and propulsion issues to chemical processing plant, which also included biophysical and biomedical attributes. I have always been somewhat concerned about the dismissive attitude of the practising engineer with the fundamental, all encompassing, physicochemical framework provided by thermodynamics, while at the same time being equally cognizant of the minimalistic utilitarian focus of the academic environment in contributing to practical solutions that the engineer has to tackle. It is on that basis I have tried to develop a mutually compatible viewpoint in providing contributions to resolve engineering issues i.e. literally, at an interface that tried to set a rigorous academic basis for solving challenging engineering problems that are almost guaranteed to require an intimate and seamless intermeshing of fundamental theory and unique creativity and applications.

Thus, a particular distinguishing feature of the current edition, which hopefully will come across forcefully in relation to this book as distinct from the large number of alternatives available in the literature, is the emphasis it places on industrial utilisation. This is demonstrated in some very practically oriented considerations that thermodynamics provides in the design and development of conversion efficient hardware: this is so important in this day and age. I would like to further stress that, due to my background and philosophy as succinctly summarised above, I have seen a large number of eye-opening examples, of such considerations in industrial settings and the innovative solutions provided by engineers and scientists of old school thermodynamics, which are as relevant today as they were then. It is with that thought that I would like to reader to appreciate the vibrancy of the subject displaying a systematic rational basis for design and development of hardware while being true to the principles laid by the originators of the subject/concepts.

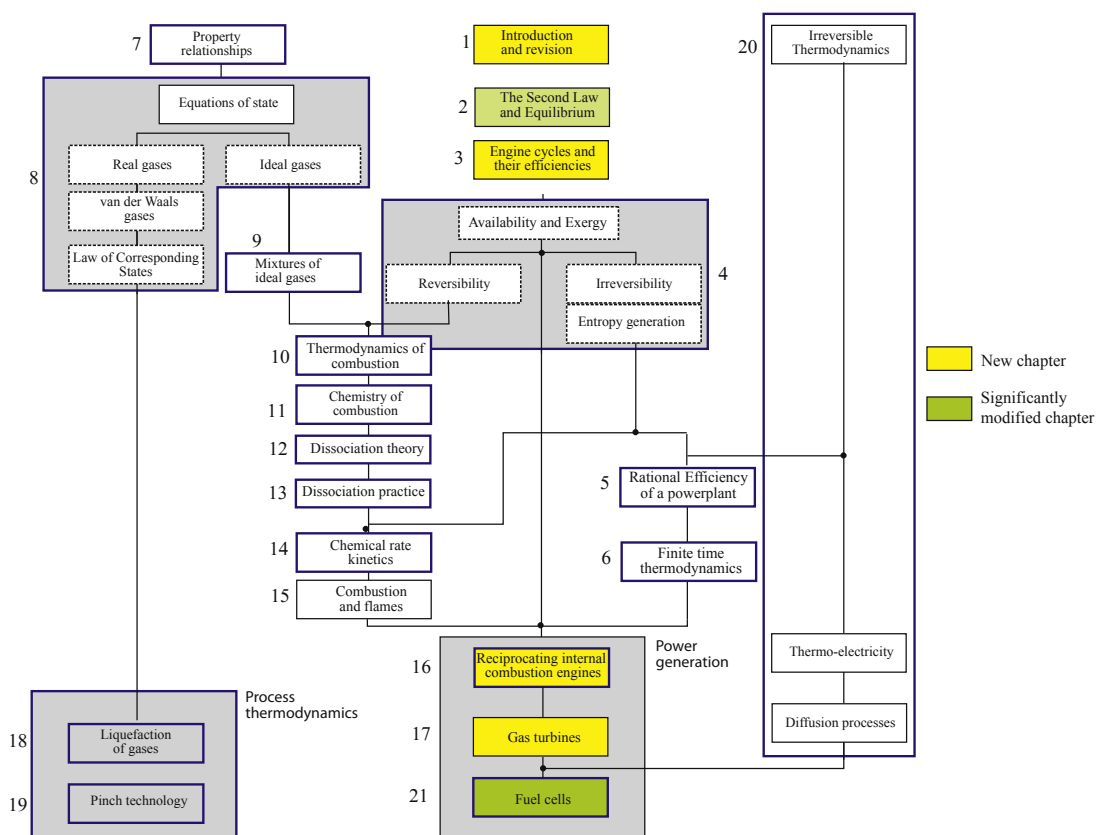
Finally, I would like to thank my wife, Ayse, and my daughter, Melissa, for being a constant source of inspiration during the effort and apologise sincerely for all the absences regarding household chores and helping with take home assignments. Unfortunately, this probably would be the norm rather than the exception as I have committed myself (foolishly) to a whole slew of writing and hope they will forgive me for it.

Ali Turan

Manchester, UK

October 2014

Structure of the Book



Notation

a	Activity coefficient
a	Specific non-flow availability
a	Coefficient in van der Waals equation
a_f	Specific flow availability
a_i	Enthalpy coefficient for gas properties
A	Non-flow availability
A	Area
A	Tafel constant
AFC	Alkaline fuel cell
b	Specific exergy
b	Coefficient in van der Waals equation
b	Bypass ratio
B	Exergy
c_p	Specific heat capacity at constant pressure (sometimes abbreviated to specific heat at constant pressure)
$\bar{c}_p$	Mean value of specific heat capacity at constant pressure over a range of temperatures
$\bar{c}_p$	Molar specific heat capacity at constant pressure (i.e. specific heat capacity at constant pressure based on <i>mols</i>)
c_v	Specific heat capacity at constant volume (sometimes abbreviated to specific heat at constant volume)
$\bar{c}_v$	Molar specific heat capacity at constant volume (i.e. specific heat capacity at constant volume based on <i>mols</i>)
C	Conductivity for heat flow into engines
CN	Cetane number
d	Increment in – usually used for definite integral, e.g. property, etc.
D	Mass diffusivity
DMFC	Direct methanol fuel cell
e	Specific internal energy
egr	Exhaust gas recirculation
E	Internal energy
E	Activation energy
E	Electromotive force of a cell (emf)
E^0	Standard emf of a cell
E_{oc}	Open circuit voltage
f	Specific Helmholtz energy (Helmholtz function)
f_t	Flame speed factor
F	Helmholtz energy (Helmholtz function)
F	Force
F	Thrust of gas turbine
F_s	Specific thrust of gas turbine
F	Faraday constant (charge carried by kmol of unit positive valency [96,487 kC/kmol])

g	Specific Gibbs energy (specific Gibbs function)
g_0	Specific Gibbs energy at datum temperature (or absolute zero)
g	Acceleration due to gravity
G	Gibbs energy (Gibbs function)
h	Specific enthalpy
h_0	Specific enthalpy at datum temperature (or absolute zero)
h	Height
H	Enthalpy
I	Irreversibility
i	Electrical current
J	Thermodynamic velocity, or flow
$\tilde{J}$	Joule's mechanical equivalent of heat
J_I	Electrical flow rate
J_Q	Heat flow rate
J_S	Entropy flow rate
k	Isothermal compressibility, isothermal bulk modulus
k	Thermal conductivity
k	Boltzmann constant (1.38062×10^{-23} J/K)
k_s	Adiabatic, or isentropic, compressibility
k	Rate of reaction
K	Karlovitz number $[(u'/\ell_T)(\delta_\ell/u_\ell)]$
K_F	Specific thrust coefficient of nozzle
K_p	Equilibrium constant
l	Length
l_T	Taylor microscale
L	Coefficient relating thermodynamic force and velocity
Le	Lewis number $[\lambda/pc_p D]$
m	Mass
$\dot{m}$	Mass flow rate
m_w	Molecular weight
MCFC	Molten carbonate fuel cell
n	Polytropic index
n	Amount of substance, chemical amount (sometimes referred to as number of moles)
n	Reaction order
N	Engine speed (rev/min)
$\tilde{N}$	Avogadro constant (6.023×10^{26} kmol ⁻¹)
p	Pressure
$\bar{p}$	Mean effective pressure
p_i	Partial pressure of component i
p_0	Datum pressure (often 1 bar or 1 atm)
P	Preparation rate (Whitehouse and Way equation.)
P	Power output
PAFC	Phosphoric acid fuel cell
PEMFC	Proton exchange membrane fuel cell
P_r	Prandtl number $[c_p \mu / k]$

q	Specific heat (energy) transfer
q_l	Electrical charge
Q	Heat (energy) transfer
Q^*	Heat of transport
Q_p	Enthalpy of reaction (energy of reaction at constant pressure)
Q_p'	Calorific value (at constant pressure) = $-Q_p$
Q_v	Internal energy of reaction (energy of reaction at constant volume)
Q_v'	Calorific value (at constant volume) = $-Q_v$
r	Compression ratio (of reciprocating engine)
r_p	Pressure ratio
r_w	Work ratio
r_{wb}	Back work ratio
R	Specific gas constant
$\mathbf{R}$	Rate of formation, rate of reaction
R	Radical
R	Electrical resistance
R	Reaction rate (Whitehouse and Way eqn.)
$\Re$	Universal gas constant
Re	Reynolds number $[\rho v \ell / \mu]$
s	Specific entropy
s_0	Specific entropy at datum temperature (or absolute zero)
S	Entropy
S^*	Entropy of transport
SOFC	Solid oxide fuel cell
SPFC	Solid polymer fuel cell
t	Temperature on discontinuous scale
t	Time
T	Temperature on absolute scale (thermodynamic temperature)
u	Specific intrinsic internal energy
u_0	Specific intrinsic internal energy at datum temperature (or absolute zero)
u'	Turbulence intensity
u_l	Laminar burning velocity
u_t	Turbulent burning velocity
U	Intrinsic internal energy
U	Overall heat transfer coefficient
v	Specific volume
V	Volume
V	Velocity
V	Voltage
$\bar{V}_p$	Mean piston speed (for reciprocating engines)
w	Specific work
$\hat{w}$	Maximum specific work
W	Work
x	Dryness fraction (quality)
x	Molar fraction

x	Distance
X	Thermodynamic force
y	Mass fraction
z	Valency

Greek characters

α	Degree of dissociation
α	$[A]/[A]_e$
α	Branching multiplication coefficient
α	Molecular thermal diffusivity
α	Crank angle (in internal combustion engines)
α	Constant volume period in dual combustion cycle
β	Coefficient of thermal expansion
β	Constant pressure period for diesel or dual combustion cycles
β	$[B]/[B]_e$
δ	Increment in – usually used for indefinite integral, e.g. work (W), heat (Q)
δ	$[D]/[D]_e$
ϵ	Potential difference, voltage
ϵ	Eddy diffusivity
ϵ	Air–fuel ratio (by mass)
$\epsilon_{A,B}$	Seebeck coefficient for material pair A, B
Δ	Increment in – usually used for indefinite integral, e.g. work (W), heat (Q)
ΔH_a	Atomisation energy
ΔH_f	Enthalpy of formation
$\Delta H()$	Dissociation energy
ϵ	Degree of reaction
ϵ	Air–fuel ratio of mixture
E	Heat exchanger effectiveness
κ	Ratio of specific heats (cp/cv)
λ	Electrical conductivity
λ	Equivalence ratio = $\epsilon_{stotic}/\epsilon$
μ	Dynamic viscosity
μ	Joule–Thomson coefficient
μ	Chemical potential
$\bar{\mu}$	Electrochemical potential
ν	Kinematic viscosity
$\pi_{A,B}$	Peltier coefficient for material pair A, B
θ	Entropy generation per unit volume
σ	Thomson coefficient
σr	Isentropic temperature ratio
σR	Pressure ratio for reheat
ν	Stoichiometric coefficient
γ	$[C]/[C]_e$
γ	Ratio of maximum to minimum temperature in cycle
η	Efficiency
η_i	Isentropic efficiency of intake

η_j	Isentropic efficiency of nozzle
η_p	Propulsive efficiency (sometimes called Froude efficiency)
ϕ	Equivalence ratio
ρ	Density
ξ	Specific exergy
ψ	Inner electric potential of a phase
τ	Temperature ratio
Ξ	Exergy

Suffices

0	Dead state conditions
0	Stagnation conditions
a	Air (for gas turbine)
Actual	Value from actual cycle, as opposed to ideal cycle
av	Available (as in energy)
b	Backward (reaction)
b	Burned (products of combustion)
b	Bypass (gas turbines)
bdc	Bottom dead centre
B	Boiler
c	At critical point, e.g. pressure, temperature, specific volume
cc	Combustion chamber
cl	Clearance (volume, of cylinder)
C	Cold (as in temperature of reservoir)
C	Compressor
d	Diagram factor in engine p – V calculation
e	Flow out of system (exit)
evo	Exhaust valve opening
[]_e	Equilibrium molar density
f	Forward (reaction)
f	Value for saturated liquid, e.g. h_f = enthalpy of saturated liquid
fg	Difference between properties on saturated vapour and saturated liquid lines, i.e. $h_{fg} = h_g - h_f$
g	Value for saturated gas, e.g. h_g = enthalpy of saturated gas
g	Gaseous state (as in reactants or products)
h	Constant enthalpy
H	Hot (as in temperature of reservoir)
i	Inversion
i	Flow into system
i	Indicated
i	i th constituent
ig	Ignition
in	Into system
isen	Isentropic (as in a process)
ivc	Inlet valve closure
j	Jet property
latent	Energy required for evaporation (equals h_{fg} or u_{fg})

<i>l</i>	Liquid state (as in reactants or products)
<i>l</i>	Laminar
max	Maximum value, or maximum useful work
mol	Specific property based on <i>mols</i>
net	Net (as in work output from system)
O	Overall
oc	Open circuit
out	Out of system
<i>p</i>	At constant pressure
P	Products
P	Pump
Rejected	Not used by cycle (usually energy)
res	Energy contained in molecules by resonance
R	Rational (as in efficiency)
R	Reactants
R	Reduced properties (in Law of Corresponding States)
R	Reversible
<i>s</i>	Shaft (as in work)
<i>s</i>	Stroke (of engine)
<i>s</i>	At constant entropy
surr	Surroundings
sys	System
T	Turbine
<i>T</i>	At constant temperature
tdc	Top dead centre
th	Thermal
u	Useful (as in work)
u	Unburned (as of reactants)
Unav	Unavailable (as in energy)
Univ	Universe (i.e. system + surroundings)
Use	Useful (as in work)
<i>v</i>	At constant specific volume

INTRODUCTION AND REVISION

1

1.1 THERMODYNAMICS

Thermodynamics is the science which defines the relationship between different forms of *energy* via characterisations of the various attributes of the enclosing system. This energy can take the form of work, heat or the energy contained within a system. Engineering thermodynamics plays a major role in the consideration of power generation, air-conditioning, chemical reactions, cryogenics (low temperatures) and low pressure systems. In general, thermodynamic concepts can be applied over a whole range of sciences, including biological systems, and they govern the way in which energy can be transformed between its various forms.

This chapter will briefly reiterate the fundamentals of the subject to make the reader familiar with the vocabulary and symbols used in this book. A more detailed version of this chapter, and its associated problems, is available on the website: <http://booksite.elsevier.com/9780444633736>.

1.1.1 MACROSCOPIC THERMODYNAMICS

There are two basic methods of studying thermodynamics, termed *classical (or macroscopic)* and *statistical thermodynamics*. Classical thermodynamics concentrates on the net changes affecting a system, without considering the detailed changes occurring within the system and the enclosing boundaries. Statistical thermodynamics considers the detailed changes occurring to and within the molecules inside the system, and can be termed *microscopic thermodynamics*. This book will concentrate on macroscopic thermodynamics, however, some concepts of statistical thermodynamics will be used to explain certain phenomena (see Chapter 21).

Classical thermodynamics considers systems at, or close to, *equilibrium*: many of the simple applications of thermodynamics are covered under this restriction. Notable cases which are not included in equilibrium situations are the production of pollutants (e.g. carbon monoxide and oxides of nitrogen) in combustion processes along with a large number of industrially important physico-chemical processes.

1.1.2 LAWS OF THERMODYNAMICS

There are *four* laws of thermodynamics, which have been developed from observations of large numbers of experiments. These laws are termed *axioms* (self-evident truths), and are the following:

Zeroth Law of Thermodynamics, which defines the concept of temperature.

First Law of Thermodynamics, which defines the concept of energy.

Second Law of Thermodynamics, which defines the ‘quality’ of energy and the direction of processes – and, even, time.

Third Law of Thermodynamics, which defines conditions at a temperature of absolute zero.

1.2 DEFINITIONS

Thermodynamics introduces new concepts and requires a new vocabulary based on a set of definitions.

1.2.1 SYSTEM

A system is a collection of matter enclosed within prescribed boundaries.

1.2.1.1 Closed system

A *closed* system is a prescribed and identifiable collection of matter enclosed *within* a prescribed **boundary**. There is *no flow* of matter across the boundary but energy exchanges can occur.

1.2.1.2 Surroundings

The surroundings are anything not contained within the system boundaries.

1.2.1.3 Open system

An open system is defined by its boundaries, and there can be mass transfer across the boundaries: the matter contained within an open system will vary with time. The space occupied by an *open system* is called a *control volume* and the boundaries of an open system are *control surfaces*.

1.2.2 PROPERTIES

A property is any quantity whose change is fixed by the end states, and is independent of the path between the end states.

Intensive properties are *independent* of the size/mass of the system.

Extensive properties are dependent on the size/mass (or *extent*) of the system.

Specific properties are defined as the extensive property *per unit mass*.

1.2.3 STATE

The *state* of a system is a complete description of all the properties of the system, i.e. both the mechanical and thermodynamic properties. e.g. a simple system is defined by its volume, pressure, velocity and position.

1.2.3.1 Change of state

When the state of a system alters, the change of state is defined by the two end states.

1.2.4 SOME IMPORTANT PROPERTIES

1.2.4.1 Pressure (p)

Pressure is a continuum concept and is the force per unit area exerted by a system on its surface in the direction normal to that surface. Typical units of pressure are N/m^2 , bar and lb_f/in^2 .

1.2.4.2 Density (ρ)

Density is defined as *mass per unit volume*. Density is also a continuum concept. Typical units of density are kilograms per cubic metre denoted by kg/m^3 .

1.2.4.3 Specific volume (v)

Specific volume is the reciprocal of density and is defined as the *volume per unit mass*; this is also a continuum concept. Typical units of specific volume are cubic metres per kilogram denoted by m^3/kg .

1.2.4.4 Temperature (t or T)

Temperature is a property introduced by thermodynamics: thermodynamic processes are driven by temperature or rather temperature differences. Temperature is measured by a device in *thermal (temperature) equilibrium* with the body.

1.3 THERMAL EQUILIBRIUM AND THE ZEROth LAW

If a system changes state slowly (compared to the reaction time of the system) it passes through a series of equilibrium states called a *path*.

1.3.1 PROCESS

The path through a succession of equilibrium points is called a *process*: it is *defined by the two end states and the path*.

1.3.2 CYCLE

A cycle is a process whose end states are identical. The concept of a cycle is an extremely important one in thermodynamics, and many of the proofs in thermodynamics are derived by considering cycles.

1.3.3 RELATIONSHIP BETWEEN PROPERTIES

The state of simple systems of constant mass and composition can be defined by two *independent* properties: this is referred to as the *two-property rule*, or the *Gibbs rule*. Any other property can be evaluated from these two properties if the characteristics of the substance inside the system boundaries are known. Hence, **two independent properties are sufficient to define the state of simple systems of constant mass**.

1.3.4 THERMAL EQUILIBRIUM

Consider two systems, A and B, which are not at the same state, connected through a wall, which can be either a perfect insulator or a perfect conductor. If the systems do not change state with time, then the wall is an *adiabatic* one. If the systems spontaneously change state then the wall is a *diathermal* one, and the systems will ultimately reach a steady state: this steady state is called *thermal equilibrium*.

1.3.5 ZEROth LAW OF THERMODYNAMICS

Two systems are in thermal equilibrium with each other if they are both in thermal equilibrium with a third system.

Systems in thermal equilibrium with each other are said to be at the same temperature.

1.4 TEMPERATURE SCALES

There are two different scales of temperature:

- The *continuous scale* of temperature is based on the Second Law of thermodynamics and is independent of the thermometric substance.
- The *discontinuous scales* of temperature are defined as the International Temperature Scale (ITS-90). The Celsius (or Centigrade) and Fahrenheit scales are the original ITS scales.

1.5 INTERACTIONS BETWEEN SYSTEMS AND SURROUNDINGS

A system can interact with its surroundings through *transfers across the system boundaries*. For a closed system there can be no mass flow across the system boundaries, and the only possible interactions are by two mechanisms: **work** and **heat** – both of these are transfers of *energy* across the boundary.

1.5.1 WORK – THERMODYNAMIC DEFINITION

Work is done by a system when the sole effect on everything external to the system (the surroundings) would be the raising of a weight.

For engineers the main interest is in using systems to produce work, and hence the following definition is adopted for the sign convention of work:

- **positive work** is done by a system on the surroundings;
- **negative work** is done by the surroundings on a system.

This sign convention is completely arbitrary and some engineering textbooks use the opposite convention, which is also used by physicists and chemists. While the convention is arbitrary it does have a significant effect on the equations of thermodynamics. It is important to use the sign convention *consistently and correctly*.

1.5.1.1 Negative work

Energy cannot be created or destroyed, so *when a system does positive work then the surroundings must do an equal amount of negative work*.

1.5.1.2 Representation of work

Positive work will be represented by an arrow pointing out of the system, and negative work will be represented by an arrow pointing into the system.

1.5.1.3 Displacement work

Displacement work is an important feature of engines operating on thermodynamic principles, and this is often generated by a piston and a cylinder.

The incremental piston, or displacement work, is

$$dW = pdV, \quad (1.1)$$

and for a process in which the pressure varies with volume the work is

$$W = \int p dV \quad (1.2)$$

1.5.1.4 Unresisted expansion

Consider a system is at a pressure of p_1 and is separated from the surroundings, at a pressure of p_2 , by a diaphragm, where $p_1 > p_2$. If the diaphragm is burst then the system expands against the surroundings: but it can only do work against a *reacting force*. If the reacting force is not equal and opposite to the internal force in the system then the work done by the system is reduced to that which can be absorbed by the surroundings: in this case, $\int p_2 dV$.

If the surroundings of the system were a vacuum then p_2 is zero and the work done by the system in expanding against the vacuum would be zero. *No work is done during an unresisted expansion.*

1.5.2 QUASI-STATIC PROCESSES

The rate of expansion is an important factor in assessing the work done. For the work to be $\int p_c dV$ it is necessary that

- the pressure in the cylinder is uniform, which means that the piston speed must be low relative to the speed of sound;
- the speed of the piston is slow relative to the velocity of the molecules.

Such processes are referred to as quasi-static (semi-equilibrium) processes.

Work is not a property of a system.

Work is a transitory phenomenon used to transfer energy.

Work exists only during the process that is causing it.

1.5.3 HEAT TRANSFER

Heat transfer is another possible form of energy transfer across system boundaries. It is an interaction that occurs across the boundary due to temperature differences.

1.5.3.1 Definition of heat (transfer)

Heat (transfer) is the interaction between systems which occurs by virtue of temperature differences.

- Heat interactions are associated with energy transfers.
- Heat interactions are transitory phenomena.
- Heat is energy usually being transmitted across a boundary.
- Heat is not a quantity of energy contained within a system.
- If two bodies at *different* temperatures are brought into contact then heat is the energy transferred; the process ceases when the temperatures are equal (zeroth law).
- If the energy of a system is increased by heat interaction then the heat transfer is positive; if the energy is decreased then the heat transfer is negative.

1.5.3.2 Unit of heat (energy)

The standard unit of heat is the unit of energy, viz. the *joule* (J). In engineering practice the *kilojoule* (kJ), is usually used, but the kilojoule is not a rational unit. The joule can be related to the calorie or kilocalorie.

One kilocalorie is the quantity of energy required to raise the temperature of 1 kg of water by 1 °C if the water is at 15 °C.

The joule will be defined later and is not based on the thermal capacity of a substance, but derives from the First Law of Thermodynamics.

One kilocalorie (kcal) is equivalent to 4.1868 kJ.

1.5.3.3 Heat (transfer) processes on a state diagram

Heat and work transfer processes both have similar effects on the changes of state. It is more difficult to see that the same change of state can be brought about by different heat transfer processes based on the different thermodynamic constraints on the system, but this is the case.

The quantity of heat energy flowing into a system is dependent on the path followed during the process: hence *heat is not a property of the system*.

1.5.4 RELATIONSHIP BETWEEN HEAT AND WORK

Both heat and work are transitory phenomena associated with interactions at the boundaries of systems. They only exist when they are taking place and are not stored per se in the system.

1.5.4.1 The First Law of Thermodynamics

The First Law of Thermodynamics is a statement of the conservation of energy. It is based on the equivalence of heat and work, which was first stated by Joule in the 1840s. The First Law enables the concept of internal energy and enthalpy to be defined as thermodynamic properties.

1.5.4.1.1 Statement of the First Law of Thermodynamics

When a system executes a cyclic process, the algebraic sum of the work transfers is proportional to the algebraic sum of the heat transfers.

This can be written mathematically as

$$\oint \delta W = \tilde{J} \oint \delta Q, \text{ where } \oint \text{ means integration around the cycle,} \quad (1.3)$$

which can be rearranged to give

$$\oint \delta W - \tilde{J} \oint \delta Q = \tilde{J} \oint \delta Q - \oint \delta W = 0. \quad (1.4)$$

In SI units the units of work and heat are both joules (J), and hence $\tilde{J} = 1$. Thus Eqn (1.4) becomes

$$\oint \delta W - \oint \delta Q = \oint \delta Q - \oint \delta W = 0,$$

which can be rewritten as

$$\oint (\delta Q - \delta W) = 0. \quad (1.5)$$

In other systems of units $\tilde{J}$ is not unity, e.g. in imperial units (foot, pound, second) the value of $\tilde{J} = 778 \text{ ft lb/Btu}$, while in the cgs (centimetre–gram–second) system the value of $\tilde{J}$ is **4.1868 g cm/cal**.

While Eqn (1.5) shows the proportionality of heat and work around a cycle, it does not give any information about intermediate states around the cycle. However, it is possible to introduce the concept of *internal energy*.

1.5.5 INTERNAL ENERGY

The quantity $\int (\delta Q - \delta W)$ is independent of the process and is dependent only on the end states. This means that $\int (\delta Q - \delta W)$ is a thermodynamic property, and it is named *internal energy* denoted by the symbol E . The change in internal energy, E , in a process from 1 to 2 is

$$E_2 - E_1 = \int_1^2 (\delta Q - \delta W), \quad (1.6)$$

or

$$dE = \delta Q - \delta W. \quad (1.7)$$

Equations (1.6) and (1.7) define the First Law in integrated or differential form. They both define the *conservation of energy*, which states that the change in energy of a system is equal to the algebraic sum of the heat and work transfers to the system.

Both Eqns (1.6) and (1.7) relate the *change in internal energy* to the heat and work transfers. They do not define the datum level of internal energy.

1.5.5.1 Relationship between E, Q and W

- The change in internal energy around a cycle is always zero.
- The net quantity of work (δW) and heat (δQ) transfers around a cycle *will not necessarily be zero*.
- The change of internal energy, $E_2 - E_1$ has a significance as a quantity associated with the state of a system.
- Work, heat and internal energy are all energy terms.
- Work and heat are both transitory energy transfers at the control surface of a system.
- Internal energy is the energy of the interior of the system.

1.5.5.2 Isolated systems

If a system executes a process in which no heat or work transfers occur then the system is said to be an *isolated system*. The internal energy of an isolated system is constant.

1.5.5.3 Energy of a system

The energy of a system was defined as E , without being specific about the form of this energy. Work transfer can bring about changes to many forms of energy: kinetic energy, potential energy, magnetic, capillary, electrical and thermal energy. In this analysis only kinetic, potential and thermal energy will be considered because these are the main forms of energy encountered by the mechanical engineer. The analysis can be expanded to include the other forms if necessary. Heat transfer can only, primarily, affect the thermal energy.

The change of internal energy, dE , of a system of mass, m , is

$$E_2 - E_1 = m \frac{V_2^2}{2} - m \frac{V_1^2}{2} + mgh_2 - mgh_1 + mu_2 - mu_1 \quad (1.8)$$

which is made up of three components:

$$d(KE) = m \frac{V_2^2}{2} - m \frac{V_1^2}{2}, \quad (1.9)$$

$$d(PE) = mgh_2 - mgh_1, \quad (1.10)$$

and

$$\text{change of thermal energy} = mu_2 - mu_1. \quad (1.11)$$

The thermal energy (u), which is based solely on the thermodynamic properties of the system, is termed the *specific intrinsic internal energy*. The total energy of a moving system in a gravitational field is given by

$$E_2 - E_1 = m \frac{V_2^2}{2} - m \frac{V_1^2}{2} + mgh_2 - mgh_1 + mu_2 - mu_1 \quad (1.12)$$

and hence, applying the First Law (Eqn (1.7)), the net transfer of work and heat is

$$\delta Q - \delta W = m \left(u_2 + \frac{V_2^2}{2} + gh_2 \right) - m \left(u_1 + \frac{V_1^2}{2} + gh_1 \right). \quad (1.13)$$

1.5.5.4 Intrinsic internal energy, U or u

The intrinsic internal energy is the energy of the system based on the molecular motion inside the system. It obeys the two-property rule, and is hence a function of any two independent properties.

The specific intrinsic internal energy is a *specific property*, defined by

$$\begin{aligned} u &= u(T, v) \\ u &= u(p, T), \text{ etc.} \end{aligned} \quad (1.14)$$

and the intrinsic internal energy

$$\begin{aligned} U &= U(m, T, v) \\ U &= U(m, p, T), \text{ etc.} \end{aligned} \quad (1.15)$$

The intrinsic internal energy is an *extensive property*.

1.5.5.5 Specific heat at constant volume, c_v

The specific heat at constant volume is a useful concept for *single-phase pure substances*. The specific heat at constant volume is defined as the *rate of change of specific intrinsic internal energy at constant volume with temperature*. This may be written mathematically as

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v = \left(\frac{\partial u}{\partial t} \right)_v = \left(\frac{\partial Q}{\partial T} \right)_v. \quad (1.16)$$

The specific heat at constant volume is a property of the system because it is a derivative of the two properties. The units of c_v in SI are J/kg K, although in engineering it is usual to quote the values in kJ/kg K.

1.5.6 THE FIRST LAW OF THERMODYNAMICS IN THE ABSENCE OF KINETIC AND POTENTIAL ENERGY EFFECTS

If the kinetic and potential energy terms are removed from Eqn (1.13) then the First Law equation becomes

$$\delta Q - \delta W = mu_2 - mu_1 \quad (1.17)$$

which in turn can be simplified to

$$\delta Q = dU + \delta W \quad (1.18)$$

Most of the applications of the First Law will be based on the formulations in Eqns (1.17) and (1.18).

1.5.6.1 The First Law of Thermodynamics and the conversion of work to heat

The First Law contains no information on the direction of transferability of heat to work and work to heat. This means that *work can be completely converted to heat, and also implies that heat can be completely converted to work*. The First Law only states that energy can only be converted from one form to another.

1.5.6.1.1 Perpetual motion machine of the first kind (PMM 1)

A perpetual motion machine of the first kind (PMM 1) is one which operates in a cycle and generates a work output without any other interaction with the surroundings. *This is impossible by the First Law.*

1.5.6.1.2 Perpetual motion machine of the second kind (PMM 2)

A perpetual motion machine of the second kind (PMM 2) does not disobey the First Law, because the heat transfer to the cyclical system is transmuted into an equal and opposite work transfer. Hence, energy is conserved. It is not until the *Second Law of Thermodynamics* has been introduced that it can be shown that a PMM 2 is impossible.

1.5.6.2 Application of First Law of Thermodynamics to three general processes

1.5.6.2.1 Constant volume process

Two processes for a constant volume (isochoric) system have the same end states, one is brought about by work transfer and the other by heat transfer, and hence the change in internal energy is the same in both cases.

The heat transfer to the system, δQ , is equal to the work transfer to the system, $-\delta W$.

1.5.6.2.2 Constant pressure process

It is easier to ensure that a system undergoes a constant pressure (isobaric) process than a constant volume one; this can be achieved by a piston cylinder arrangement.

(a) Heating process

The First Law gives

$$\delta Q = dU + pdV \quad (1.19)$$

(b) Work process

In this case the work (δW_s) is done on the system is in the form of a paddle wheel stirring the fluid contained in the system. If the system is insulated from the surroundings, the process is adiabatic and $\delta Q = 0$. Hence, applying the First Law (Eqn (1.18)) gives

$$\delta Q = dU + \delta W$$

but in this case, while $\delta Q = 0$, the work term, δW , is made up of two components:

- the stirring work, δW_s ,
- the pdV work done in raising the weight due to the change in properties of the substance, e.g. temperature.

Equations (1.18) then becomes

$$0 = dU + pdV - \delta W_s, \quad (1.20)$$

which may be rewritten to give

$$\delta W_s = dU + pdV. \quad (1.21)$$

Since this was a constant pressure process it is possible to write Eqn (1.21) as

$$\delta W_s = d(U + pV) = dH. \quad (1.22)$$

where H is termed the *enthalpy* of the system.

If the end states of the two processes are the same, then the heat and work transfer processes are equivalent. Thus both the heat and work transferred to the system are equal to the change of *enthalpy*. Thus Eqn (1.19) can be written

$$\delta Q = dH. \quad (1.23)$$

1.5.7 ENTHALPY, H , AND SPECIFIC ENTHALPY, h

Enthalpy is a *property* because it is defined as

$$H = U + pV, \quad (1.24)$$

which is the sum of a property, U , and the product of two other properties, pV . The *specific enthalpy*, h , of a substance can be defined in a similar way to the specific internal energy, etc. and it is

$$h = \frac{H}{m} = \frac{U + pV}{m} = \frac{U}{m} + \frac{pV}{m} = u + pv. \quad (1.25)$$

1.5.7.1 Specific heat at constant pressure, c_p

The specific heat at constant pressure is defined in a similar manner to that at constant volume. It is defined as the *rate of change of specific enthalpy at constant pressure with temperature*. The mathematical definition of c_p is

$$c_p = \left(\frac{dh}{dT} \right)_p = \left(\frac{dh}{dt} \right)_p = \left(\frac{\delta Q}{dT} \right)_p \quad (1.26)$$

Again, the value of c_p can be obtained from either the continuous or discontinuous scales of temperature. The units of c_p are the same as those of c_v , namely J/kg K, or more commonly in engineering kJ/kg K.

1.5.7.1.1 Constant temperature processes

Constant temperature processes are referred to as *isothermal* processes. There are a number of isothermal processes encountered in common usage.

- Boiling and condensing processes occur at constant temperature and are accompanied by a change of phase of the working fluid.
- Slow expansion and compression processes in equilibrium with constant temperature surroundings will be isothermal.
- Isothermal processes require heat or work transfer to or from the surroundings. They are not adiabatic.

1.5.7.1.2 Constant internal energy processes

A constant internal energy process occurs when $dU = 0$. This can occur if the following circumstances exist:

- Heat and work transfers are both equal to zero, i.e. $\delta Q = 0$; $\delta W = 0$.
- Heat and work transfers are equal and opposite, so that $\delta Q - \delta W = 0$.

An example of a constant internal energy system is the expansion of an insulated system against a vacuum.

1.5.8 APPLICATION OF THE FIRST LAW OF THERMODYNAMICS TO OPEN SYSTEMS

The First Law of Thermodynamics *for Closed Systems* can be extended to open systems. At this stage it is necessary to reconsider the definitions of closed and open systems.

A *closed system* is a quantity of matter contained within prescribed boundaries, i.e. it has a fixed mass.

An *open system* is defined by its boundaries, or control surface, i.e. it has variable mass.

1.5.8.1 Unsteady Flow Energy Equation (USFEE)

$$\delta Q - \delta W = \delta \left(U + \frac{\bar{V}^2}{2} + gZ \right)_{cv} - \delta m_i \left(u_i + p_i v_i + \frac{V_i^2}{2} + g z_i \right) + \delta m_e \left(u_e + p_e v_e + \frac{V_e^2}{2} + g z_e \right) \quad (1.27)$$

Giving further consideration to the flow energy term $p_i v_i$, it can be seen that this is the *specific enthalpy*, h , of a substance. The *enthalpy*, H , of a system is given by

$$H = mh \quad (1.28)$$

where m = mass of the system.

This equation can be written as a rate equation giving

$$\dot{Q} - \dot{W} = \frac{\partial}{\partial t} \left(U + \frac{\bar{V}^2}{2} + gz \right)_{cv} - \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) + \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) \quad (1.29)$$

Equation (1.29) may be simplified to

$$\dot{Q} - \dot{W} = \frac{\partial}{\partial t} (E)_{cv} - \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) + \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) \quad (1.30)$$

Equation (1.30) is called the *unsteady flow energy equation (USFEE)*. It is unsteady because the conditions existing in the control volume may be functions of time, i.e. $\frac{\partial}{\partial t} (E)_{cv} \neq 0$.

1.5.8.2 Steady flow energy equation

The *steady flow energy equation* is a particular case of the USFEE, and may be derived from Eqn (1.30) by making the following assumptions:

- $\dot{m}_e = \dot{m}_i$;
- all velocities, enthalpies and elevations remain constant with time;
- $\frac{\partial}{\partial t} (E)_{cv} = 0$.

Then

$$\dot{Q} - \dot{W} = \dot{m} \left(h_e - h_i + \frac{V_e^2 - V_i^2}{2} + g(z_e - z_i) \right) \quad (1.31)$$

These assumptions mean that to an observer there appears to be no change in the state of the system with the passage of time, even though the fluid inside the system is continuously changing.

1.5.8.3 Applications of steady flow energy equation

Applications of the steady flow energy equation are discussed in the web version (<http://booksite.elsevier.com/9780444633736>) of Chapter 1.

1.6 CONCLUDING REMARKS

This chapter has summarised the basic definitions of thermodynamics. It has also introduced the concepts of work and heat – and most importantly emphasised that these are forms of energy transfer. Work and heat are transitory phenomena that exist only when a system interacts with its surroundings. However, the net effect of work and heat transfers is to change the energy of the system. The chapter has also introduced the concepts of open and closed systems, and derived forms of the energy conservation equation for both types of system. This chapter provides the building blocks of engineering thermodynamics up to the First Law: the Second Law is introduced in Chapter 2.

1.7 PROBLEMS

Revision problems relating to this chapter are given in the web version (<http://booksite.elsevier.com/9780444633736>) of Chapter 1.

THE SECOND LAW AND EQUILIBRIUM

The First Law of Thermodynamics states that energy cannot be created or destroyed: it can simply be transformed from one form of energy to another. This means that work can be transformed completely into heat. The Second Law of Thermodynamics relates to the reverse transformation of heat into work, and it will be shown that it is not possible to completely transform heat to work. In its simplest form for engineers, the Second Law is useful for considering the thermal efficiency of heat engines. In a more general form, the Second Law introduces the concept of the ‘quality’ of energy.

Some of the ideas introduced in Chapter 2 are discussed in greater depth in the web version of this book available on <http://booksite.elsevier.com/9780444633736>.

2.1 THERMAL EFFICIENCY

The definition of mechanical efficiency is

$$\text{Efficiency, } \eta = \frac{\text{Work output}}{\text{Work input}} \quad (2.1)$$

It was not possible to derive a similar relationship for thermal efficiency until Joule showed the equivalence between heat and work in 1848. Then thermal efficiency could be stated as

$$\text{Thermal efficiency, } \eta_{\text{th}} = \frac{\text{Useful work output}}{\text{Thermal energy input, for a heat engine operating in a cycle}} \quad (2.2)$$

2.2 HEAT ENGINE

A **heat engine** is a continuously operating thermodynamic system across the boundaries of which only heat and work flow: it is a closed system. The term *continuously operating* means that the heat engine operates in a *cycle*, and that a number of integral cycles is/are performed.

2.3 SECOND LAW OF THERMODYNAMICS

Two statements of the Second Law will be given here. The first is the Kelvin–Planck statement which says

It is impossible to construct an engine which will operate in a complete cycle and produce no other effects than to transfer heat with a single reservoir and raise a weight (i.e. do work).

The other statement of the Second Law, attributed to Clausius, states

It is impossible to construct a system which will operate in a cycle and transfer heat from a cooler to a hotter body without work being done on the system by the surroundings.

It is possible to derive six corollaries of the Second Law, and these will simply be stated here.

Corollary 1

It is impossible to construct a heat engine to work between two heat reservoirs which has an efficiency which exceeds that of a reversible engine operating between the same two reservoirs.

Corollary 2

All reversible heat engines operating between the same two heat reservoirs have the same thermal efficiency.

Corollary 3

A temperature scale may be defined which is independent of the thermometric substance.

Corollary 4

This is often referred to as the Clausius inequality and defines a relationship for the net heat transfer of a cyclic process.

Whenever a system executes a complete cyclic process (i.e. a cycle) $\oint_{\text{cycle}} \frac{dQ}{T} \leq 0$

Corollary 5

This corollary defines the property *entropy*, which is the property associated with the Second Law of thermodynamics. Entropy is a measure of the transformation brought about by a process and is also an indicator of the direction of a process.

$\oint_{\text{cycle}} \frac{dQ_R}{T} = 0$ for any *reversible*, cyclic process. Hence, $\int \frac{dQ_R}{T}$ is a property of any reversible process between a reference state 0 and any other state 1. This property is called *entropy*.

Corollary 6

This is an important concept which shows that the degree of disorder in the universe will increase. If there is an increase in the order of a part of the universe, then it is accompanied by a decrease in the order of the remainder of the universe.

The entropy of an isolated system increases, or in the limit remains constant.

2.4 THE CONCEPT OF THE HEAT ENGINE: DERIVED BY ANALOGY WITH A HYDRAULIC DEVICE (TABLE 2.1)

Table 2.1 A Comparison of Parameters Defining Power Output and Efficiency for Engines

	Hydraulic Machine	Thermodynamic Machine
'Forcing' quantity	Head of water ($h_1 - h_2$)	Temperature difference ($T_1 - T_2$)
'Flowing' quantity	Weight flow rate $\dot{m}g$	Entropy flow rate $\dot{s} = \dot{Q}/T$
Work output rate	$\dot{m}g(h_1 - h_2)$	$\dot{s}(T_1 - T_2)$
Efficiency	$\eta = \frac{h_1 - h_2}{h_1}$	$\eta = \frac{T_1 - T_2}{T_1}$

2.5 THE ABSOLUTE TEMPERATURE SCALE

Carnot introduced the concept of absolute temperature from consideration of the reversible heat engine.

Kelvin realised that an absolute scale of temperature could be defined in terms of the reversible heat engine, and would be independent of the working fluid. This must be the case, or reversible heat engines operating between the same two temperature reservoirs with different working fluids would have different efficiencies, which would violate the first and second corollaries.

Kelvin defined a scale such that the same quantity of work is produced by a unit fall (1°) in temperature irrespective of the temperature level. This means that $\dot{Q}/T$ must be constant irrespective of the absolute temperature, T . Hence

$$\frac{\dot{Q}}{T} = \text{const} = \frac{\dot{Q}_0}{T_0} = \frac{\dot{Q}_1}{T_1} = \text{etc.}$$

This relationship between temperature and heat flow gives the efficiency as

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad (2.3)$$

The maximum value of efficiency is achieved when $T_C = 0$, when $\eta = 100\%$. An engine of this type would be a perpetual motion machine of the second kind, denoted a PMM2. Such a device has never been built and would violate the Kelvin–Planck statement of the Second Law.

2.6 ENTROPY

Section 2.4 shows that the ‘thermodynamic flow’ quantity to be considered in heat engines has the value of $\dot{Q}/T$. This quantity is conserved in a reversible engine; and is referred to as the ‘entropy’ flow rate. If the heat engine is ‘irreversible’ there is a production of entropy as the energy passes through the machine. There is no tangible analogue between this entropy production and the flow of ‘energy’ in the hydraulic machine. A direct consequence of this is the Clausius inequality which has no counterpart in any other field of physical science.

$$\oint \frac{\delta Q}{T} \leq 0. \quad (2.4)$$

The significance of the inequality sign is that

$$\begin{aligned} \text{for reversible processes} \quad \oint \frac{\delta Q}{T} &= 0 \\ \text{while, for irreversible processes} \quad \oint \frac{\delta Q}{T} &< 0. \end{aligned} \quad (2.5)$$

Consideration of a cycle for a **reversible engine** leads to the conclusion that

$$\oint \frac{\delta Q_R}{T} = 0.$$

This can only be the case if $\int \frac{\delta Q_R}{T}$ is a property of the system: it is called the **entropy** and is denoted by the symbol S , while specific entropy (i.e. entropy per unit mass) is s .

$$\text{The change of entropy between states 1 and 2 is } S_2 - S_1 = \int_1^2 \frac{\delta Q_R}{T} \quad (2.6)$$

2.6.1 THE SIGNIFICANCE OF ENTROPY

1. Entropy is evaluated from **reversible processes**.
2. Entropy can be used with irreversible processes.
3. The factor $1/T$ is the integrating factor that turns δQ_R from an indefinite integral into a definite one.
4. Entropy is a measure of the order or disorder of a system.

2.6.2 EVALUATION OF ENTROPY CHANGE FOR AN IRREVERSIBLE PROCESS

The change of entropy for an irreversible process must be evaluated by considering the change of entropy for a reversible process (or processes) that achieves the same two end states. A good example of such a process occurs in a throttling process: this is discussed in the web version (<http://booksite.elsevier.com/9780444633736>) of Chapter 2.

2.6.3 ENTROPY CHANGE AS ENVISAGED BY CLAUSIUS

Clausius suggested that the change of entropy could be considered to be made up of two terms.

$$dS = \frac{d(IE)}{T} + dZ \quad (2.7)$$

where $d(IE)$ is the change of ‘internal heat’ of the system $= \delta Q - \delta W_S$ and dZ is the change in disgregation of the molecules of the system i.e. a measure of the molecular spacing.

2.6.4 ENTROPY CHANGES FOR PURE SUBSTANCES

$$TdS = dU + pdV \quad (2.8)$$

Also, $H = U + pV$, giving $dH = dU + pdV + Vdp$, and

$$TdS = dH - Vdp \quad (2.9)$$

Specific entropy is the entropy per unit mass, hence $s = S/m$ and

$$ds = \frac{du + pdv}{T} = \frac{dh - vdp}{T} \quad (2.10)$$

Since this is a relationship between the properties u , p , T and h it is possible to evaluate the entropy of a fluid at any state defined by two independent properties. Also, since entropy is a property it can be used as a co-ordinate in a state diagram.

2.6.4.1 Temperature–entropy diagram for a pure substance

In these diagrams, entropy is usually used as the abscissa (i.e. the x -axis) of the diagram.

2.7 REPRESENTATION OF HEAT ENGINES

A heat engine which operates in a cyclical manner can be represented diagrammatically as shown in Fig. 2.1.

The direct heat engine, Fig. 2.1(a), receives heat (energy) from the high temperature reservoir at temperature, T_1 , and rejects it to the low temperature reservoir at temperature, T_2 . The reversed heat engine, Fig. 2.1(b), receives heat from the low temperature reservoir at T_2 , and pumps it to the high temperature reservoir at T_1 .

2.7.1 EFFICIENCY OF A HEAT ENGINE

The efficiency of a direct heat engine, often referred to as the thermal efficiency, η_{th} , is defined as the ratio of useful work to the heat supplied.

$$\text{Thermal efficiency, } \eta_{th} = \frac{\text{Net Work}}{\text{Heat supplied}} \quad (2.11)$$

This can be defined as

$$\eta_{th} = \frac{W_s}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad (2.12)$$

The 'efficiency' of reversed heat engines is normally called the coefficient of performance.

The coefficient of performance of a refrigerator is designated β , where this is defined as

$$\text{Coefficient of performance, } \beta = \frac{Q_2}{W_s} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} \quad (2.13)$$

The coefficient of performance of a heat pump is designated β' , where this is defined as

$$\text{Coefficient of performance, } \beta' = \frac{Q_1}{W_s} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2} \quad (2.14)$$

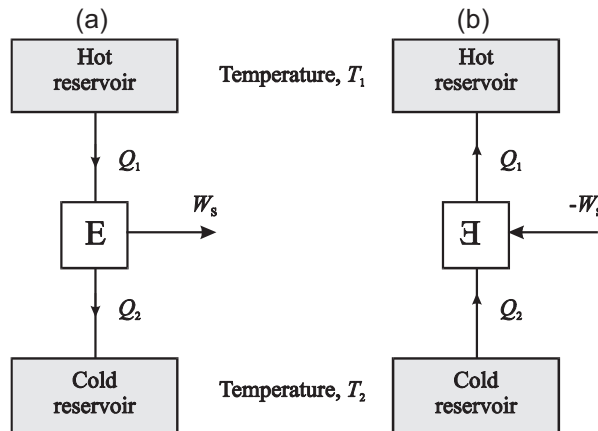


FIGURE 2.1

Schematic representation of a heat engine, (a) direct heat engine, (b) reversed heat engine.

The coefficient of performance of a heat pump can be related to that of a refrigerator by the simple equation

$$\beta' = 1 + \frac{Q_2}{W_S} = 1 + \beta \quad (2.15)$$

2.7.2 ENGINE WITH THERMAL EFFICIENCY OF 100%

The efficiency of a heat engine is defined in Eqn (2.12) as

$$\eta_{th} = \frac{W_S}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

The efficiency of a heat engine can be 100% if $Q_2 = 0$. This would be a PMM2 and violate the Kelvin–Planck statement of the Second Law.

2.7.3 REVERSIBLE HEAT ENGINE

The concept of reversible processes is a very important one and is discussed in the web version (<http://booksite.elsevier.com/9780444633736>) of Chapter 2.

It is possible to define a cycle made up of such processes, and because each of the processes in the cycle is reversible then the cycle will be reversible. A heat engine could execute such a cycle, and this heat engine would be called a reversible heat engine. Since all the processes are reversible, then an engine operating on this cycle can work with equal ‘efficiency’ in either direction, i.e. it could operate either as an engine or a heat pump or refrigerator.

2.8 REVERSIBILITY AND IRREVERSIBILITY (FIRST COROLLARY OF SECOND LAW)

As stated previously, the Second Law defines the direction of energy transfer during a process. All real processes are irreversible, due to friction, turbulence, mixing, electrical resistance, etc. However, it is useful to postulate what would happen in reversible processes, because these will give a yardstick at which to aim when designing engines. This is similar to neglecting friction at bearings when assessing the operation of a mechanism.

2.8.1 REVERSIBLE PROCESSES

A reversible process is one which can be taken from its initial state to another state, and then back to the initial state without any change to either the system or the surroundings. Examples of these are the following:

- frictionless motion of solids (no friction between mating surfaces)
- extension of springs (no hysteresis losses in the materials)
- slow adiabatic compression or expansion of gases (so that no pressure waves are set up in the gas)

- slow isothermal compression or expansion of gases (so that no temperature gradient is required to transfer the heat into or out of the system)
- electrolysis (with no resistance in the electrolyte)

2.8.2 IRREVERSIBLE PROCESSES

In reality all the processes have some losses, which might be friction, heat losses, hysteresis, etc. Hence, all real processes are irreversible. This does not mean that it is impossible for a system to perform a cycle made up of irreversible processes but simply that the surroundings will have been altered by the cycle having been performed. A number of common irreversible processes will be listed.

- friction between solids, or in fluids
- unresisted expansions
- heat transfer across finite temperature differences
- combustion – because the fuel and air are turned into carbon dioxide and water
- mixing of unlike, and miscible fluids
- hysteresis processes (internal friction in metals, hysteresis in electrical systems)
- plastic deformation of materials
- electrical resistance to current flow (production of heat through I^2R losses)

2.9 EQUILIBRIUM

Most texts on thermodynamics restrict themselves to dealing exclusively with equilibrium thermodynamics. This book will also focus on equilibrium thermodynamics but the effects of making this assumption will be explicitly borne in mind. The majority of processes met by engineers are in thermodynamic equilibrium, but some important processes have to be considered by nonequilibrium thermodynamics. Most of the combustion processes that generate atmospheric pollution include nonequilibrium effects, and carbon monoxide (CO) and oxides of nitrogen (NO_x) are both the result of the inability of the system to reach thermodynamic equilibrium in the time available.

There are four kinds of equilibrium, and these are most easily understood by reference to simple mechanical systems shown in Fig. 2.2. Here a marble is placed on a number of different surfaces, and the effect of a perturbation is considered: the result is then related to systems in similar thermodynamic states.

1. Stable equilibrium: marble in bowl (depicted in Fig. 2.2(a)):

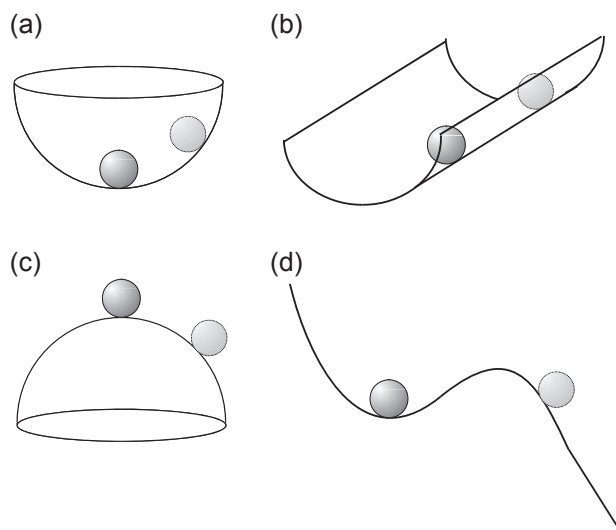
For stable equilibrium $\Delta E)_S > 0$ and $\Delta S)_E < 0$, where Δ indicates the sum of terms in the Taylor's series.¹

In this case any deflection results in motion back to the stable condition.

2. Neutral equilibrium: marble in trough (depicted in Fig 2.2(b)):

$\Delta E)_S = 0$ and $\Delta S)_E = 0$ along the trough axis. The marble is in equilibrium at any point along the axis.

¹The difference between ΔS and dS . Consider the Taylor's series $\Delta S = \frac{dS}{dx}\Delta x + \frac{1}{2}\frac{d^2S}{dx^2}\Delta x^2 + \frac{1}{6}\frac{d^3S}{dx^3}\Delta x^3 + \dots \cong dS + \frac{1}{2}\frac{d^2S}{dx^2}\Delta x^2$. Thus dS is the first term only of the Taylor's series, and dS would equal zero at the top of the bowl in Fig. 2.2(c), but $\Delta S = \frac{1}{2}\frac{d^2S}{dx^2}\Delta x^2$ would not be zero because the second derivative $\frac{d^2S}{dx^2}$ is not zero.

**FIGURE 2.2**

The four types of equilibrium for a mechanical system.

3. Unstable equilibrium: marble sitting on top of an upturned bowl (depicted in Fig. 2.2(c)): $\Delta E)_S < 0$ and $\Delta S)_E > 0$; any movement causes the marble to move farther from its 'equilibrium' position.
4. Metastable equilibrium: marble in higher of two 'troughs' (depicted in Fig. 2.2(d)): Relatively small variations of position will take the marble over the local maxima, and then it will be in an unstable state.

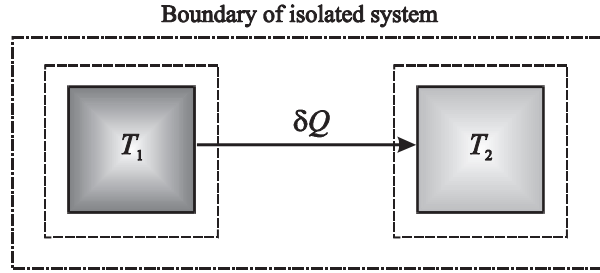
Hence the following statements can be derived for certain classes of problem (see Hatsopoulos and Keenan (1972)):

i. Stable equilibrium:	$dS)_E = 0$ and $\Delta S)_E < 0$
ii. Neutral equilibrium:	$dS)_E = 0$ and $\Delta S)_E = 0$
iii. Unstable equilibrium:	$dS)_E = 0$ and $\Delta S)_E > 0$

2.9.1 EQUILIBRIUM OF A THERMODYNAMIC SYSTEM

The type of equilibrium in a mechanical system can be judged by considering the variation in energy due to an infinitesimal disturbance. If the energy (potential energy) increases then the system will return to its previous state, if it decreases it will not return to that state. A similar method for examining the equilibrium of thermodynamic systems is required. This will be developed from the Second Law of Thermodynamics and the definition of entropy.

Consider a system comprising two identical blocks of metal at different temperatures (see Fig 2.3), but connected by a conducting medium. From experience the block at the higher temperature will

**FIGURE 2.3**

Heat transfer between two blocks.

transfer ‘heat’ to that at lower temperature. If the two blocks together constitute an isolated system the energy transfers will not affect the total energy in the system. If the high temperature block is at a temperature T_1 and the other at T_2 and if the quantity of energy transferred is δQ then the change in entropy of the high temperature block is

$$dS_1 = -\frac{\delta Q}{T_1} \quad (2.16)$$

and that of the lower temperature block is

$$dS_2 = +\frac{\delta Q}{T_2} \quad (2.17)$$

Both Eqns (2.16) and (2.17) contain the assumption that the heat transfers from block 1, and into block 2 are reversible. If the transfers were irreversible then Eqn (2.16) would become

$$dS_1 > -\frac{\delta Q}{T_1} \quad (2.16a)$$

and Eqn (2.17) would be

$$dS_2 > +\frac{\delta Q}{T_2} \quad (2.17a)$$

Since the system is isolated the energy transfer to the surroundings is zero, and hence the change of entropy of the surroundings is zero. Hence the change in entropy of the system is equal to the change in entropy of the universe and is, using Eqns (2.16) and (2.17)

$$dS = dS_1 + dS_2 = -\frac{\delta Q}{T_1} + \frac{\delta Q}{T_2} = \delta Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2.18)$$

Since $T_1 > T_2$, then the change of entropy of both the system and the universe is $dS = \frac{\delta Q}{T_2 T_1} (T_1 - T_2) > 0$.

The same solution, viz. $dS > 0$, is obtained from Eqns (2.16a) and (2.17a). The previous way of considering the equilibrium condition shows how systems will tend to go towards such a state. A slightly different approach, which is more analogous to the one used to investigate the equilibrium of

mechanical systems, is to consider the two blocks of metal to be in equilibrium and for heat transfer to occur spontaneously (and reversibly) between one and the other. Assume the temperature change in each block is δT , with one temperature increasing and the other decreasing, and the heat transfer is δQ . Then the change of entropy, dS , is given by

$$\begin{aligned} dS &= \frac{\delta Q}{T + \delta T} - \frac{\delta Q}{T - \delta T} = \frac{\delta Q}{(T + \delta T)(T - \delta T)} (T - \delta T - T - \delta T) \\ &= \frac{\delta Q}{T^2 - \delta T^2} (-2\delta T) \approx -2\delta Q \frac{\delta T}{T^2} \end{aligned} \quad (2.19)$$

This means that the entropy of the system would have decreased. Hence maximum entropy is obtained when the two blocks are in equilibrium and are at the same temperature. The general criterion of equilibrium according to Keenan (1963) is

For stability of any system it is necessary and sufficient that, in all possible variations of the state of the system which do not alter its energy, the variation of entropy shall be negative.

This can be stated mathematically as

$$\Delta S)_E < 0 \quad (2.20)$$

It can be seen that the statements of equilibrium based on energy and entropy, viz. $\Delta E)_S > 0$ and $\Delta S)_E < 0$, are equivalent by applying the following simple analysis. Consider the marble at the base of the bowl, as shown in Fig. 2.2(a): if it is lifted up the bowl its potential energy will be increased. When it is released it will oscillate in the base of the bowl until it comes to rest as a result of 'friction', and if that 'friction' is used solely to raise the temperature of the marble then its temperature will be higher after the process than at the beginning. A way to ensure the end conditions, i.e. the initial and final conditions, are identical would be to cool the marble by an amount equivalent to the increase in potential energy before releasing it. This cooling is equivalent to lowering the entropy of the marble by an amount ΔS , and since the cooling has been undertaken to bring the energy level back to the original value this proves that $\Delta E)_S > 0$ and $\Delta S)_E < 0$.

Equilibrium can be defined by the following statements:

- i. If the properties of an isolated system change spontaneously there is an increase in the entropy of the system.
- ii. When the entropy of an isolated system is at a maximum the system is in equilibrium.
- iii. If for all the possible variations in state of the isolated system there is a negative change in entropy then the system is in stable equilibrium.

These conditions may be written mathematically as

- i. $\Delta S)_E > 0$, spontaneous change (unstable equilibrium)
- ii. $\Delta S)_E = 0$, equilibrium (neutral equilibrium)
- iii. $\Delta S)_E < 0$, **criterion of stability** (stable equilibrium)

2.10 HELMHOLTZ ENERGY (HELMHOLTZ FUNCTION)

There are a number of ways of obtaining an expression for Helmholtz energy, but the one based on the Clausius derivation of entropy gives the most insight.

In the previous section the criteria for equilibrium were discussed and these were derived in terms of ΔS_E . The variation of entropy is not always easy to visualise, and it would be more useful if the criteria could be derived in a more tangible form related to other properties of the system under consideration. Consider the arrangements in Fig. 2.4(a) and (b). Figure 2.4(a) shows a system A, which is a general system of constant composition in which the work output, δW , can be either shaft or displacement work, or a combination of both. Figure 2.4(b) is a more specific example in which the work output is displacement work, $p dV$; the system in Fig. 2.4(b) is easier to understand.

In both arrangements, system A is a closed system (i.e. there are no mass transfers) which delivers an infinitesimal quantity of heat, δQ , in a reversible manner to the heat engine E_R . The heat engine then rejects a quantity of heat δQ_0 to a reservoir, e.g. the atmosphere, at temperature T_0 .

Let dE , dV and dS denote the changes in internal energy, volume and entropy of the system, which is of constant, invariant composition. For a specified change of state these quantities, which are changes in properties, would be independent of the process or work done. Applying the First Law of Thermodynamics (Eqn (1.7)) to system A gives

$$\delta W = -dE + \delta Q \quad (2.21)$$

If the heat engine (E_R) and system A are considered to constitute another system, system B. Then, applying the First Law of Thermodynamics to system B gives

$$\delta W_{\text{net}} = \delta W + \delta W_R = -dE + \delta Q_0 \quad (2.22)$$

where $\delta W + \delta W_R$ = net work done by the heat engine and system A. Since the heat engine is internally reversible, and the entropy flow on either side is equal, then

$$\frac{\delta Q_0}{T_0} = \frac{\delta Q}{T} \quad (2.23)$$

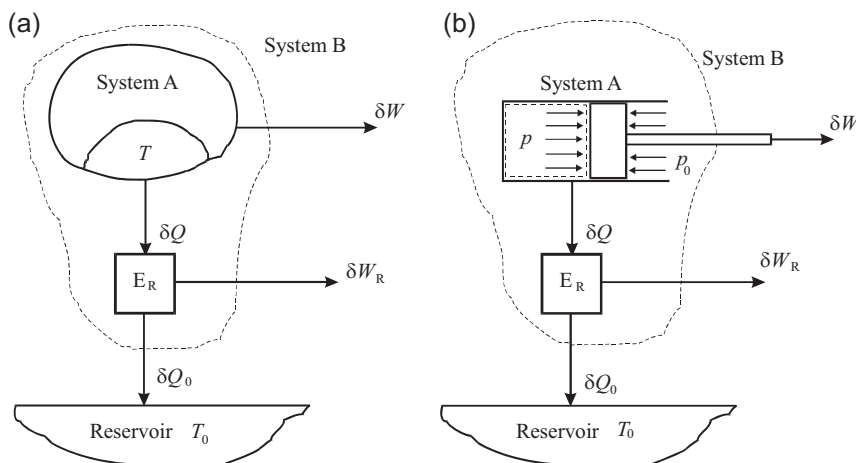


FIGURE 2.4

Maximum work achievable from a system.

and the change in entropy of system A during this process, because it is reversible, is $dS = \frac{\delta Q_R}{T}$.

$$\text{Hence } \delta W_{\text{net}} = -dE + T_0 dS = -d(E - T_0 S), \text{ because } T_0 \text{ is constant.} \quad (2.24)$$

The expression $E - T_0 S$ is called the *Helmholtz energy* or *Helmholtz function*. In the absence of motion and gravitational effects the energy, E , may be replaced by the intrinsic internal energy, U , giving

$$\delta W_{\text{net}} = -d(U - T_0 S) \quad (2.25)$$

The significance of δW_{net} will now be examined. The changes executed were considered to be reversible and δW_{net} was the net work obtained from system B (i.e. system A + heat engine E_R). **Thus δW_{net} must be the maximum quantity of work that can be obtained from the combined system.** The expression for δW_{net} is called the change in the Helmholtz energy, where the Helmholtz energy is defined as

$$F = U - TS \quad (2.26)$$

Helmholtz energy is a property which has the units of energy and indicates the maximum work that can be obtained from a system. It can be seen that this is less than the internal energy, U , and it will be shown that the product TS is a measure of the unavailable energy.

2.11 GIBBS ENERGY

In the previous section the maximum work that can be obtained from system B, comprising system A and heat engine E_R was derived. It was also stipulated that system A could change its volume by δV , and while it is doing this it must perform work on the atmosphere equivalent to $p_0 \delta V$, where p_0 is the pressure of the atmosphere. This work detracts from the work previously calculated and gives the **maximum useful work**, δW_u as

$$\delta W_u = \delta W_{\text{net}} - p_0 dV \quad (2.27)$$

if the system is in pressure equilibrium with surroundings,

$$\delta W_u = -d(E - T_0 S) - p_0 dV = -d(E + p_0 V - T_0 S) \text{ because } p_0 \text{ is constant.}$$

Hence,

$$\delta W_u = -d(H - TS) \quad (2.28)$$

The quantity $H - TS$ is called the **Gibbs energy**, **Gibbs potential** or the **Gibbs function**, G .

Hence,

$$G = H - TS \quad (2.29)$$

Gibbs energy is a property which has the units of energy, and indicates the maximum useful work that can be obtained from a system. It can be seen that this is less than the enthalpy, H , and it will be shown that the product TS is a measure of the unavailable energy.

2.11.1 THE USE AND SIGNIFICANCE OF THE HELMHOLTZ AND GIBBS ENERGIES

It should be noted that the definitions of Helmholtz and Gibbs energies, Eqns (2.26) and (2.29), have been obtained for systems of invariant composition. The more general form of these basic thermodynamic relationships, in differential form, is

$$\begin{aligned}dU &= TdS - pdV + \sum \mu_i dn_i \\dH &= TdS + Vdp + \sum \mu_i dn_i \\dF &= -SdT - pdV + \sum \mu_i dn_i \\dG &= -SdT + Vdp + \sum \mu_i dn_i\end{aligned}\tag{2.30}$$

The additional term, $\sum \mu_i dn_i$, is the product of the chemical potential of component, i , and the change of the amount of substance (measured in moles) of component i . (The chemical potential of a substance has the same numerical value as the specific Gibbs energy of the substance, and is introduced in Section 12.2 when dissociation is discussed. It is used extensively in the later chapters where it can be seen to be the driving force of chemical reactions). Obviously if the amount of substance of the constituents does not change then this term is zero. However, if there is a reaction between the components of a mixture then this term will be nonzero and must be taken into account.

2.11.2 HELMHOLTZ ENERGY

- i. The change in Helmholtz energy is the maximum work that can be obtained from a closed system undergoing a reversible process whilst remaining in temperature equilibrium with its surroundings.
- ii. A decrease in Helmholtz energy corresponds to an increase in entropy, hence the minimum value of the function signifies the equilibrium condition.
- iii. A decrease in entropy corresponds to an increase in F ; hence the criterion $dF)_T > 0$ is that for stability. This criterion corresponds to work being done on the system.
- iv. For a constant volume system in which $\delta W = 0$, $dF = 0$.
 - v. For reversible processes $F_1 = F_2$; for all other processes there is a decrease in Helmholtz energy.
- vi. The minimum value of Helmholtz energy corresponds to the equilibrium condition.

2.11.3 GIBBS ENERGY

- i. The change in Gibbs energy is the maximum useful work that can be obtained from a system undergoing a reversible process whilst remaining in pressure and temperature equilibrium with its surroundings;
- ii. The equilibrium condition for the constraints of constant pressure and temperature can be defined as
 - a. $dG)_{p,T} < 0$ spontaneous change
 - b. $dG)_{p,T} = 0$ equilibrium
 - c. $dG)_{p,T} > 0$ criterion of stability;
- iii. The minimum value of Gibbs energy corresponds to the equilibrium condition.

2.12 GIBBS ENERGY AND PHASES

An extremely important feature of Gibbs energy is that it defines the interaction of coexisting phases (see Atkins (1994)). Figure 2.5 is a typical p - v - T diagram for H_2O (water). All stable equilibrium states of H_2O are represented by points on the surface of the diagram: any points that are not on the surface would be in unstable or metastable equilibrium. If the p - v - T diagram is viewed from the right, normal to the p - v plane, the phase diagram for H_2O is seen: this is shown in Fig. 2.6. This diagram shows the phase boundary lines where the changes between the various phases take place, and it can be used to analyse what happens to water as it is cooled at constant pressure from superheated steam (at A) to ice (at E). Experience tells us that the steam will start to condense at B, on the saturated vapour line; it will remain as a liquid (water) as it passes through point C, with the temperature reducing, until it becomes a saturated liquid at point D. Further cooling at constant pressure will result in a reduction in temperature and solid H_2O (ice) will form.

An interesting question is how many properties are required to define the state of the system when a number of components, C , in a number of different phases, P , are present. This problem was solved by Gibbs, and his phase rule states that for a system at equilibrium the number of degrees of freedom, D , (equal to the number of independent intensive properties) is

$$D = C - P + 2 \quad (2.31)$$

Most mechanical engineering problems only deal with multiple phase mixtures of single components, e.g. H_2O . Hence, for the regions shown in Fig. 2.6, where there is a single component present

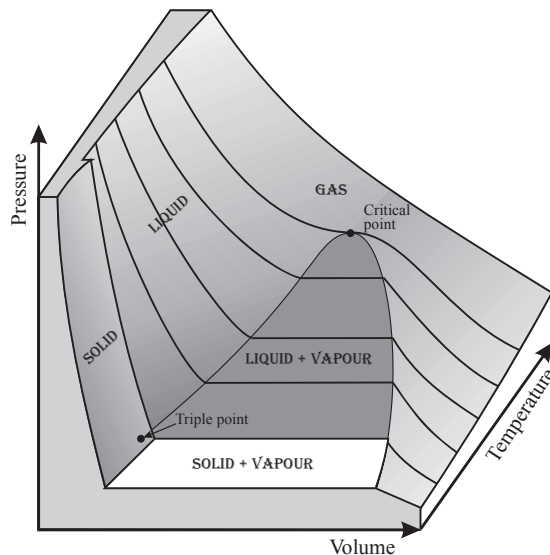
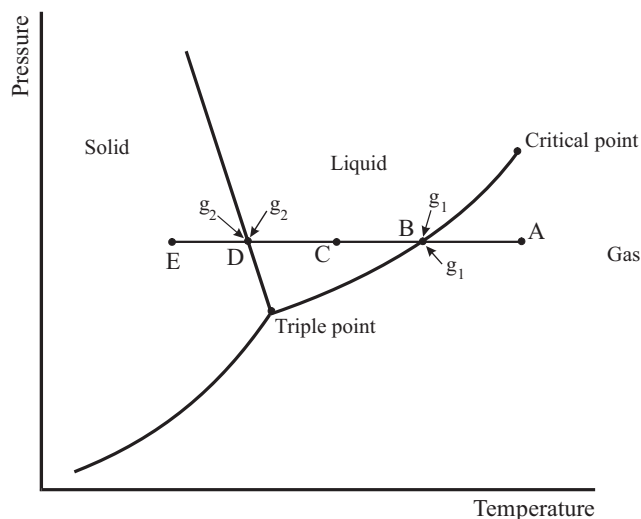


FIGURE 2.5

p - v - T surface for H_2O (a substance that expands on freezing).

**FIGURE 2.6**Phase diagram for H_2O .

(steam, water, ice) $P = 1$, and $C = 1$, Eqn (2.31) gives $D = 2$. This means that it is necessary to have two independent properties, e.g. p and T , to define the state of the substance.

If the substance is changing phase, i.e. from water to steam, on one of the boundary lines then $P = 2$, and $D = 1$: hence, the state of the substance can be defined by a single property during the phase change because p and T are not independent properties in this region. Another characteristic of phase change which comes from Gibbs energy (or, more correctly, chemical potential) is that the Gibbs energy of both phases is equal during the phase change process. This means that in Fig. 2.6, as shown at the phase boundaries, the specific Gibbs energy is equal for both phases.

2.13 EXAMPLES OF DIFFERENT FORMS OF EQUILIBRIUM MET IN THERMODYNAMICS

Stable equilibrium is the most frequently met state in thermodynamics, and most systems exist in this state.

Most of the theories of thermodynamics are based on stable equilibrium, which might be more correctly named 'thermostatics' (Tribus, 1961). The measurement of thermodynamic properties relies on the measuring device being in equilibrium with the system. For example, a thermometer must be in thermal equilibrium with a system if it is to measure its temperature, which explains why it is not possible to assess the temperature of something by touch because there is heat transfer either to or from the fingers – the body 'measures' the heat transfer rate. A system is in a stable state if it will permanently stay in this state without a tendency to change. Examples of this are a mixture of water and water vapour at constant pressure and temperature, the mixture of gases from an internal combustion engine when they exit the exhaust pipe; and many forms of crystalline structures in metals. Basically, stable equilibrium states are defined by state diagrams, e.g. the p - v - T diagram for water

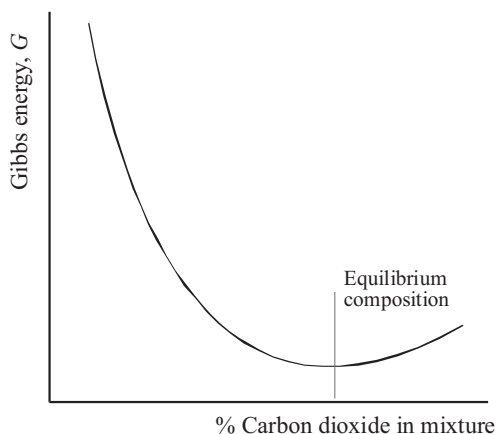
shown in Fig. 2.5. Equilibrium of mixtures of elements and compounds is defined by the state of maximum entropy or minimum Gibbs or Helmholtz energy; this is discussed in Chapter 12. The concepts of stable equilibrium can also be used to analyse the operation of fuel cells and these are considered in Chapter 21.

Another form of equilibrium met in thermodynamics is metastable equilibrium. This is where a system exists in a 'stable' state without any tendency to change until it is perturbed by an external influence through a finite perturbation. A good example of this is met in combustion in spark-ignition engines, where the reactants (air and fuel) are induced into the engine in a premixed form. They are ignited by a small spark and convert rapidly into products, releasing many thousands of times the energy of the spark used to initiate the combustion process. Another example of metastable equilibrium is encountered in the Wilson 'cloud chamber' used to show the tracks of α particles in atomic physics. The Wilson cloud chamber consists of supersaturated water vapour which has been cooled down below the dewpoint without condensation – it is in a metastable state. If an α particle is introduced into the chamber it provides sufficient perturbation to bring about condensation along its path. Other examples include explosive boiling which can occur if there are not sufficient nucleation sites to induce sufficient bubbles at boiling point to induce normal boiling, and some of the crystalline states encountered in metallic structures.

Unstable states cannot be sustained in thermodynamics because the molecular movement will tend to perturb the systems and cause them to move towards a stable state. Hence, unstable states are only transitory states met in systems which are moving towards equilibrium. The gases in a combustion chamber are often in unstable equilibrium because they cannot react quickly enough to maintain the equilibrium state, which is defined by minimum Gibbs or Helmholtz energy. The 'distance' of the unstable state from the state of stable equilibrium defines the rate at which the reaction occurs; this is referred to as rate kinetics, and will be discussed in Chapter 14. Another example of unstable 'equilibrium' occurs when a partition is removed between two gases which are initially separated. These gases then mix due to diffusion, and this mixing is driven by the difference in chemical potential between the gases; chemical potential is introduced in Chapter 12 and the process of mixing is discussed in Chapter 20. Some thermodynamic situations never achieve stable equilibrium, they exist in a steady state with energy passing between systems in stable equilibrium, and such a situation can be analysed using the techniques of irreversible thermodynamics developed in Chapter 20.

2.13.1 SIGNIFICANCE OF THE MINIMUM GIBBS ENERGY AT CONSTANT PRESSURE AND TEMPERATURE

It is difficult for many mechanical engineers to readily see the significance of Gibbs and Helmholtz energy. If systems are judged to undergo change while remaining in temperature and pressure equilibrium with their surroundings then most mechanical engineers would feel that no change could have taken place in the system. However, consideration of Eqn (2.30) shows that, if the system were a multicomponent mixture, it would be possible for changes in Gibbs (or Helmholtz) energies to take place if there were changes in composition. For example, an equilibrium mixture of carbon dioxide, carbon monoxide and oxygen could change its composition by the carbon dioxide breaking down into carbon monoxide and oxygen, in their stoichiometric proportions; this breakdown would change the composition of the mixture. If the process happened at constant temperature and pressure, in equilibrium with the surroundings, then an increase in the Gibbs energy, G , would have occurred; such a

**FIGURE 2.7**

Variation of Gibbs energy with chemical composition, for a system in temperature and pressure equilibrium with the environment.

process would be depicted by Fig. 2.7. This is directly analogous to the marble in the dish, which was discussed in Section 2.9.

The formation of equilibrium mixtures by dissociation is considered in much more depth in Chapter 12, where the combustion processes in engines are evaluated. Dissociation and equilibrium are the driving forces in the formation of pollution from all combustion processes.

2.14 CONCLUDING REMARKS

This chapter has revised the important features resulting from the Second Law of Thermodynamics, and introduced some new ideas relating to equilibrium. The concepts of the heat engine and Carnot cycle have been introduced, and these will be returned to in Chapters 3 and 6: they also introduced reversibility and the Carnot efficiency. A new property, entropy, has been developed and this will be used throughout this book to analyse a broad range of thermodynamic situations. Entropy is probably the most useful property in thermodynamics because it often enables complex problems to be analysed philosophically without resorting to complex numerical calculations.

Having developed these ideas it was possible to define thermodynamic equilibrium in terms of Helmholtz and Gibbs energies. These concepts will become essential when analysing the more complex problems developed in the later chapters. It was also shown that Gibbs energy can define equilibrium in multicomponent and multiphase mixtures, although we will limit ourselves to the latter in this book.

2.15 PROBLEMS

Problems P2.1–P2.5 are revision problems and are relatively easy. The remainder relate to equilibrium in the later part of the chapter.

P2.1 A mass of 10 kg of water at 0 °C is brought into contact with a large heat reservoir at 100 °C.

- a. When the water has reached 100 °C what has been
 - the change of entropy of the water;
 - the change of entropy of the reservoir;
 - the change of entropy of the universe?
- b. If the water had been heated from 0 to 100 °C by first bringing it into contact with a reservoir at 30 °C and then a reservoir of 100 °C, what would have been the change in the entropy of the universe?
- c. Explain how the water could have been heated to give no change in the entropy of the universe.

[13.11 kJ/K; −11.26 kJ/kg K; 1.85 kJ/kg K; 1.070 kJ/kg K; infinite number of reservoirs]

P2.2 A system contains a fluid at a temperature of 70 °C and 1 bar. It undergoes a reversible process during which the temperature of the system remains constant. Given that the heat transfer to the fluid during the process is 100 kJ, evaluate

- a. the increase in entropy.
- b. if the system has a mass of 2.31 kg. Evaluate the increase in specific entropy of the system.
- c. If a second fluid system, identical to the first one undergoes an irreversible isothermal process from the same initial state to the same final state as above; and the heat transfer to the fluid in this irreversible process is 180 kJ; evaluate the increase in entropy of the fluid.

[0.2915 kJ/K; 0.1262 kJ/kg K; 0.2915 kJ/kg K]

P2.3 Calculate the gain in entropy when 1 kg of water at 30 °C is converted into steam at 150 °C and then superheated to 300 °C, with the process taking place at constant pressure.

Take $c_p(\text{water}) = 4.2 \text{ kJ/kg K}$, $c_p(\text{steam}) = 2.1 \text{ kJ/kg K}$, $h_{fg} = 2600 - 1.5t$, where $t = \text{temperature in } ^\circ\text{C}$.

[7.6533 kJ/kgK]

P2.4 A mass of a liquid, m , at temperature, T_1 , is mixed with an equal mass of the same liquid at temperature, T_2 . The system is thermally insulated. Show that the change of entropy of the Universe is

$$2m c_p \ln \left(\frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}} \right)$$

and prove that this is necessarily positive.

[Hint: Do not specifically consider the mixing of the fluids.]

P2.5 A substance has the following physical properties at a certain pressure:

Saturation temperature, $t_s = 76 ^\circ\text{C}$; $h_{fg} = 61.1 \text{ kJ/kg}$

$c_{p(\text{liquid})} = 0.21 \text{ kJ/kg K}$; $c_{p(\text{vapour})} = 0.14 + 0.00036T \text{ kJ/kg K}$, where $T = \text{temperature in K}$

Determine the enthalpy and entropy of superheated vapour at 150 °C assuming these properties are zero for the fluid in liquid state at −40 °C.

[106.10 kJ/kg; 0.31348 kJ/kg K]

- P2.6** Determine the criteria for equilibrium for a thermally isolated system at (a) constant volume; (b) at constant pressure. Assume that the system is
- constant, and invariant, in composition;
 - variable in composition.
- P2.7** Determine the criteria for isothermal equilibrium of a system at (a) constant volume, and (b) constant pressure. Assume that the system is:
- constant, and invariant, in composition;
 - variable in composition.
- P2.8** A system at constant pressure consists of 10 kg of air at a temperature of 1000 K. This is connected to a large reservoir which is maintained at a temperature of 300 K by a reversible heat engine. Calculate the maximum amount of work which can be obtained from the system. Take the specific heat at constant pressure of air, c_p , as 0.98 kJ/kg K
[3320.3 kJ]
- P2.9** A thermally isolated system at constant pressure consists of 10 kg of air at a temperature of 1000 K and 10 kg of water at 300 K, connected together by a heat engine. What would be the equilibrium temperature of the system if
- the heat engine has a thermal efficiency of zero;
 - the heat engine is reversible?

[Hint: consider the definition of equilibrium defined by the entropy change of the system.]
Assume

$$\text{for water : } c_v = 4.2 \text{ kJ/kg K;}$$

$$\kappa = c_p/c_v = 1.0;$$

$$\text{for air : } c_v = 0.7 \text{ kJ/kg K;}$$

$$\kappa = c_p/c_v = 1.4.$$

[432.4 K; 376.7 K]

- P2.10** A thermally isolated system at constant pressure consists of 10 kg of air at a temperature of 1000 K and 10 kg of water at 300 K, connected together by a heat engine. What would be the equilibrium temperature of the system if the maximum thermal efficiency of the engine is only 50%?

Assume

$$\text{for water : } c_v = 4.2 \text{ kJ/kg K;}$$

$$\kappa = c_p/c_v = 1.0;$$

$$\text{for air : } c_v = 0.7 \text{ kJ/kg K;}$$

$$\kappa = c_p/c_v = 1.4.$$

[385.1 K]

- P2.11** Show that if a liquid is in equilibrium with its own vapour and an inert gas in a closed vessel, then

$$\frac{dp_v}{dp} = \frac{\rho_v}{\rho_l}$$

where p_v is the partial pressure of the vapour, p is the total pressure, ρ_v is the density of the vapour, ρ_l is the density of the liquid.

- P2.12** An incompressible liquid of specific volume v_l , is in equilibrium with its own vapour and an inert gas in a closed vessel. The vapour obeys the law

$$p(v - b) = \Re T$$

Show that

$$\ln\left(\frac{p_v}{p_0}\right) = \frac{1}{\Re T} \{ (p - p_0)v_l - (p_v - p_0)b \}$$

where p_0 is the vapour pressure when no inert gas is present, and p is the total pressure.

- P2.13 a.** Describe the meaning of the term thermodynamic equilibrium. Explain how entropy can be used as a measure of equilibrium and also how other properties can be developed which can be used to assess the equilibrium of a system.

If two phases of a component coexist in equilibrium (e.g. liquid and vapour phase H_2O) show that

$$T \frac{dp}{dT} = \frac{l}{v_{fg}}$$

where

T = temperature,

p = pressure,

l = latent heat

and v_{fg} = difference between liquid and vapour phases

Show the significance of this on a phase diagram.

- b.** The melting point of tin at a pressure of 1 bar is 505 K, but increases to 508.4 K at 1000 bar. Evaluate
- the change of density between these pressures and
 - the change in entropy during melting.

The latent heat of fusion of tin is 58.6 kJ/kg.

[254,100 kg/m³; 0.1157 kJ/kg K]

- P2.14** Show that when different phases are in equilibrium the specific Gibbs energy of each phase is equal.

Using the following data, show the pressure at which graphite and diamond are in equilibrium at a temperature of 25 °C. The data for these two phases of carbon at 25 °C and 1 bar are given in the following table:

	Graphite	Diamond
Specific Gibbs energy, g /(kJ/kg)	0	269
Specific volume, v /(m ³ /kg)	0.446×10^{-3}	0.285×10^{-3}
Isothermal compressibility, k /(bar ⁻¹)	2.96×10^{-6}	0.158×10^{-6}

It may be assumed that the variation of kv with pressure is negligible, and the lower value of the solution may be used.

[17,990 bar]

P2.15 Van der Waals equation for water is given by

$$p = \frac{0.004619T}{v - 0.0016891} - \frac{0.017034}{v^2}$$

where p = pressure (bar), v = specific volume (m³/kmol), T = temperature (K).

Draw a p - v diagram for the following isotherms: 250 °C, 270 °C, 300 °C, 330 °C, 374 °C, 390 °C.

Compare the computed specific volumes with Steam Table values and explain the differences in terms of the value of $p_c v_c / \Re T_c$.

ENGINE CYCLES AND THEIR EFFICIENCIES

The concept of internally reversible cycles was introduced in Section 2.7: these are sometimes known as *endoreversible cycles*. The advantage of considering endoreversible cycles is that the area of the cycle on a T – s diagram represents the work done by, or on, the fluid when it executes that cycle. If a cycle is *not endoreversible* then the area on the T – s diagram of the cycle is not equivalent to the work done. There are a number of important endoreversible cycles and these are introduced below.

3.1 HEAT ENGINES

3.1.1 CARNOT CYCLE

The Carnot cycle, as originally proposed, is both internally and externally reversible. It consists of two isentropic and two isothermal processes, as shown in Fig. 3.1, for a cycle based on a perfect gas.

Fig. 3.1(b) has been based on processes for a perfect gas. The reversible, adiabatic processes obey the law $pV^\kappa = c$, and the reversible, isothermal processes obey the law $pV = c$. It can be seen from

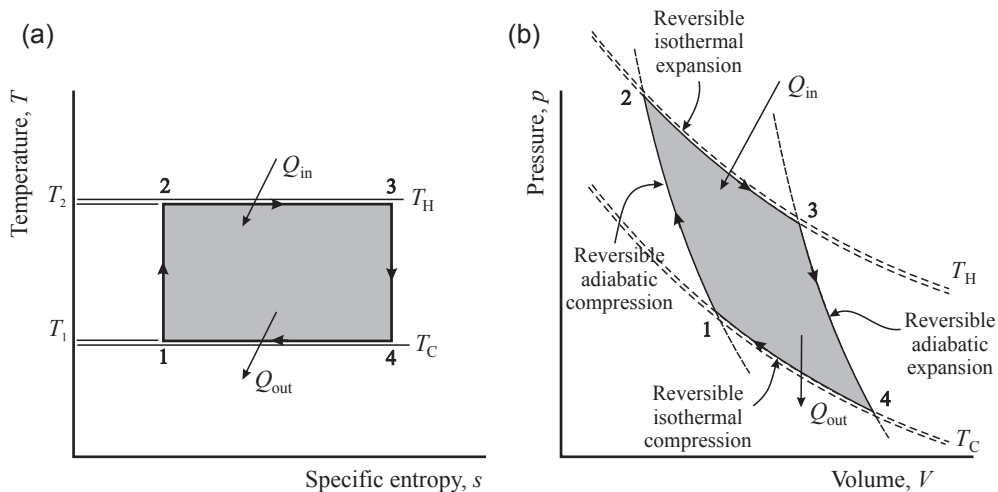


FIGURE 3.1

Carnot cycle based on a perfect gas as the working fluid. (a) Temperature–entropy (T – s) diagram; (b) pressure–volume (p – V) diagram.

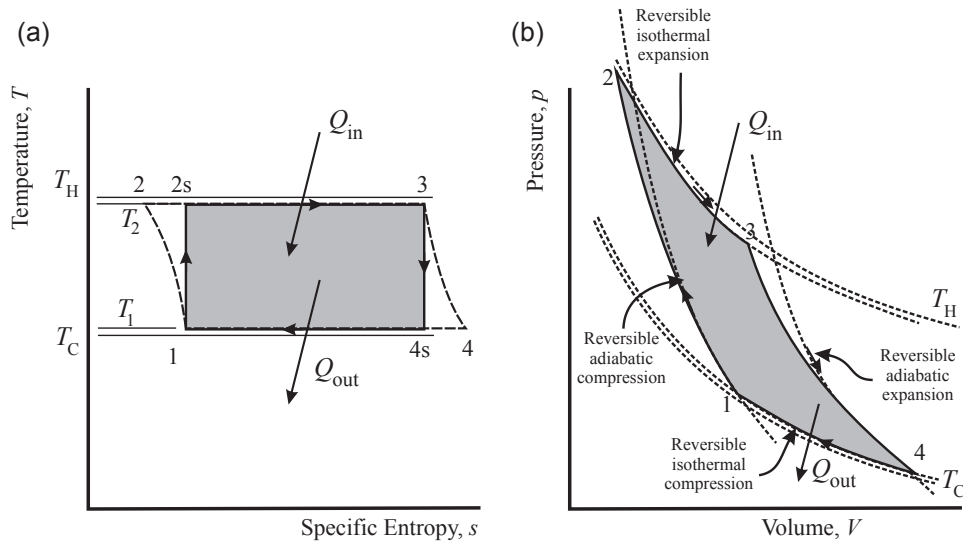


FIGURE 3.2

'Carnot cycle' depicting processes using a perfect gas working fluid with irreversibilities.

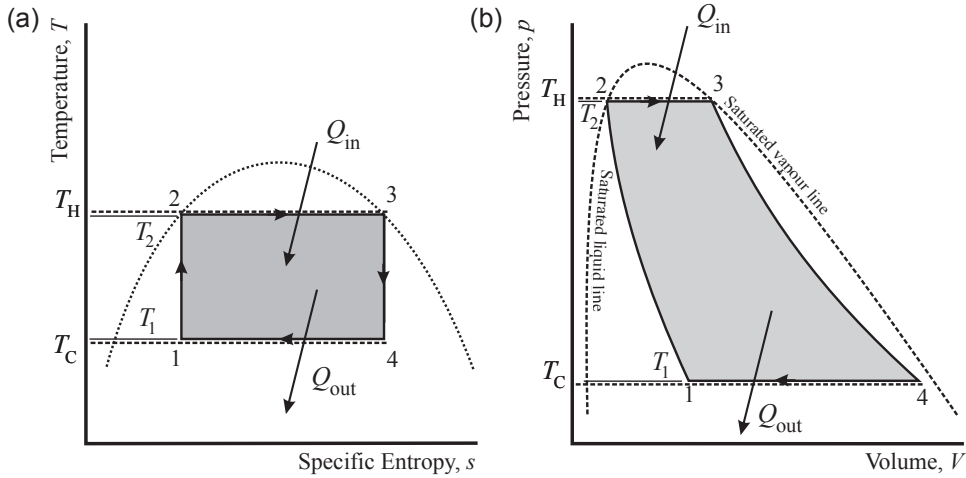
Fig. 3.1(b) that the p - V diagram for the cycle is very 'thin'. This means that if the processes are not reversible the effect on the area of the diagram, shown in Fig. 3.2, is dramatic. In Fig. 3.1(a), the temperatures of the hot and cold reservoirs are also shown: T_H is only infinitesimally higher than T_1 , while T_C is only infinitesimally lower than T_2 . This is necessary if the cycle is to be both *internally and externally reversible*. The consequence of this is that the heat transfer rates associated with the Carnot cycle are very low, and *the Carnot cycle produces no power!* The effects of external irreversibilities on engine efficiency are discussed in Chapter 6.

One difficulty with using a perfect gas as the working fluid is that it can only absorb heat by changing temperature. For this reason, many of the cycles used in engines, particularly heat engines, are based on a fluid that can change phase during the working cycle. The working fluid most commonly used in power generation is water that can receive heat during the isothermal heat addition process (2–3) by evaporation, and can reject it during the isothermal heat rejection (4–1) by condensation. The diagrams of these cycles are shown in Fig. 3.3.

It can be seen that the isothermal heating process now takes place between the saturated liquid and saturated vapour lines: in other words the liquid is evaporated at the high-pressure state. This is depicted in the p - V diagram shown in Fig. 3.3(b).

The fluid is then expanded from state 3, on the saturated vapour line, to state 4, which is in the two-phase liquid + vapour region. The heat rejection takes place between 4 and 1, and the fluid 'condenses' isothermally at constant pressure. The cycle is completed by a process from 1 to 2, when the fluid is compressed reversibly and adiabatically to the saturated liquid line.

The energy transfers during the cycle can be evaluated for both cases by consideration of the T - s diagram.

**FIGURE 3.3**

Carnot cycle for a working fluid which changes phase during the heat addition and rejection processes.

(a) T - s diagram for cycle; (b) p - V diagram for cycle.

$$\text{The heat addition is } Q_{23} = T_2(s_3 - s_2); \quad (3.1)$$

$$\text{the heat rejection is } Q_{41} = T_1(s_4 - s_1); \quad (3.2)$$

$$\text{and the work output is } W = Q_{23} + Q_{41} = (T_2 - T_1)(s_3 - s_2) \quad (3.3)$$

The thermal efficiency of the cycle is

$$\eta = \frac{W}{Q_{23}} = \frac{(T_2 - T_1)(s_3 - s_2)}{T_2(s_3 - s_2)} = \frac{T_2 - T_1}{T_2} = \frac{T_H - T_C}{T_H} \quad (3.4)$$

This is the same as the thermal efficiency of a reversible cycle derived from the definition of the absolute scale of temperature in Section 2.5, Eqn 2.3. These energy transfers can be illustrated on a T - s diagram, as shown on Fig. 3.4.

$$\text{Heat addition, } Q_{23} = \text{area } 6-2-3-5-6$$

$$\text{Heat rejection, } Q_{41} = \text{area } 6-1-4-5-6$$

$$\text{Work output, } W = \text{area } 1-2-3-4-1$$

The thermal efficiency of the reversible cycle based on a perfect gas can also be evaluated. It should be realised that the thermodynamic scale of temperature and 'absolute temperature' defined by the perfect gas law are the same by coincidence rather than definition. Considering the processes shown in Fig. 3.1(B), the work transfers are defined by the areas of the p - V diagram.

Work done

$$W_{12} = \frac{p_1 V_1 - p_2 V_2}{\kappa - 1}; \quad W_{23} = p_2 V_2 \ln \frac{V_3}{V_2}; \quad W_{34} = \frac{p_3 V_3 - p_4 V_4}{\kappa - 1}; \quad W_{41} = p_4 V_4 \ln \frac{V_1}{V_4};$$

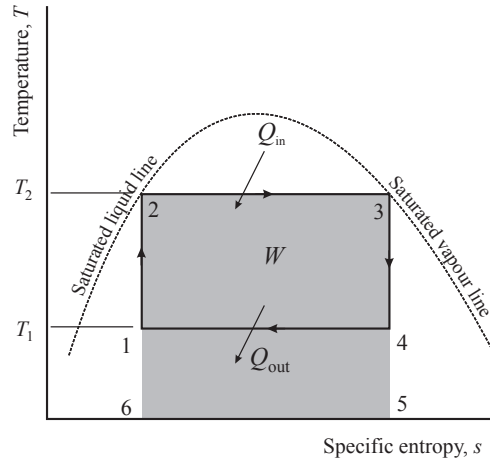


FIGURE 3.4

Energy transfer processes depicted on T - s diagram.

which gives the work from the cycle as

$$\oint_{\text{cycle}} W = W_{12} + W_{23} + W_{34} + W_{41}.$$

giving

$$\oint_{\text{cycle}} W = R \ln \frac{V_3}{V_2} (T_2 - T_1). \quad (3.5)$$

The energy addition to the cycle can be evaluated from process 2 to 3. Applying the First Law gives

$$\begin{aligned} \delta Q_{23} &= dU_{23} + \delta W_{23} = c_v(T_3 - T_2) + \delta W_{23} = \delta W_{23} \\ &= RT_2 \ln \frac{V_3}{V_2} \end{aligned} \quad (3.6)$$

$$\text{Hence, the thermal efficiency of the cycle is } \eta = \frac{\oint_{\text{cycle}} W}{Q_{23}} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2} = 1 - \frac{T_C}{T_H}. \quad (3.7)$$

This is the same as evaluated from the previous analysis, and given as [Eqn \(3.4\)](#), which is not surprising because *all reversible cycles operating between the same temperature limits have the same thermal efficiency*. Hence, the efficiency of a reversible cycle is independent of the working fluid.

It can be seen that there are a number of benefits in using a working fluid which can change phase, including

- constant pressure isothermal heat addition;
- a diagram that is less sensitive to inefficiencies than the perfect gas one;
- it is possible to replace the compression of a gaseous phase by the pumping of a liquid, in which case the compression work is significantly reduced.

The work output of a Carnot cycle is defined by the areas of either a p - V or a T - s diagram, and it can be seen that these are finite. However, while the Carnot cycle can produce a finite work output, *the power output is zero because the rate of heat transfer to the engine across an infinitesimal temperature difference is zero*, to achieve external reversibility. This means that the *Carnot efficiency defines the maximum efficiency of a heat engine between two temperature levels*. This is never achieved in practice because all engines are, at least, significantly irreversible in the external heat transfer processes: this is discussed in Chapter 6.

3.1.2 RANKINE CYCLE

It was shown above that the Carnot cycle for a fluid which changes phase during the working cycle requires an expansion device which operates with a fluid with a low quality (x) at the end of the expansion process. This creates problems in the design of the expansion device because of the amount of liquid in the working fluid. In the case of a steam turbine there can be very bad erosion of the low-pressure turbine blades due to water droplets in the steam, and this can reduce the reliability of the machine. Similarly, the compression depicted in Fig. 3.3 goes from a low-quality mixture of water and water vapour (at state 1) to saturated liquid water (at state 2). This requires careful control of state 1 to ensure that state 2 lies on the saturated liquid line, and also a compressor that can deal with a mixture that changes phase during the compression process.

The Rankine cycle attempts to solve these problems and is the basis of all steam turbine power plants, and a schematic diagram of a steam turbine power plant is shown in Fig. 3.5. It is an adaptation of the Carnot cycle to remove some of the latter's limitations. The basic Rankine cycle (see Fig. 3.6(a)) removes the problem of compressing a two-phase liquid from 1 to 2, because the fluid is condensed right up to the saturated liquid line (state 1). It is then compressed in the liquid phase from 1 to 2, where it is a compressed liquid. Heating, at constant pressure, commences at 2, and the fluid is raised in temperature from 2 to 3, with evaporation occurring from 3 to 4. At state 4, the liquid is fully

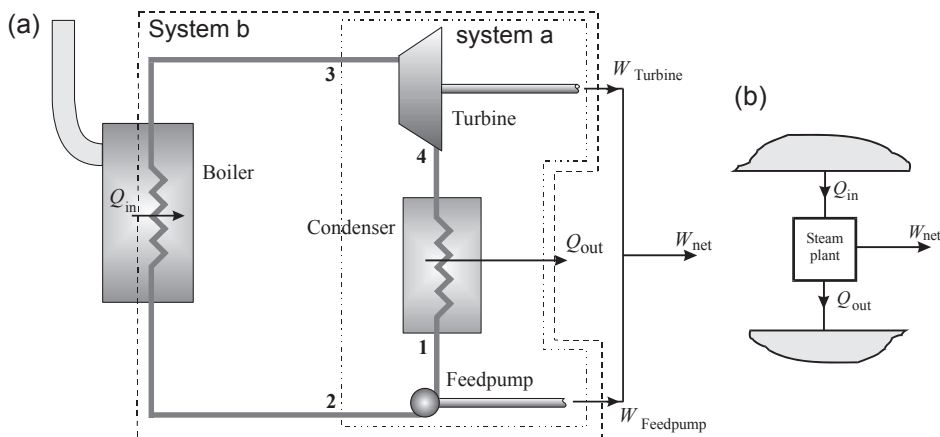


FIGURE 3.5

Steam turbine power plant (a) schematic diagram (b) heat engine equivalent.

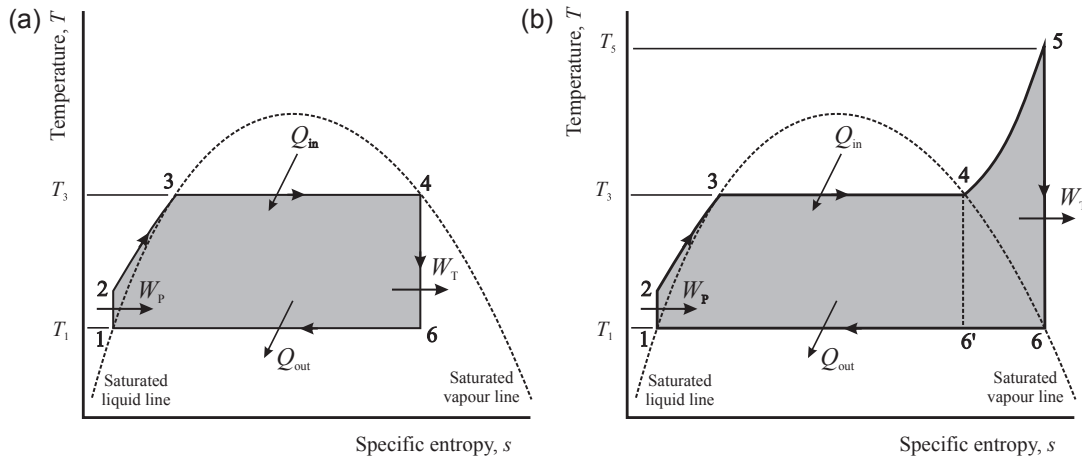


FIGURE 3.6

The Rankine cycle. (a) The basic Rankine cycle; (b) the Rankine cycle with superheat.

evaporated, and state 4 is on the saturated vapour line. The fluid is expanded from 4 to 6 in the turbine, when it experiences the same change of state as in the Carnot cycle, with wet fluid at 6. This situation can be improved by *superheating* the fluid from state 4 to state 5, as shown in Fig. 3.6(b). The effect of this is to raise the maximum temperature achieved by the fluid in executing the cycle, and the peak temperature is now T_5 rather than T_3 , as it was in the other cycles up till now.

The work output of an endoreversible Rankine cycle is defined by the area of the T - s diagram. This means that for the same pressures it is possible to increase the power output of the cycle by superheating, because the area of the diagram in Fig. 3.6(b) is greater than that in Fig. 3.6(a). Hence, superheating increases the work output, but what is the effect on the efficiency? First, it must be recognised that the energy input is greater in the superheat cycle than the standard one, and is defined by the enthalpy difference between 2 and 5, rather than 2 and 4. The real question is has the energy added between 4 and 5 in Fig. 3.6(b) been used more efficiently than that between 2 and 4. This can be answered by considering the superheat cycle to be made up of two cycles: 1-2-3-4-5-6-1 and 6'-4-5-6-6'. The first cycle here is the basic Rankine cycle while the second is a superheated cycle. Since the efficiency of a heat engine cycle is dependent on the *temperature at which energy is received*, the efficiency of cycle 6'-4-5-6-6' is greater than that of cycle 1-2-3-4-5-6-1, and hence, the efficiency of the superheated cycle is greater than that of the basic one.

3.1.3 COMPARISON OF EFFICIENCIES OF CARNOT AND RANKINE CYCLES

It is possible to use a simple analysis to compare the efficiencies of Carnot and Rankine cycles operating between the same temperature limits. Two cycles are shown superimposed in Fig. 3.7(a) and (b) that show the basic and superheated cycles respectively.

The Carnot cycle operating between the same temperature limits produces more work than the Rankine cycle, but this does not guarantee that the efficiency is higher. The efficiency can be considered by examining the work output and the *heat rejected*. By definition, the efficiency of a heat

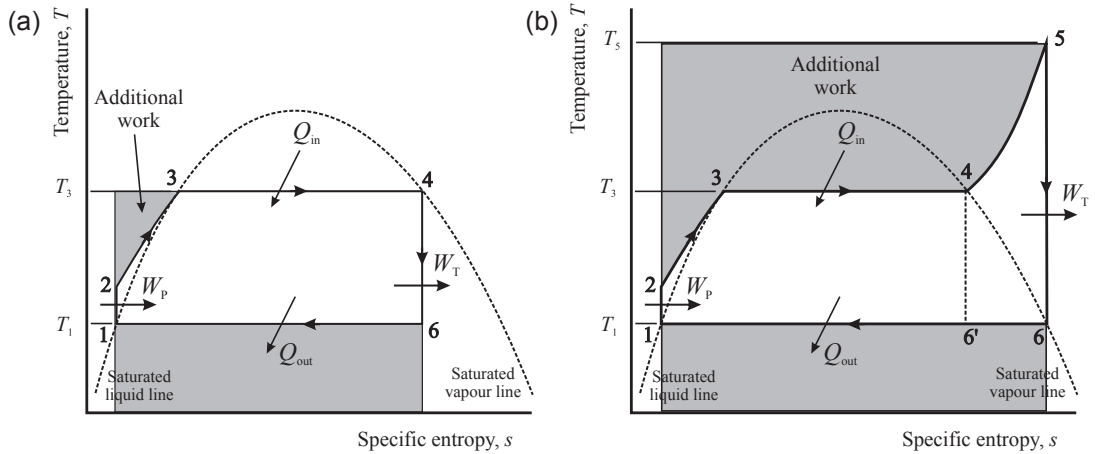


FIGURE 3.7

Comparison of Carnot and Rankine cycles. (a) Basic Rankine cycle; (b) Rankine cycle with superheat.

engine is $\eta = \frac{W}{Q_{in}} = \frac{W}{W + Q_{out}}$. In these cases, the values of Q_{out} for the Carnot and Rankine cycles are the same, and hence, the efficiency of the Carnot cycle must be greater than that of the Rankine cycle.

$$\eta_{Carnot} > \eta_{Rankine} \quad (3.8)$$

Another way of looking at this problem is to consider the mean temperature of energy addition.

3.1.4 MEAN TEMPERATURE OF ENERGY ADDITION AND REJECTION

It was shown in Fig. 3.7(a) and (b) that the Carnot cycle has a greater thermal efficiency than a Rankine cycle operating between the same temperature limits. This is because the heat addition for the Carnot cycle takes place at the maximum temperature of the cycle, and the heat rejection occurs at the minimum temperature. Hence, the Carnot cycle takes maximum advantage of the temperature difference. The Carnot cycle in Fig. 3.8(a) has been broken down into an infinite number of infinitesimal cycles and the efficiency of the cycle is given by

$$\eta = \frac{\sum_{cycles} W}{\sum_{cycles} Q}. \quad (3.9)$$

Since all the cycles are identical in this case, the efficiency of the whole cycle is equal to the individual efficiencies of the incremental cycles.

The situation changes with the superheated Rankine cycle in Fig. 3.8(b). Three incremental cycles have been depicted. Cycle *a* is in the region where the liquid water is being heated, and the efficiency is low because the peak temperature is low. The next cycle, *b*, is in the evaporation region, and the efficiency in this region will be the same as the Carnot cycle shown in Fig. 3.8(a). The final cycle, *c*, has been drawn in the superheat region, where the temperature is again rising. The efficiency of this cycle will be higher than during the evaporation region but lower than that of a Carnot cycle operating

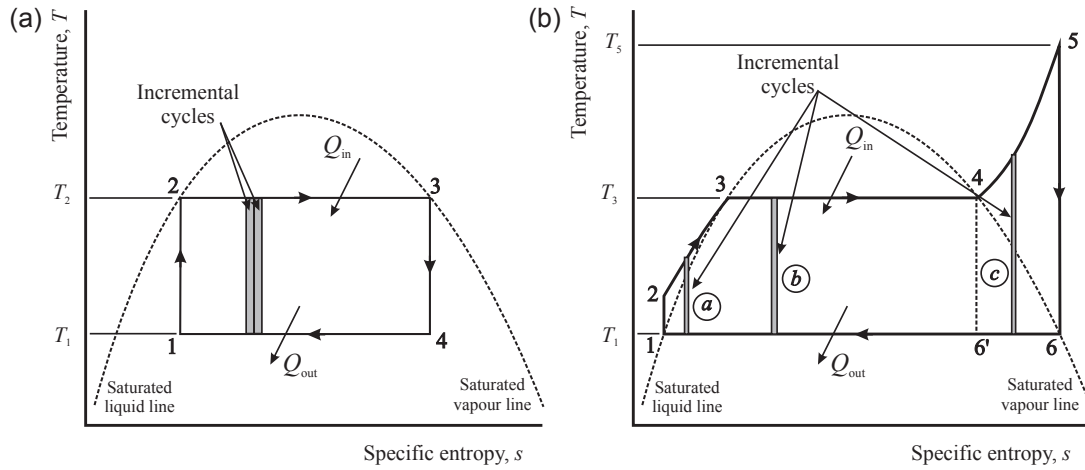


FIGURE 3.8

Cycles broken down to incremental Carnot cycles (a) basic Carnot cycle (b) reheated Rankine cycle.

between T_1 and T_5 . Hence, the efficiency of the Rankine cycle in Fig. 3.8(b) will be an ‘average’ of the incremental cycles which make up the whole Rankine cycle. Since the temperature of heat rejection in this diagram is the same for all incremental cycles then the efficiency is governed by the temperature of energy addition. The efficiency of each incremental cycle is equivalent to that of the equivalent Carnot cycle, and the work output of each cycle is

$$\delta W = \delta Q(1 - T_r/T_a), \quad (3.10)$$

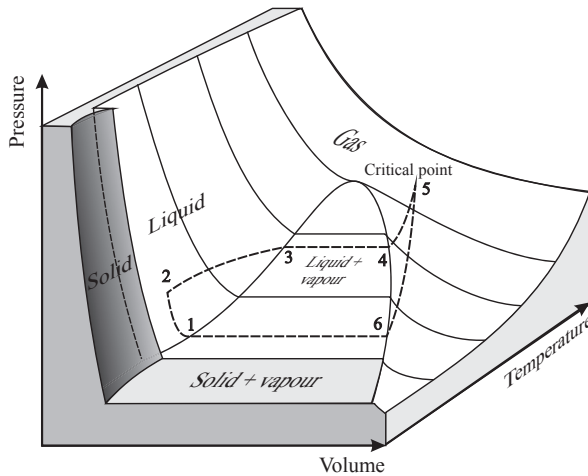
where

T_a = temperature of heat addition

T_r = temperature of heat rejection.

Now, the heat addition for each incremental cycle is $\delta Q = T\delta s$, and hence, the work done over the cycle is

$$\begin{aligned} W_{\text{cycle}} &= \oint_{\text{cycle}} \delta W = \oint_{\text{cycle}} T_a(1 - T_r/T_a)ds \\ &= \int_2^5 T_a ds - T_r(s_5 - s_2) \\ &= \left(\frac{\int_2^5 T_a ds}{(s_5 - s_2)} - T_r \right) (s_5 - s_2) \end{aligned} \quad (3.11)$$

**FIGURE 3.9**Rankine cycle shown on p - V - T surface.

This equation is equivalent to Eqn (3.3), but the value of the high temperature has been replaced by the term $\frac{\int_2^5 T_a ds}{(s_5 - s_2)}$, which is the mean temperature of heat addition.

Mean temperature of energy addition, or rejection; $\bar{T} = \frac{\int_1^2 T ds}{s_2 - s_1}$ (3.12)

Hence, any cycle can be made equivalent to a Carnot cycle, and the efficiency of that cycle is the same as that of a Carnot cycle with the same mean temperatures of heat addition and rejection. This shows that any cycle in which the temperature of heat addition and rejection are not constant cannot achieve the same efficiency as a Carnot cycle with the same temperature limits.

3.1.5 RANKINE CYCLE DEPICTED ON p - v - T SURFACE

The diagrams given above show the Rankine cycle on T - s diagrams. This is the normal manner in which the cycle is shown. It is also possible to draw the Rankine cycle on the p - v - T surface for water, as shown in Fig. 3.9.

3.2 AIR-STANDARD CYCLES

The Rankine cycle is based on a working fluid which changes phase during the cycle, and in which the regions of heat addition and rejection occur at constant temperature. However, the most readily available working fluid is air, which is a superheated gas at normal operating conditions. This results in a series of cycles in which the energy is received and rejected at variable temperature. These cycles can be used to examine the performance of internal combustion engines, e.g. petrol and diesel engines and gas turbines. It should be realised that internal combustion engines and gas turbines are *not* heat engines – because mass flows across the boundaries as air and fuel to enter the engines, and exhaust gases leave. More realistic cycles for these engines are considered in Chapters 16 and 17, respectively.

However, it is possible to define ‘engines’ which can be analysed by endoreversible cycles: these ‘engines’ replace the energy flows brought about by gas flows and combustion by heat transfer processes. Such cycles will be described below.

There are three air-standard cycles:

- constant volume ‘combustion’ (Otto),
- constant pressure ‘combustion’ (Diesel) and
- dual ‘combustion’ – this is a combination of constant volume and constant pressure combustion, and results in a slightly more realistic cycle.

These are the heat engine equivalent of the reciprocating engine and different from the actual engine cycle because:

- the cycle is a closed one with heat transfer;
- the working fluid does not change composition;
- the energy addition obeys closely defined rules, e.g. constant volume energy addition;
- the rates of heat release (energy addition) are unrealistic;
- indicated work outputs are evaluated.

The effect of two differences between ideal and real cycles will be examined in Chapter 16:

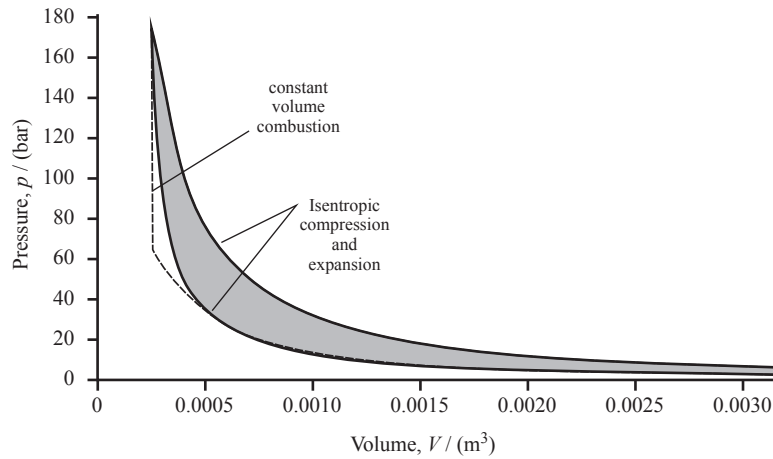
1. frictional losses and
2. the finite rate of heat release.

3.2.1 OTTO CYCLE

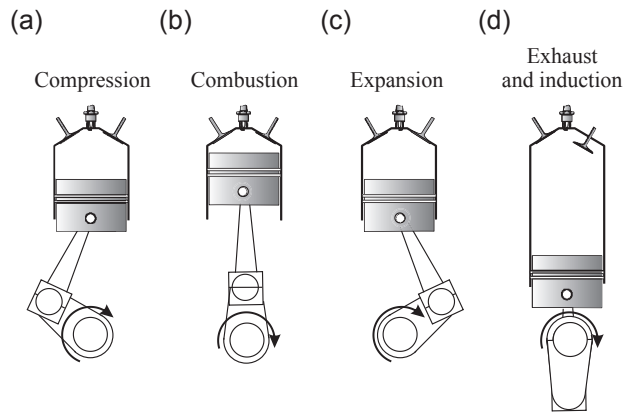
The Otto cycle is an air-standard cycle which approximates the processes in petrol or diesel engines. It is based on constant volume heat addition (combustion) and heat rejection processes, and isentropic compression and expansion. The diagram is shown in Fig. 3.10, where it is superimposed on an actual p – V diagram for a diesel engine.

The actual p – V diagram for an engine has rounded corners because of the processes of combustion take place at a finite rate. The Otto cycle has sharp corners because the ‘combustion’ is switched on and off instantaneously. It can be seen from Fig. 3.10 that the area of the Otto cycle is larger than that of the actual cycle, and this has to be taken into account when analysing engine cycles – the actual engine cycle will always produce less work output than the Otto cycle.

A typical engine ‘cycle’ is defined in Fig. 3.11. It consists of a compression stroke (Fig. 3.11(a)), followed by a period of combustion close to top dead centre (tdc) (Fig. 3.11(b)) and then by expansion (Fig. 3.11(c)). These two strokes form the power producing processes, but afterwards the products of combustion have to be replaced by fresh air. This is symbolised in Fig. 3.11(d), where the exhaust valve is open at the beginning of the exhaust stroke. In a four-stroke engine the piston executes two complete revolutions of the crankshaft, and uses two strokes while the gas is pushed out by the piston on the up stroke, and then the intake valve is opened to enable air to be induced. In a two-stroke engine the intake and exhaust strokes occur at the end and the beginning of the expansion and compression strokes, respectively. These processes are called the *gas exchange processes*, and are one of the main reasons why real engines are not heat engines. The other reason is the combustion process, when the air is used to burn the fuel. This process of combustion means that the fluid in the engine cannot undergo a cycle.

**FIGURE 3.10**

Otto cycle and engine cycle on p - V diagram.

**FIGURE 3.11**

Processes in a reciprocating engine (i.e. a diesel or petrol engine). (a) compression (b) combustion (c) expansion (d) exhaust and induction.

The Otto, Diesel and dual-combustion cycles are air-standard cycles that approximate the processes in a real engine. They can be achieved in the following way:

- The combustion process is replaced by a heat transfer process in which an amount of energy equivalent to the energy released by combustion is added to the air;
- The gas exchange process is replaced by a heat transfer process to a cold reservoir, so that the hot gases after expansion are returned to the state of the air after induction.

The resulting air-standard cycle is defined in [Fig. 3.12](#).

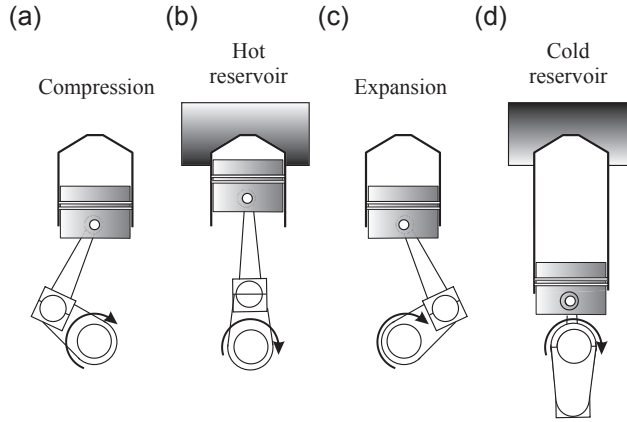


FIGURE 3.12

Method of achieving air-standard cycle for Otto cycle. (a) compression (b) heat addition (combustion) (c) expansion (d) heat extraction (gas exchange).

The basic Otto cycle is made up of four processes:

- Isentropic compression;
- Constant volume heat addition;
- Isentropic expansion and
- Constant volume heat rejection.

These can be depicted on T - s and p - V diagrams as shown in Fig. 3.13.

Since all the processes in Fig. 3.13 are reversible, the areas of the diagrams (a and b) are equal, and depict the work done in the cycle. The work done is

$$\begin{aligned} W &= \oint p dV = \int_1^2 p dV + \int_3^4 p dV \\ &= \frac{p_1 V_1 - p_2 V_2}{\kappa - 1} + \frac{p_3 V_3 - p_4 V_4}{\kappa - 1} = \frac{mR}{\kappa - 1} \{ (T_1 - T_2) + (T_3 - T_4) \} \end{aligned} \quad (3.13)$$

The energy added to the cycle is that added at constant volume between 2 and 3, and is given by

$$Q_{23} = mc_v (T_3 - T_2) = \frac{mR}{\kappa - 1} (T_3 - T_2) \quad (3.14)$$

Hence the thermal efficiency is

$$\begin{aligned} \eta_{\text{Otto}} &= \frac{\oint p dV}{Q_{23}} = \frac{(T_1 - T_2) + (T_3 - T_4)}{T_3 - T_2} = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} \\ &= 1 - \frac{\text{heat rejected}}{\text{heat added}}. \end{aligned} \quad (3.15)$$

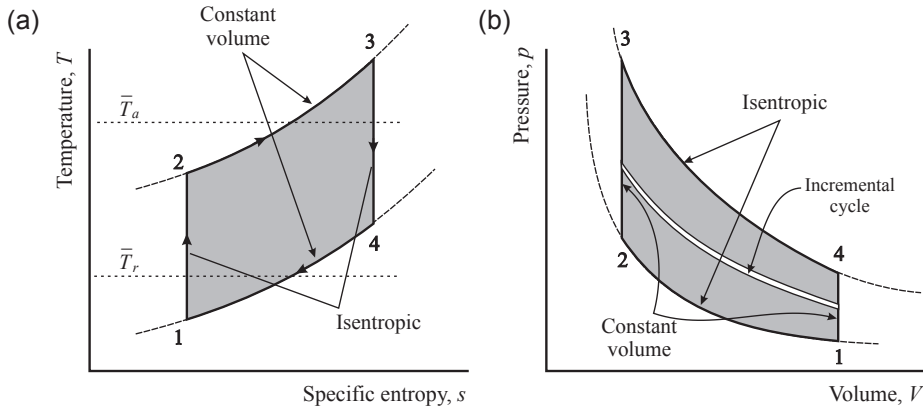


FIGURE 3.13

Otto cycle. (a) T - s diagram; (b) p - V diagram.

This equation can be rearranged into a more familiar one for the Otto cycle in the following way. First, it is necessary to define the compression ratio, r , which is based on the ratio of the volume at tdc to that at bottom dead centre (bdc), i.e. $r = V_2/V_1$. It is then possible to write the temperatures around the cycle in terms of T_1 and T_3 , and the compression ratio, r . This gives

$T_4 = \frac{T_3}{r^{(\kappa-1)}}$, and $T_2 = T_1 r^{(\kappa-1)}$, which may be substituted into Eqn (3.15) to give

$$\eta_{\text{Otto}} = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} = 1 - \frac{1}{r^{(\kappa-1)}} \quad (3.16)$$

$$\text{Now, the term } \frac{1}{r^{(\kappa-1)}} = \frac{T_1}{T_2} = \frac{T_4}{T_3}, \quad \text{and hence } \eta_{\text{Otto}} = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3}. \quad (3.17)$$

Thus, the efficiency of an Otto cycle is also related to a temperature ratio, but in this case it is the temperature ratio due to isentropic compression or expansion. Consideration of Fig. 3.13(b) shows that this is significantly less than the temperature ratio of the hot and cold reservoirs, and hence the efficiency of the Otto cycle is less than that of a Carnot cycle operating between the same two temperature limits which has an efficiency, $\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{T_1}{T_3}$. The reason for this is simply that the heat is added and rejected over varying temperatures, and it can be shown that *the efficiency of an engine operating on an Otto cycle is the same as a Carnot cycle operating between reservoirs at the mean temperatures of heat addition ($\bar{T}_a$) and rejection ($\bar{T}_r$)*. It is interesting to note that the efficiency of the Otto cycle approaches that of the Carnot cycle if $T_3 \cong T_2$; such a cycle produces no output because lines 1-2 and 3-4 in Fig. 3.13 become coincident.

3.2.2 DIESEL CYCLE

The Diesel cycle also applies to reciprocating engines, and is similar to the Otto cycle except that the heat is applied at *constant pressure* rather than constant volume. This removes the limitation of infinite

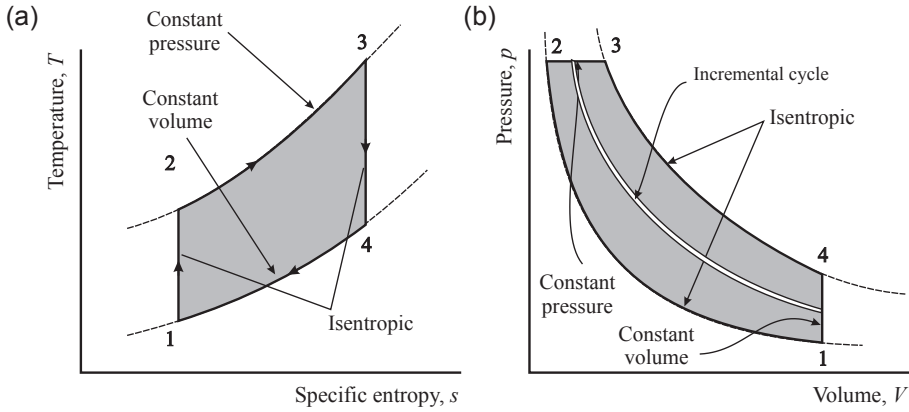


FIGURE 3.14

Diesel cycle. (a) T - s diagram; (b) p - V diagram.

rates of combustion implied by the Otto cycle, but still results in an unrealistic combustion pattern. The Diesel cycle is shown in Fig. 3.14.

The work done in a Diesel cycle is

$$\begin{aligned} W &= \oint p dV = \frac{p_1 V_1 - p_2 V_2}{\kappa - 1} + p_2 (V_3 - V_2) + \frac{p_3 V_3 - p_4 V_4}{\kappa - 1} \\ &= p_2 V_2 \left\{ (\beta - 1) + \frac{1}{\kappa - 1} \left[\frac{p_1 V_1}{p_2 V_2} - 1 + \frac{p_3 V_3}{p_2 V_2} - \frac{p_4 V_4}{p_2 V_2} \right] \right\} \\ &= \frac{mRT_2}{\kappa - 1} \left\{ \kappa(\beta - 1) - \frac{1}{r^{\kappa-1}} (\beta^\kappa - 1) \right\} \end{aligned} \quad (3.18)$$

where β defines the size of the constant pressure heat addition region, $\beta = V_3/V_2$. The effect of the constant pressure heat addition region is to reduce the *expansion ratio of the cycle*, $r_e = V_4/V_3 = r/\beta$. This has a large effect on the efficiency of the cycle.

The heat addition is

$$Q_{23} = mc_p(T_3 - T_2) = \frac{m\kappa R}{\kappa - 1}(T_3 - T_2) = \frac{m\kappa RT_2}{\kappa - 1}(\beta - 1). \quad (3.19)$$

The efficiency of the cycle is

$$\eta_{\text{diesel}} = \frac{\oint p dV}{Q_{23}} = \frac{\kappa(\beta - 1) - \frac{(\beta^\kappa - 1)}{r^{\kappa-1}}}{\kappa(\beta - 1)} = 1 - \frac{1}{r^{\kappa-1}} \cdot \frac{\beta^\kappa - 1}{\kappa(\beta - 1)} \quad (3.20)$$

This efficiency is less than that of the Otto cycle because the term $\frac{\beta^\kappa - 1}{\kappa(\beta - 1)} > 1$.

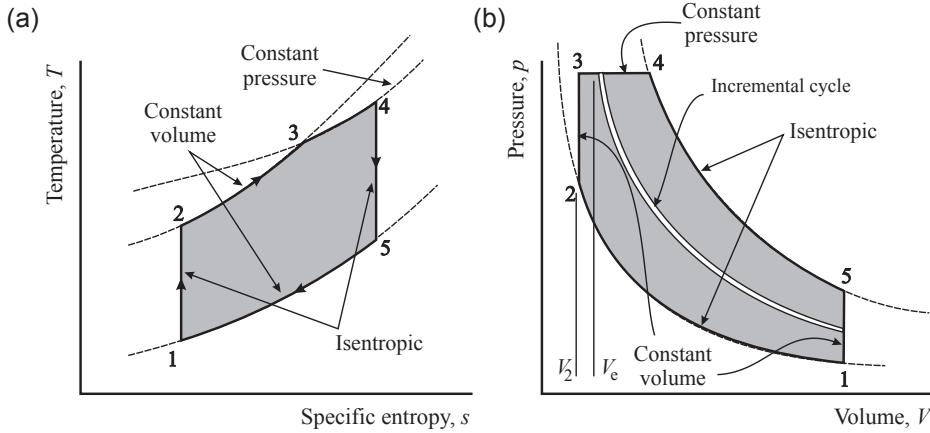


FIGURE 3.15

The dual-combustion cycle. (a) T - s diagram (b) p - V diagram.

3.2.3 DUAL-COMBUSTION CYCLE

The dual-combustion cycle is shown in Fig. 3.15. The cycle gets its name because a proportion of the ‘combustion’ (heat addition) takes place at constant volume, from 2 to 3, and then the remainder occurs at constant pressure, from 3 to 4. This cycle is the most representative of real engine cycles, in which the initial combustion takes place rapidly, and then slows down later in the process (although the dual-combustion cycle requires the heat release to increase as the volume increases). It can be shown (this is left to the reader) that the efficiency of a dual-combustion cycle is

$$\eta_{th} = 1 - \frac{1}{r^{(\kappa-1)}} \left[\frac{\alpha\beta^\kappa - 1}{(\alpha - 1) + \alpha\kappa(\beta - 1)} \right] \quad (3.21)$$

where $\alpha = p_3/p_2$, the pressure ratio caused by constant volume combustion.

3.2.4 THE MOST EFFICIENT INTERNAL COMBUSTION ENGINE CYCLE BASED ON VARIOUS CONSTRAINTS

Equations (3.16), (3.20) and (3.21) define the efficiency of air-standard cycles. These can be generalised as:

$$\eta_{th} = 1 - \frac{C}{r^{(\kappa-1)}} \quad (3.22)$$

where

$$C = 1 \quad \text{for Otto cycle} \quad (3.23)$$

$$C = \left[\frac{\alpha\beta^\kappa - 1}{(\alpha - 1) + \alpha\kappa(\beta - 1)} \right] > 1 \quad \text{for a dual combustion cycle;} \quad (3.24)$$

$$C = \left[\frac{\beta^\kappa - 1}{\kappa(\beta - 1)} \right] > 1, \quad \text{for a diesel (constant pressure) cycle.} \quad (3.25)$$

Hence, for a given *compression ratio* (r) the thermal efficiencies are related by

$$(\eta_{\text{th}})_{\text{Otto}} > (\eta_{\text{th}})_{\text{dual comb}} > (\eta_{\text{th}})_{\text{diesel}} \quad (3.26)$$

However, the situation changes if the maximum pressure is limited: in fact, *if all three cycles are compared for the same peak pressure and same work output, then*

$$(\eta_{\text{th}})_{\text{diesel}} > (\eta_{\text{th}})_{\text{dual comb}} > (\eta_{\text{th}})_{\text{Otto}} \quad (3.27)$$

Why is this the case? Considering first the cycles with the same compression ratio, then it is apparent that the *average* expansion ratio of each of the cycles is different. The average expansion ratio of the Otto cycle is equal to the compression ratio, r . In Fig. 3.15, V_e represents a typical cycle and the typical expansion ratio $r_e = V_1/V_e$ and, since $V_e > V_2$, then $r_e < r$. So if there is any constant pressure combustion then there must be a lower mean expansion ratio than in the case of the Otto cycle.

Figure 3.16 shows a comparison of two cycles (an Otto and a Diesel cycle). These have the same peak pressure and *the same work output*. It can be seen that the compression ratio of the diesel engine is higher than that of the Otto cycle engine: in fact, the expansion ratio of the Diesel cycle throughout the cycle is higher than the compression ratio of the Otto cycle. This means that the thermal efficiency of each element of the Diesel cycle is more efficient than the Otto cycle, and hence this Diesel cycle is more efficient than the Otto cycle. A similar argument applies for the dual-combustion cycle, which lies between the Diesel and Otto cycles.

These idealised cycles enable general concepts to be understood. They have enabled us to see why a Diesel engine cycle can be more efficient than an Otto one if the peak pressure is limited. They have shown that expansion ratio is a more relevant parameter than compression ratio when considering the efficiency of a cycle. However, they have not allowed us to see how the performance of real engines, with finite rates of combustion, varies when parameters are changed. These are considered in

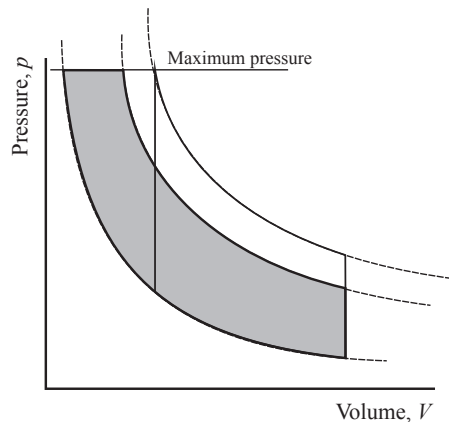


FIGURE 3.16

Comparison of Otto and Diesel cycles with the same maximum pressure and work outputs.

Chapter 16, by means of an engine simulation program. The results of the simulation are presented in a form that should be intelligible to the reader of this chapter, without having assimilated all necessary theory to understand the detailed workings of the program.

In the previous sections, engines have been compared based on their efficiencies. Another way of assessing the output of reciprocating engines is to compare them on the basis of mean effective pressure (mep). The indicated mean effective pressure of an engine ($\bar{p}_i$) is defined as the average (mean) pressure that would have to operate over the whole stroke ($V_S = V_1 - V_2$) to give the same work output as the actual cycle, i.e.

$$\bar{p}_i = \frac{\oint p dV}{V_S} \quad (3.28)$$

The concept of meps will be returned to in Chapter 16.

3.2.5 JOULE (OR BRAYTON) CYCLE

The Joule cycle is the air-standard cycle which describes the processes in the gas turbine. The Joule cycle has constant pressure combustion and constant pressure heat rejection. It is depicted in Fig. 3.17.

This cycle, which is examined in exactly the same manner as the Otto and Diesel cycles in Section 16.2, results in the following expression for efficiency Eqn (17.8).

$$\eta_{\text{Joule}} = 1 - \frac{1}{r_p^{\frac{\kappa-1}{\kappa}}}, \quad (3.29)$$

where $r_p = p_2/p_1$ the pressure ratio for the gas turbine.

The term $\frac{1}{r_p^{\frac{\kappa-1}{\kappa}}}$ is equivalent to the temperature ratio, $\frac{T_1}{T_2}$, and the significance of this is discussed below.

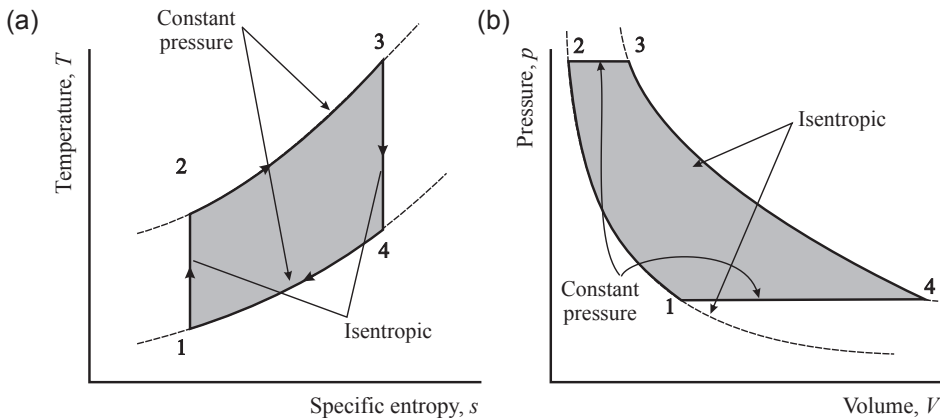


FIGURE 3.17

Joule (gas turbine) cycle. (a) T - s diagram; (b) p - V diagram.

3.3 GENERAL COMMENTS ON EFFICIENCIES

The efficiency of the Carnot cycle is directly related to the temperature ratio of the hot and cold reservoirs. Examination of the other efficiencies will show that they are also related to temperature ratios of the cycle. The efficiency of the Otto cycle is (Eqn (3.17))

$$\eta_{\text{Otto}} = 1 - \frac{1}{r^{(\kappa-1)}} = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3}.$$

The equation for the diesel engine is more complex and will not be considered here. However, the efficiency of the Joule cycle can also be related to the temperature ratio because $r_p^{\frac{\kappa-1}{\kappa}} = \frac{T_2}{T_1}$, and hence

$$\eta_{\text{Joule}} = 1 - \frac{1}{r_p^{\frac{\kappa-1}{\kappa}}} = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3}, \text{ in Fig. 3.17.}$$

Hence, all heat engines have efficiencies of the form

$$\eta_{\text{th}} = 1 - \frac{T_n}{T_m},$$

where T_n and T_m are particular temperatures relating to the individual cycle.

3.4 REVERSED HEAT ENGINES

Reversed heat engines were introduced in Section 2.7, and comprise refrigerators and heat pumps. The objectives of these devices are to transfer energy from a low temperature reservoir to a higher temperature one. In the case of the refrigerator, the aim is to cool the ice box and reject the energy extracted from it into ambient conditions at a higher temperature. The purpose of the heat pump is to warm a building by ‘pumping’ low-grade energy up to a higher temperature. Both of these devices work by using power input to drive the processes: it is not possible, by the Second Law, for energy to pass spontaneously from a low to a high-temperature reservoir. The cycles used to analyse reversed heat engines are similar to those introduced above for heat engines producing power – the processes are simply executed in reverse order.

3.4.1 REVERSED CARNOT CYCLE

If the Carnot cycle shown in Fig. 3.1 is operated in reverse, i.e. the arrows on the diagram are turned round, as in Fig. 3.18, then the directions of the work and heat transfer terms are also reversed. This means that net work is provided to the cycle during processes 1-2 and 3-4, and that energy (Q_{in}) is ‘pumped’ from the low-temperature reservoir (T_C), and energy (Q_{out}) is delivered to the high-temperature reservoir (T_H). Hence, the addition of work to the cycle is able to raise the ‘quality’ of the energy in the low-temperature reservoir.

3.4.2 ACTUAL REFRIGERATOR AND HEAT PUMP CYCLES

A device which would execute this cycle is shown schematically in Fig. 3.19(a): in this case, unlike that of the steam turbine, the pumping work is significantly larger than the work obtained from the

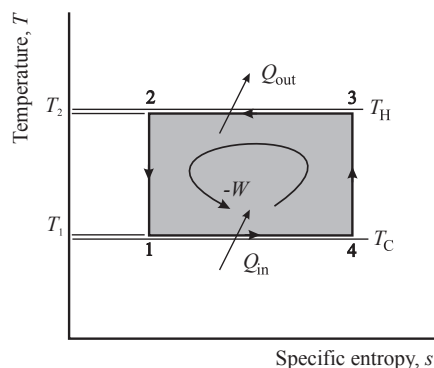


FIGURE 3.18

T - s diagram for reversed heat engine (refrigerator or heat pump) operating on reversed Carnot cycle.

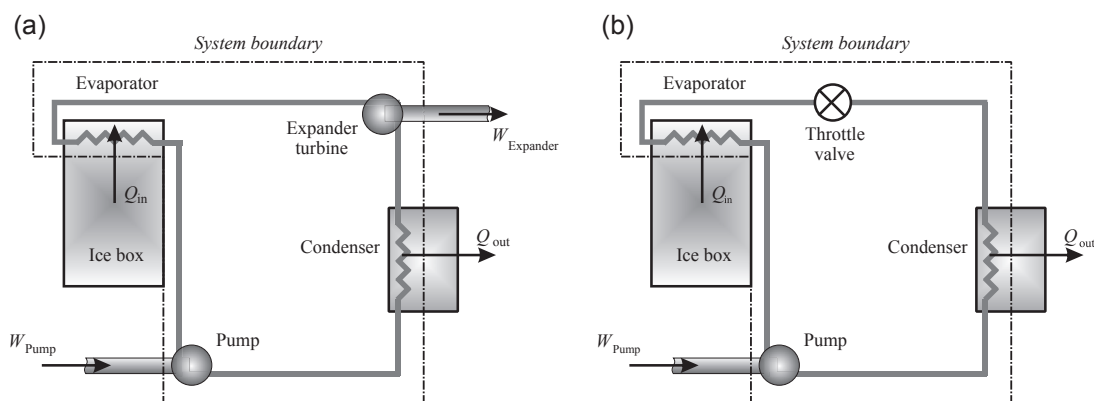


FIGURE 3.19

Schematic diagrams of refrigerator (or heat pump) (a) with expander turbine and (b) with throttle.

expander turbine. In most small, domestic, refrigeration plants, the expander turbine is replaced with a throttle, as shown in Fig. 3.19(b). This modifies the T - s diagram for the refrigerator to that given in Fig. 3.20(a). Many refrigeration plants operate with subcooling of the working fluid that further modifies the cycle to that in Fig. 3.20(b).

As described in Section 2.7.1, thermal efficiency is not the correct parameter to define the ‘efficiency’ of a reversed cycle, and the parameter used in this case is the *coefficient of performance*, which is defined as

$$\beta = \frac{Q_C}{W_{\text{net}}} = \frac{Q_C}{Q_H - Q_C}, \quad \text{for a refrigerator}$$

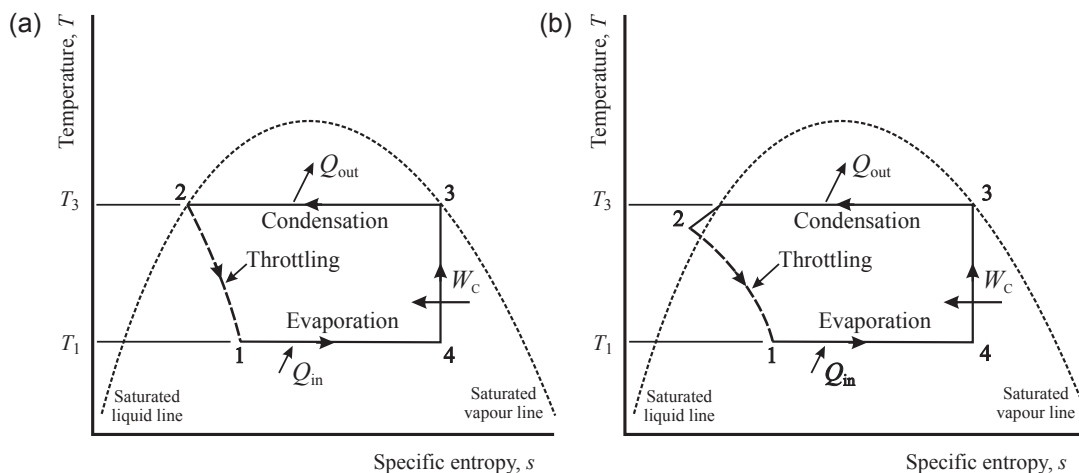


FIGURE 3.20

Irreversible refrigeration cycles (a) with simple throttle (see Fig. 3.19(b)) and (b) with throttle and subcooling.

$$\beta' = \frac{Q_H}{W_{\text{net}}} = \frac{Q_H}{Q_H - Q_C}, \quad \text{for heat pump.}$$

It was also shown in Section 2.7.1 that $\beta' = \beta + 1$. The coefficients of performance of all reversible heat engines operating between the same two temperature reservoirs will be equal, irrespective of the working fluid. This can be defined in terms of the reservoir temperatures *if the devices are internally and externally reversible*. Substituting for temperatures gives

$$\beta = \frac{T_C}{T_H - T_C}, \quad \text{and} \quad \beta' = \frac{T_H}{T_H - T_C}.$$

3.4.3 EXAMPLE

Calculate the coefficients of performance of the refrigerator and heat pump working with ammonia as the refrigerant. The evaporation takes place at a pressure of 0.7177 bar, after which the ammonia is compressed isentropically to the saturated vapour line at a pressure of 15.54 bar. After constant pressure condensation to a temperature of 28 °C, the fluid is expanded irreversibly through a throttle to the evaporator pressure.

Solution:

The T - s diagram for the cycle is shown in Figs. 3.20 and 3.21.

The values of properties at the salient points can be obtained from tables of properties.

Conditions at 4:

$$p_4 = p_1 = 0.7177 \text{ bar};$$

$$h_f = 0 \text{ kJ/kg}; \quad h_g = 1390 \text{ kJ/kg}; \quad h_{fg} = 1390 \text{ kJ/kg}.$$

$$s_f = 0 \text{ kJ/kgK}; \quad s_{fg} = 5.962 \text{ kJ/kgK}; \quad s_g = 5.962 \text{ kJ/kgK}.$$

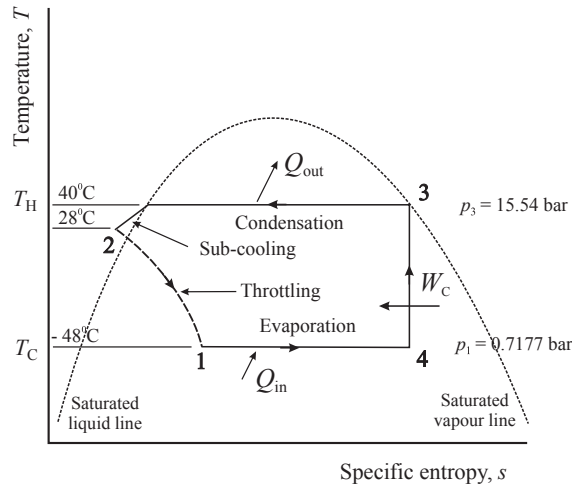


FIGURE 3.21

T-s diagram for reversed heat pump cycles.

The values of enthalpy and entropy on the saturated liquid line at 40 °C have been arbitrarily set at zero in the tables.

Conditions at 3:

$$p_3 = p_2 = 15.54 \text{ bar}$$

$$h_f = 371.9 \text{ kJ/kg}; \quad h_g = 1473.3 \text{ kJ/kg}.$$

$$s_f = 1.360 \text{ kJ/kgK}; \quad s_g = 4.877 \text{ kJ/kgK}.$$

Conditions at 2:

This is a subcooled state where the liquid is compressed, and it will be assumed that the enthalpy is equal to the enthalpy on the saturated liquid line at 28 °C. Hence

$$h_f = 313.4 \text{ kJ/kg}$$

Now, since the compression from 4 to 3 is isentropic $s_4 = s_3$. Hence,

$$s_3 = 4.877 = xs_g + (1 - x)s_f = 5.962x$$

$$\text{giving } x = 4.877/5.962 = 0.8180$$

and

$$h_4 = xh_g + (1 - x)h_f = 0.8180 \times 1390 = 1137 \text{ kJ/kg}$$

Work done in compressor

$$W_C = W_{43} = h_4 - h_3 = 1137 - 1473.3 = -336.3 \text{ kJ/kg}$$

Heat extracted from the evaporator (cold reservoir)

$$Q_C = Q_{41} = h_4 - h_1 = h_4 - h_2 = 1137 - 313.4 = 823.6 \text{ kJ/kg.}$$

Hence, *coefficient of performance of refrigerator*, $\beta = \frac{h_4 - h_1}{h_3 - h_4} = \frac{823.6}{336.3} = 2.449$.

Heat transferred from the condenser (hot reservoir)

$$Q_H = Q_{32} = h_2 - h_3 = 313.4 - 1473.3 = -1159.9 \text{ kJ/kg}$$

Hence, *coefficient of performance of heat pump*, $\beta' = \frac{h_2 - h_3}{h_4 - h_3} = \frac{1159.9}{336.3} = 3.449$.

Thus, both the coefficients of performance are greater than unity, and the coefficient of performance of the heat pump is one greater than that of the refrigerator – even though the devices are not reversible. If the devices had been reversible, i.e. had followed the reversed Carnot cycle, then the values would have been

$$\beta = \frac{T_C}{T_H - T_C} = \frac{T_1}{T_3 - T_1} = \frac{233}{313 - 233} = 2.913$$

$$\beta' = \frac{T_H}{T_H - T_C} = \frac{T_3}{T_3 - T_1} = \frac{313}{313 - 233} = 3.913$$

It can be seen that the reversible reversed heat engines, operating on the Carnot cycle, have higher coefficients of performance than those undergoing cycles with irreversibilities.

3.5 CONCLUDING REMARKS

This chapter has introduced a range of different cycles, from the fundamental Carnot cycle through more realistic cycles for simulating actual power plant. It is possible to evaluate the thermal efficiency of these cycles, and these efficiencies can be compared to that of the Carnot cycle. The Carnot cycle is shown to be the most efficient cycle operating between two temperature levels, simply because it is able to receive and reject energy at the upper and lower temperatures. None of the other cycles can achieve this, although the basic Rankine cycle can come close.

Air-standard cycles have been introduced, and cycles that can be used to analyse reciprocating engines, e.g. spark-ignition and diesel engines and gas turbines have been described. It has been explained that engines following these cycles are usually not heat engines because working fluid flows across their boundaries. It has also been demonstrated that they can never achieve the Carnot efficiency because the energy addition and rejection occurs at varying temperature, and the efficiency of the cycles is related to the *mean* temperatures of energy addition and rejection.

Finally, reversed heat engine cycles, i.e. refrigerators and heat pumps, have been introduced and their ‘efficiency’ has been defined as the coefficient of performance. Reciprocating engines and gas turbines will be discussed further in Chapters 16 and 17 respectively.

3.6 PROBLEMS

P3.1 A steam turbine operates on a Carnot cycle, with a maximum pressure of 20 bar and a condenser pressure of 0.5 bar. Calculate the salient points of the cycle, the energy addition and work output per unit mass, and hence the thermal efficiency of the cycle.

Compare this value to the Carnot efficiency based on the temperatures of energy addition and rejection.

[26.98%; 27.0%]

- P3.2** A steam power plant operating on a basic Rankine cycle has the following parameters: maximum (boiler) pressure 20 bar; minimum (condenser) pressure 0.5 bar. Calculate the thermal efficiency of the cycle, and compare it to that of a Carnot cycle operating between the same temperature limits (see P3.1). Calculate the specific power output and the back work ratio (defined as $\dot{w}_P/\dot{w}_T$) for the cycle in this question and that in P3.1. Comment on the results obtained.

(Assume the pump and turbine operate isentropically.)

[24.26%; 27.0%; 598.5 kW/(kg/s); 0.34%; 14.7%]

- P3.3** Recalculate P3.1 assuming that the pump efficiency, $\eta_P = 0.8$, and the turbine efficiency, $\eta_T = 0.9$. Comment on the effect on the thermal efficiency of the plant, and also the back work ratio.

[22.64%; 20.48%]

- P3.4** Recalculate P3.2 assuming that the pump efficiency $\eta_P = 0.8$, and the turbine efficiency $\eta_T = 0.9$. Comment on the effect on the thermal efficiency of the plant, and also the back work ratio.

[21.81%; 0.47%]

- P3.5** The engine designed by Lenoir was essentially an atmospheric engine based on the early steam engines. In this, a combustible mixture was contained in a cylinder: it was ignited and the pressure increased isochorically to the maximum level. After this the gas expanded isentropically through an expansion ratio, r_e , during which it produced work output. The air-standard cycle returned the gas to state 1 through an isochoric expansion to p_1 and an isobaric compression to V_1 .

Assume $p_1 = 1$ bar, $T_1 = 15^\circ\text{C}$, $p_2 = 10$ bar and the expansion ratio, $r_e = 5$. Calculate the specific work output and thermal efficiency of this cycle. How does this compare with the efficiency of an equivalent Carnot cycle?

[650.30 kJ/kg; 34.97%; 90.0%]

- P3.6** A Lenoir engine (described in P3.5) operates with inlet conditions of $p_1 = 1$ bar and $T_1 = 27^\circ\text{C}$. The energy added to the charge is 1000 kJ/kg, and the expansion ratio, r_e , is 3.0. Calculate the maximum pressure and temperature achieved in the cycle and its thermal efficiency.

[5.65 bar; 1422 °C; 26.00%]

- P3.7** A cycle is proposed as a development of the Lenoir cycle, in which the working fluid is expanded isentropically from its peak pressure down to a point where its temperature is equal to T_1 , the initial temperature. The gas is then compressed isothermally back to the initial pressure. Prove that the thermal efficiency of the cycle is given by

$$\eta_{\text{th}} = 1 - \frac{T_1}{T_2 - T_1} \ln \frac{T_2}{T_1}$$

where T_2 is the maximum temperature achieved in the cycle.

Calculate the thermal efficiency of the cycle if the initial pressure is 10 bar and the maximum pressure is 35 bar. Compare this to the Carnot efficiency achievable between the temperature limits and explain why this cycle would not be used in practice.

[49.9%; 71.4%]

- P3.8** Yet another cycle is proposed in which energy is added at constant volume until the fluid achieves state 2, the gas is then expanded to its initial pressure (state 3) before being compressed isobarically back to its initial conditions (state 1). Show that the thermal efficiency of this cycle is

$$\eta_{\text{th}} = 1 - \frac{\kappa(T_3 - T_1)}{(T_2 - T_1)}$$

If the initial conditions are 27 °C and 1.0 bar, and the energy added is 2000 kJ/kg, calculate the thermal efficiency of the cycle. What is the specific work output of the cycle?
[35.4%; 708 kJ/kg]

Examples P3.2 and P3.9–P3.13 follow the development of a basic Rankine cycle to demonstrate how the efficiency of such cycles can be improved.

- P3.9** The condenser pressure of the turbine in P3.2 is reduced to 0.15 bar. Calculate the same parameters for this cycle as in the previous example. Why have the parameters improved so much?
[28.97%; 32.65%; 744.8 kW/(kg/s)]
- P3.10** Both cycles in P3.2 and P3.9 resulted in extremely ‘wet’ steam (low quality) at the exit to the turbine. This would cause erosion of the blades, and should be avoided. One way of achieving this is to superheat the steam before it leaves the boiler: assuming that the temperature of the steam leaving the superheater is 400 °C, calculate the same parameters for this cycle using the basic data in P3.9. What is the quality of the steam leaving the turbine?
Also calculate the mean temperatures of energy addition and rejection, and show that a Carnot cycle with these temperatures would have the same efficiency as this Rankine cycle.
[31.02%; 51.40%; 937 kW/(kg/s); 0.878; 474 K; 326.9 K]
- P3.11** Problems P3.2, P3.9 and P3.10 have shown how the efficiency of a basic Rankine cycle can be improved, but even after superheating the steam leaving the turbine is still wet. This situation could be alleviated by using two turbine stages and reheating the steam between them. Calculate the basic parameters for the cycle if the steam is withdrawn from the HP turbine at 10 bar and reheated to 400 °C.
What are the specific power outputs of each turbine?
[32.14%; 51.40%; 1039 kW/(kg/s); 0.925; 845 kW; 196 kW]
- P3.12** Recalculate P3.11 with the pressure at which steam is reheated and reduced to 5 bar. What have been the benefits of using this lower pressure?
[32.36%; 51.40%; 1101 kW/(kg/s); 0.970; 745 kW; 358 kW]
- P3.13** Problem P3.12 seems to demonstrate that the efficiency of the reheated Rankine cycle gets better as the work distribution between the high pressure (HP) and low pressure (LP) turbines becomes more equal. Do some calculations to see if this proposition is true. At what reheat pressure are the turbine power outputs approximately equal, and what are the salient parameters of the cycle?
[1.5 bar; 32.69%; 51.40%; 1180 kW/(kg/s); 0.983; 590 kW; 592 kW]
- P3.14** What has the development of the basic Rankine cycle carried out in Problems P3.9–P3.14 shown you about the effect of the salient parameters on the efficiency of the cycle? Evaluate the mean temperature of energy addition and rejection for the cycles.

- P3.15** The previous examples, P3.9–P3.13, have all been based on a boiler pressure of 20 bar. What is the effect of raising the boiler pressure to (a) 40 bar and (b) 80 bar on the steam plant described in P3.10?
[(a) 34.16%; 1020 kW/(kg/s); (b) 37.0%; 1077 kW/(kg/s)]
- P3.16** Recalculate P3.15(a) with the condenser pressure lowered to 0.07 bar.
[36.41%; 1110 kW/(kg/s)]
- P3.17** Considering P3.15 and P3.16, which is the most effective method for increasing the thermal efficiency of the plant – raising the boiler pressure or decreasing the condenser pressure? Explain your answer.
- P3.18** An air-standard Otto cycle operates with a compression ratio, $r = 10:1$. If the initial conditions at bdc are 1 bar and 27 °C, and the energy addition is 2000 kJ/kg of air, calculate the salient points around the cycle and the thermal efficiency. Show that the efficiency calculated from the cycle calculation is equal to that from Eqn (3.16). Assume the compression and expansion are isentropic and $\kappa = 1.4$. How does this compare with the efficiency of a Carnot cycle between the two temperature limits?
[60.2%; 91.5%]
- P3.19** Recalculate P3.18 by assuming that the energy addition results from the combustion of fuel in the cylinder – this increases the mass of gas after ignition. The combustion occurs when an air-fuel mixture with a strength, ϵ , of 20:1 is burned at tdc: the calorific value (Q'_p) of the fuel is 40,000 kJ/kg. How does this compare with the efficiency of a Carnot cycle between the two temperature limits?
[61.0%; 91.2%]
- P3.20** An air-standard Diesel cycle operates with a compression ratio, $r = 10:1$. If the initial conditions at bdc are 1 bar and 27 °C, and the energy addition is 2000 kJ/kg of air, calculate the salient points around the cycle, and the thermal efficiency. Show that the efficiency calculated from the cycle calculation is equal to that from Eqn (3.20). Assume the compression and expansion are isentropic and $\kappa = 1.4$. How does this compare with the efficiency of a Carnot cycle between the two temperature limits, and what is the value of β ?
[45.02%; 89.07%; 3.6453]
- P3.21** The Otto cycle in P3.18 achieved a peak pressure of 118.1 bar, whilst the Diesel cycle in P3.20 only reached 25.12 bar. If the compression ratio of the Diesel cycle was increased to reach 118.1 bar at the end of compression, what would be the cycle efficiency? How does this fit in with the analysis in this chapter?
[67.57%]
- P3.22** The final air-standard cycle associated with reciprocating engines is the dual-combustion cycle. Assume the Otto cycle in P3.18 is modified so that half the energy is added at constant volume and the other half at constant pressure. What is the efficiency of this cycle based on the ratio of work output to energy addition? Evaluate α and β , defined in the text, and calculate the efficiency using Eqn (3.21)?
[58.49%; 2.850; 1.465]

There are more problems relating to reciprocating engines in Chapter 16, and gas turbines in Chapter 17.

AVAILABILITY AND EXERGY

Many of the analyses performed by engineers are based on the First Law of Thermodynamics, which is a law of energy conservation. Most mechanical engineers use the Second Law of Thermodynamics simply through its derived property – entropy (S). However, it is possible to introduce other ‘Second Law’ properties to define the maximum amounts of work achievable from certain systems. Previously, in Chapter 2, the properties Helmholtz energy (F) and Gibbs energy (G) were derived as means of assessing the equilibrium of various systems. This section considers how the maximum amount of work available from a system, when interacting with surroundings, can be estimated. This shows, as expected, that all the energy in a system cannot be converted to work: the Second Law stated that it is impossible to construct a heat engine that does not reject energy to the surroundings.

4.1 DISPLACEMENT WORK

The work done by a system can be considered to be made up of two parts: that done against a resisting force and that done against the environment. This can be seen in Fig. 4.1. The pressure inside the system, p , is resisted by a force, F , and the pressure of the environment. Hence, for System A, which is in equilibrium with the surroundings,

$$pA = F + p_0A \quad (4.1)$$

where A is the area of cross-section of the piston.

If the piston moves a distance, dx , then the work done by the various components shown in Fig. 4.1 is

$$pAdx = Fdx + p_0Adx \quad (4.2)$$

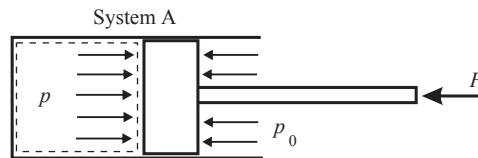


FIGURE 4.1

Forces acting on a piston.

where

$$pAdx = pdV = \delta W_{\text{sys}} = \text{work done by the fluid in the system},$$

$$Fdx = \delta W_{\text{use}} = \text{work done against the resisting force},$$

$$p_0Adx = p_0dV = \delta W_{\text{surr}} = \text{work done against the surroundings}.$$

Hence the work done by the system is not all converted into useful work, but some of it is used to do displacement work against the surroundings, i.e.

$$\delta W_{\text{sys}} = \delta W_{\text{use}} + \delta W_{\text{surr}} \quad (4.3)$$

which can be rearranged to give

$$\delta W_{\text{use}} = \delta W_{\text{sys}} - \delta W_{\text{surr}}. \quad (4.4)$$

4.2 AVAILABILITY

It was shown above that not all the displacement work done by a system is available to do useful work. This concept will now be generalised to consider all the possible work outputs from a system which is not in thermodynamic and mechanical equilibrium with its surroundings (i.e. not at the ambient or dead-state conditions).

Consider the system introduced earlier to define Helmholtz and Gibbs energy: this is basically the method which was used to prove the Clausius inequality.

Fig. 4.2(a) shows the general case where the work can be either displacement or shaft work, while Fig. 4.2(b) shows a specific case where the work output of System A is displacement work. It is easier

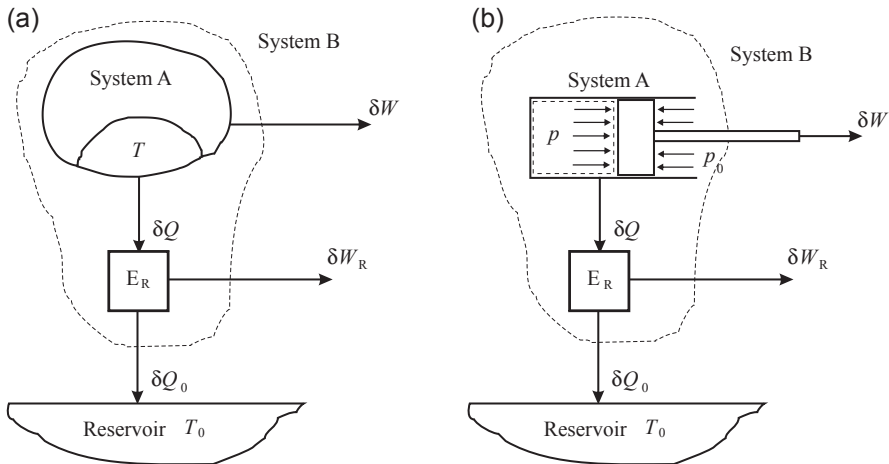


FIGURE 4.2

System transferring heat to a reservoir through a reversible heat engine.

to follow the derivation using the specific case, but a more general result is obtained from the arrangement shown in Fig. 4.2(a).

First consider that System A is a *constant volume system* which transfers heat with the surroundings via a small reversible heat engine. Applying the First Law to the System A

$$dU = \delta Q - \delta W = \delta Q - \delta W_s, \quad (4.5)$$

where δW_s indicates the shaft work done (e.g. System A could contain a turbine).

Let System B be System A plus the heat engine, E_R . Then applying the First Law to System B gives

$$dU = \Sigma(\delta Q - \delta W) = \delta Q_0 - (\delta W_s + \delta W_R) \quad (4.6)$$

As System A transfers energy with the surroundings, it undergoes a change of entropy defined by

$$dS = \frac{\delta Q}{T} = \frac{\delta Q_0}{T_0}, \quad (4.7)$$

because the heat engine transferring the heat to the surroundings is reversible and there is no change of entropy across it.

$$\text{Hence} \quad (\delta W_s + \delta W_R) = -(dU - T_0 dS) \quad (4.8)$$

As stated previously, $(\delta W_s + \delta W_R)$ is the maximum work that can be obtained from a *constant volume, closed system* when interacting with the surroundings. If the volume of the system was allowed to change, as would have to happen in the case depicted in Fig. 4.2(b), then the work done against the surroundings would be $p_0 dV$ where p_0 is the pressure of the surroundings. This work, done against the surroundings, reduces the maximum useful work from the system in which a change of volume takes place to $\delta W + \delta W_R - p_0 dV$, where δW is the sum of the shaft work and the displacement work.

Hence, the *maximum useful work* which can be achieved from a closed system is

$$\delta W + \delta W_R = -(dU + p_0 dV - T_0 dS) \quad (4.9)$$

This work is given the symbol, dA . Since the surroundings are at fixed pressure and temperature (i.e. p_0 and T_0 are constant) dA can be integrated to give

$$A = U + p_0 V - T_0 S \quad (4.10)$$

A is called the *non-flow availability function*. Although it is a combination of properties, A is not itself a property because it is defined in relation to the arbitrary datum values of p_0 and T_0 . Hence it is not possible to tabulate values of A without defining both these datum levels. The datum levels are what differentiate A from Gibbs energy, G . Hence the maximum useful work achievable from a system changing state from 1 to 2 is given by

$$W_{\max} = -\Delta A = -(A_2 - A_1) = A_1 - A_2 \quad (4.11)$$

The specific availability, a , i.e. the availability per unit mass is

$$a = u + p_0 v - T_0 s \quad (4.12a)$$

If the value of a were based on unit amount of substance (i.e. kmol) it would be referred to as the molar availability.

The change of specific (or molar) availability is

$$\begin{aligned}\Delta a &= a_2 - a_1 = (u_2 + p_0 v_2 - T_0 s_2) - (u_1 + p_0 v_1 - T_0 s_1) \\ &= (h_2 + v_2(p_0 - p_2)) - (h_1 + v_1(p_0 - p_1)) - T_0(s_2 - s_1)\end{aligned}\quad (4.12b)$$

4.3 EXAMPLES

Example 4.3.1: reversible work from a piston-cylinder arrangement (this example is based on Haywood (1980))

System A, in Figure 4.1, contains air at a pressure and temperature of 2 bar and 550 K respectively. The pressure is maintained by a force, F , acting on the piston. The system is taken from state 1 to state 2 by the reversible processes depicted in Fig. 4.3, and state 2 is equal to the dead-state conditions with a pressure, p_0 , and temperature, T_0 , of 1 bar and 300 K respectively. Evaluate the following work terms assuming that the air is a perfect gas and that $c_p = 1.005$ kJ/kg K and the ratio of specific heats, $\kappa = 1.4$.

- a. The air follows the process 1-a-2 in Fig. 4.3, and transfers heat reversibly with the environment during an isobaric process from 1-a. Calculate the following specific work outputs for processes 1-a and a-2.
 - (i) The work done by the system, δW_{sys} ;
 - (ii) The work done against the surroundings, δW_{surr} ;
 - (iii) The useful work done against the resisting force F , δW_{use} and
 - (iv) The work done by a reversible heat engine operating between the system and the surroundings, δW_{R} .

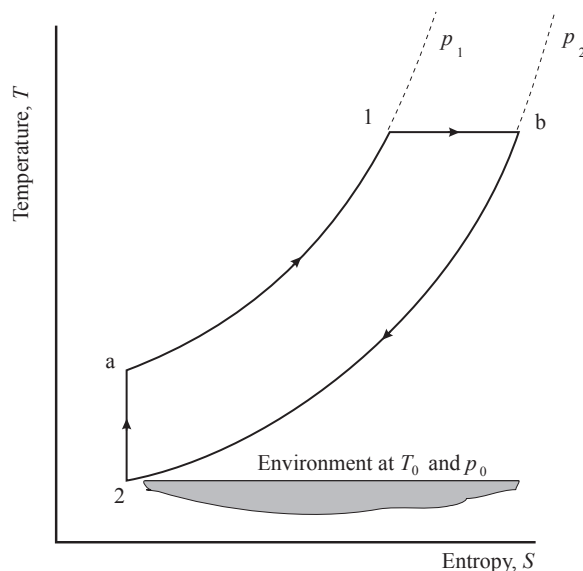


FIGURE 4.3

Processes undergone by system.

Then evaluate for the total process, 1-2, the following parameters.

- (v) The gross work done by the system, $\Sigma(\delta W_{\text{sys}} + \delta W_{\text{R}})$;
- (vi) The net useful work output against the environment, $\Sigma(\delta W_{\text{use}} + \delta W_{\text{R}})$;
- (vii) The total displacement work against the environment, $\Sigma(\delta W_{\text{surr}})$ and
- (viii) The work term $p_0(v_2 - v_1)$.

Solution:

It is necessary to evaluate the specific volume at the initial condition, state 1.

$$p_1 v_1 = RT_1, \text{ hence } v_1 = RT_1/p_1.$$

The gas constant, R , is given by $R = \frac{\kappa-1}{\kappa} c_p = \frac{0.4 \times 1.005}{1.4} = 0.287 \text{ kJ/kg K}$, and hence

$$v_1 = \frac{0.287 \times 10^3 \times 550}{2 \times 10^5} = 0.7896 \text{ m}^3/\text{kg}$$

The intermediate temperature, T_a , should now be evaluated. Since the process a-2 is isentropic then T_a must be isentropically related to the final temperature, T_2 . Hence

$$T_a = T_2 \left(\frac{p_a}{p_2} \right)^{(\kappa-1)/\kappa} = 300 \left(\frac{2}{1} \right)^{0.4/1.4} = 365.7 \text{ K}$$

Thus

$$v_a = \frac{p_1 T_a}{p_a T_1} v_1 = \frac{365.7}{550} v_1 = 0.6649 v_1$$

Consider process 1-a:

$$\begin{aligned} w_{\text{sys}}|_{1-a} &= \int_1^a p dv = p_a(v_a - v_1), \text{ for an isobaric process} \\ &= \frac{2 \times 10^5}{10^3} (0.6649 - 1.0) \times 0.7896 = -52.96 \text{ kJ} \\ w_{\text{surr}}|_{1-a} &= \int_1^a p_0 dv = \frac{1 \times 10^5}{10^3} (0.6649 - 1.0) \times 0.7896 \\ &= -26.46 \text{ kJ/kg} \end{aligned}$$

The useful work done by the system against the resisting force, F , is the difference between the two work terms given above, and is

$$w_{\text{use}}|_{1-a} = w_{\text{sys}}|_{1-a} - w_{\text{surr}}|_{1-a} = -26.46 \text{ kJ/kg}$$

The work terms derived above relate to the mechanical work that can be obtained from the system as it goes from state 1 to state a. However, in addition to this mechanical work the system could also do thermodynamic work by transferring energy to the surroundings through a reversible heat engine. This work can be evaluated in the following way. In going from state 1 to state a the system has had to transfer energy to the surroundings because the temperature of the fluid has decreased from 550 to 365.7 K. This heat transfer could have been simply to a reservoir at a temperature below T_a , in which case no useful work output would have been achieved. It could have also been to the environment

through a reversible heat engine, as shown in Fig. 4.2(b). In the latter case, useful work would have been obtained, and this would be equal to

$$\delta w_R = -\eta_R \delta Q,$$

where η_R is the thermal efficiency of a reversible heat engine operating between T and T_0 , and δQ is the heat transfer to the system,

$$= -\frac{T - T_0}{T} \delta Q.$$

Hence, the work output obtainable from this reversible heat engine as the system changes state from 1 to a is

$$\begin{aligned} w_R &= -\int_1^a \frac{T - T_0}{T} \delta Q = -\int_1^a \frac{T - T_0}{T} c_p dT \\ &= -c_p \left\{ (T_a - T_1) - T_0 \ln \frac{T_a}{T_1} \right\} \\ &= -1.005 \times \left\{ (365.7 - 550) - 300 \ln \frac{365.7}{550} \right\} = 62.18 \text{ kJ/kg} \end{aligned}$$

Now consider process a to 2.

First, evaluate the specific volume at 2, v_2 .

$$v_2 = \frac{p_1 T_2}{p_2 T_1} v_1 = \frac{2 \times 300}{1 \times 550} v_1 = 1.0909 v_1$$

The expansion from a to 2 is isentropic and hence obeys the law $p v^\kappa = \text{constant}$. Thus the system work is

$$\begin{aligned} w_{\text{sys}}|_{a-2} &= \frac{(1 \times 1.0909 - 2 \times 0.6649)}{1 - 1.4} \times \frac{0.7896 \times 10^5}{10^3} = 47.16 \text{ kJ/kg} \\ w_{\text{surr}}|_{a-2} &= \int_a^2 p_0 dv = \frac{1 \times 10^5}{10^3} (1.0909 - 0.6649) \times 0.7896 = 33.63 \text{ kJ/kg} \\ w_{\text{use}}|_{a-2} &= w_{\text{sys}}|_{a-2} - w_{\text{surr}}|_{a-2} = 13.52 \text{ kJ/kg} \end{aligned}$$

The energy available to drive a reversible heat engine is zero for this process because it is adiabatic; hence

$$w_R|_{a-2} = 0.$$

The work terms for the total process from 1 to 2 can be calculated by adding the terms for the two subprocesses. This enables the solutions to questions (v) to (viii) to be obtained.

The gross work done by the system is

$$w_{\text{gross}} = \sum (w_{\text{sys}} + w_R) = -52.96 + 47.16 + 62.18 + 0 = 56.38 \text{ kJ/kg}$$

The net useful work done by the system is

$$w_{u.net} = \sum (w_{use} + w_R) = -26.46 + 13.52 + 62.18 = 49.24 \text{ kJ/kg}$$

The total displacement work done against the surroundings is

$$w_{surr} = -26.46 + 33.63 = 7.17 \text{ kJ/kg}$$

The displacement work of the surroundings evaluated from

$$p_0(v_2 - v_1) = 1 \times 10^5 \times (1.0909 - 1) \times 0.7896/10^3 = 7.17 \text{ kJ/kg}$$

Example 4.3.2: change of availability in reversible piston-cylinder arrangement

Calculate the change of availability for the process described in example 4.3.1. Compare the value obtained with the work terms evaluated in example 4.3.1.

Solution:

The appropriate definition of availability for System A is the non-flow availability function, defined in Eqn (4.12a), and the maximum useful work is given by Eqns (4.11) and (4.12b). Hence, w_{use} is given by

$$\begin{aligned} w_{use} &= -\Delta a = -(a_2 - a_1) = a_1 - a_2 \\ &= u_1 - u_2 + p_0(v_1 - v_2) - T_0(s_1 - s_2) \end{aligned}$$

The change of entropy, $s_1 - s_2$ can be evaluated from

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p}$$

which for a perfect gas becomes

$$\begin{aligned} s_1 - s_2 &= c_p \ln \frac{T_1}{T_2} - R \ln \frac{p_1}{p_2} \\ &= 1.005 \times \ln \frac{550}{300} - 0.287 \times \ln \frac{2}{1} = 0.41024 \text{ kJ/kg K} \end{aligned}$$

Substituting gives

$$\begin{aligned} w_{use} &= c_v(T_1 - T_2) + p_0(v_1 - v_2) - T_0(s_1 - s_2) \\ &= (1.005 - 0.287)(550 - 300) + \frac{1 \times 10^5}{10^3} (1 - 1.0909) \times 0.7896 - 300 \times 0.41024 \\ &= 179.5 - 7.17 - 123.07 = 49.25 \text{ kJ/kg.} \end{aligned}$$

This answer is identical to the net useful work done by the system evaluated in part (vi) above; this is to be expected because the change of availability was described and defined as the maximum useful work that could be obtained from the system. Hence, the change of availability can be evaluated directly to give the maximum useful work output from a number of processes without having to evaluate the components of work output separately.

Example 4.3.3: availability of water vapour

Evaluate the specific availability of water vapour at 30 bar, 450 °C if the surroundings are at $p_0 = 1$ bar and $t_0 = 35$ °C. Evaluate the maximum useful work that can be obtained from this vapour if it is expanded to (i) 20 bar, 250 °C; (ii) the dead state.

Solution:

From Rogers and Mayhew tables (Rogers and Mayhew (1994)):

$$\text{at } p = 30 \text{ bar; } t = 450^\circ\text{C}$$

$$u = 3020 \text{ kJ/kg; } h = 3343 \text{ kJ/kg; } v = 0.1078 \text{ m}^3/\text{kg; } s = 7.082 \text{ kJ/kg K}$$

Hence the specific availability at these conditions is

$$\begin{aligned} a &= u + p_0 v - T_0 s \\ &= 3020 + 1 \times 10^5 \times 0.1078 / 10^3 - 308 \times 7.082 \\ &= 849.5 \text{ kJ/kg} \end{aligned}$$

- (i) Change of availability if expanded to 20 bar, 250 °C.

From Rogers and Mayhew tables:

$$\text{at } p = 20 \text{ bar; } t = 250^\circ\text{C}$$

$$u = 2681 \text{ kJ/kg; } h = 2904 \text{ kJ/kg; } v = 0.1115 \text{ m}^3/\text{kg; } s = 6.547 \text{ kJ/kg K}$$

The specific availability at these conditions is

$$\begin{aligned} a &= u + p_0 v - T_0 s \\ &= 2681 + 1 \times 10^5 \times 0.1115 / 10^3 - 308 \times 6.547 \\ &= 675.7 \text{ kJ/kg} \end{aligned}$$

Thus the maximum work that can be obtained by expanding the gas to these conditions is

$$w_{\max} = a_1 - a_2 = 849.5 - 675.7 = 173.8 \text{ kJ/kg}$$

This could also be evaluated using Eqn (4.12b), giving

$$\begin{aligned} w_{\max} &= -\Delta a = h_1 + v_1(p_0 - p_1) - (h_2 + v_2(p_0 - p_2)) - T_0(s_1 - s_2) \\ &= 3343 - 2904 + 0.1078 \times (1 - 30) \times 10^2 - 0.1115 \times (1 - 20) \\ &\quad \times 10^2 - 308 \times (7.082 - 6.547) \\ &= 439 - 312.6 + 211.9 - 164.78 = 173.5 \text{ kJ/kg} \end{aligned}$$

The values obtained by the different approaches are the same to the accuracy of the figures in the tables.

- (ii) Change of availability if expanded to datum level at $p_0 = 1 \text{ bar; } t_0 = 35^\circ\text{C}$.

$$u = 146.6 \text{ kJ/kg; } h = 146.6 \text{ kJ/kg; } v = 0.1006 \times 10^{-2} \text{ m}^3/\text{kg; } s = 0.5045 \text{ kJ/kg K.}$$

The specific availability at the dead state is

$$\begin{aligned} a &= u + p_0 v - T_0 s \\ &= 146.6 + 1 \times 10^5 \times 0.001006 / 10^3 - 308 \times 0.5045 \\ &= -8.7 \text{ kJ/kg} \end{aligned}$$

and the maximum work that can be obtained by expanding to the dead state is

$$w_{\max} = a_1 - a_2 = 849.5 - (-8.7) = 858.2 \text{ kJ/kg}$$

Again, this could have been evaluated using Eqn (4.12b) to give

$$\begin{aligned} w_{\max} &= -\Delta a = h_1 + v_1(p_0 - p_1) - (h_2 + v_2(p_0 - p_2)) - T_0(s_1 - s_2) \\ &= 3343 - 146.6 + 0.1078 \times (1 - 30) \times 10^2 - 0.001006 \times (1 - 1) \times 10^2 \\ &\quad - 308 \times (7.082 - 0.5045) \\ &= 3196.4 - 312.6 + 0 - 2025.9 = 857.9 \text{ kJ/kg} \end{aligned}$$

This shows that although the energy available in the system was 3020 kJ/kg (the internal energy) it is not possible to convert all this energy to work. It should be noted that this 'energy' is itself based on a datum of the triple point of water, but the dead state is above this value. However, even if the datum levels were reduced to the triple point the maximum useful work would still only be

$$w_{\max} = -\Delta a = (3343 - 0) + 0.1078 \times (0.00612 - 30) \times 10^2 - 273(7.082 - 0) = 1086.3 \text{ kJ/kg.}$$

It is also possible to evaluate the availability of a steady-flow system and this is defined in a similar manner to that used above, but in this case the reversible heat engine extracts energy from the flowing stream. If the kinetic and potential energies of the flowing stream are negligible compared to the thermal energy then the steady-flow availability is

$$a_f = h - T_0 s \quad (4.13a)$$

The change in steady flow availability is

$$\Delta a_f = a_{f2} - a_{f1} = h_2 - T_0 s_2 - (h_1 - T_0 s_1) \quad (4.13b)$$

Thus the maximum work which could be obtained from a steady-flow system is the change in flow availability, which for the previous example is

$$\begin{aligned} w_{\max} &= -\Delta a_f = -(a_{f2} - a_{f1}) = h_1 - T_0 s_1 - (h_2 - T_0 s_2) \\ &= (3343 - 146.6) - 308 \times (7.082 - 0.5045) \\ &= 1170.4 \text{ kJ/kg.} \end{aligned}$$

4.4 AVAILABLE AND NON-AVAILABLE ENERGY

If a certain portion of energy is available, then obviously another part is unavailable – the unavailable part is that which must be thrown away. Consider Fig. 4.4; this diagram indicates an internally reversible process from a to b. This can be considered to be made up of an infinite number of strips 1-m-n-4-1 where the temperature of energy transfer is essentially constant, i.e. $T_1 = T_4 = T$. The energy transfer obeys

$$\frac{\delta Q}{T} = \frac{\delta Q_0}{T_0}$$

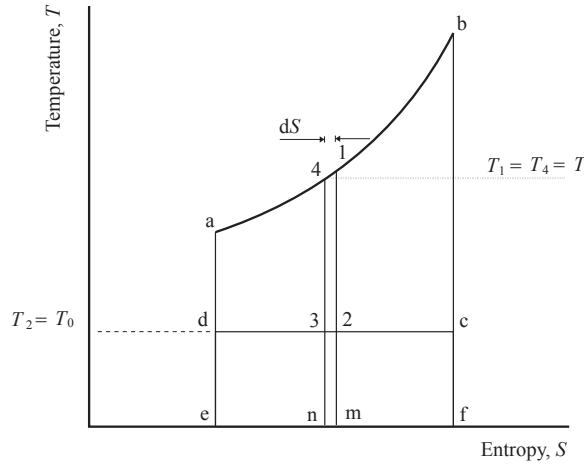


FIGURE 4.4

Available and unavailable energy shown on a T - s diagram.

where δQ = heat transferred to system and δQ_0 = heat rejected from system, as in an engine (E_R) undergoing an infinitesimal Carnot cycle.

In reality, δQ_0 is the minimum amount of heat that can be rejected because processes 1 to 2 and 3 to 4 are both isentropic, i.e. adiabatic and *reversible*.

Hence the amount of energy that must be rejected is

$$E_{\text{unav}} = \int dQ_0 = T_0 \int \frac{dQ}{T} \Big|_R = T_0 \Delta S \quad (4.14)$$

Note that the quantity of energy, δQ , can be written as a definite integral because the process is an isentropic (reversible) one. Then E_{unav} is the energy that is unavailable and is given by **cdefc**. The available energy on this diagram is given by **abcd** and is given by

$$E_{\text{av}} = Q - E_{\text{unav}} = Q - T_0 \Delta S \quad (4.15)$$

where Q is defined by the area **abfea**.

4.5 IRREVERSIBILITY

The concept of reversible engines has been introduced and these have operated on reversible cycles, e.g. isentropic and isothermal reversible processes. However, all real processes are irreversible and it is possible to obtain a measure of this irreversibility using the previous analysis. This will be illustrated by two examples: a turbine that produces a work output; and a compressor that absorbs a work input.

Example 4.5.1: a turbine

An aircraft gas turbine with an isentropic efficiency of 85% receives hot gas from the combustion chamber at 10 bar and 1000 °C. It expands this to the atmospheric pressure of 1 bar. If the temperature of the atmosphere is 20 °C, determine (a) the change of availability of the working fluid, and the work done by the turbine *if the expansion were isentropic*. Then, for the actual turbine, determine (b) the

change of availability and the work done, (c) the change of availability of the surroundings and (d) the net loss of availability of the universe (i.e. the irreversibility).

Assume that the specific heat at constant pressure, $c_p = 1.100$ kJ/kg K, and that the ratio of specific heats, $\kappa = 1.35$.

Solution:

The processes involved are shown on Fig. 4.5.

(a) Isentropic expansion

From the steady flow energy equation the specific work done in the isentropic expansion is

$$w_{T|_{\text{isen}}} = c_p(T_1 - T_{2'})$$

$$\text{For the isentropic expansion } T_{2'} = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} = 1273 \left(\frac{1}{10} \right)^{\frac{0.35}{1.35}} = 700.8 \text{ K}$$

$$\text{giving } w_{T|_{\text{isen}}} = 1.100 \times (1273 - 700.8) = 629.5 \text{ kJ/kg}$$

The change in availability of the working fluid is given by Eqn (4.13b), $\Delta a = a_{f2'} - a_{f1}$, where

$$a_{f2'} = h_{2'} - T_0 s_{2'}$$

$$a_{f1} = h_1 - T_0 s_1$$

For an isentropic change, $s_{2'} = s_1$, and hence $\Delta a = h_{2'} - h_1 = -w_{T|_{\text{isen}}} = -629.5$ kJ/kg.

The change of availability of the surroundings is 629.5 kJ/kg, and hence the change of availability of the universe is zero for this *isentropic* process. This means that the energy can be transferred between the system and the environment without any degradation, and the processes are reversible – this would be expected in the case of an isentropic process.

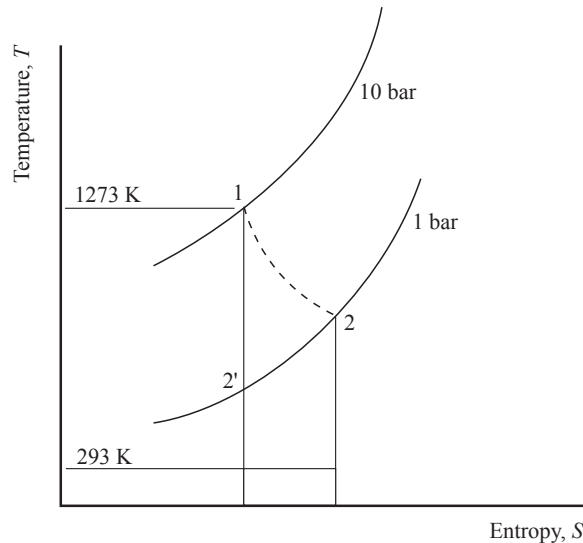


FIGURE 4.5

Turbine expansion process on T - s diagram.

(b) Non-isentropic expansion

If the isentropic efficiency of the turbine is 85%, i.e. $\eta_T = 0.85$, then the turbine work is

$$w_T = \eta_T w_{T|_{\text{isen}}} = 0.85 \times 629.5 = 535.0 \text{ kJ/kg}$$

The temperature at the end of the expansion is $T_2 = T_1 - w_T/c_p = 1273 - 535.0/1.100 = 786 \text{ K}$.

The change of availability is given by Eqn (4.13b) as

$$\begin{aligned}\Delta a &= a_{f2} - a_{f1} \\ &= h_2 - T_0 s_2 - (h_1 - T_0 s_1) \\ &= h_2 - h_1 - T_0(s_2 - s_1) = -w_T - T_0(s_2 - s_1)\end{aligned}$$

The change of entropy for a perfect gas is given by

$$\Delta s_{12} = s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}$$

where, from the perfect gas law,

$$R = \frac{(\kappa - 1)c_p}{\kappa} = \frac{(1.35 - 1) \times 1.100}{1.35} = 0.285 \text{ kJ/kg K}$$

Thus the change of entropy during the expansion process is

$$s_2 - s_1 = 1.1 \times \ln \frac{786}{1273} - 0.285 \times \ln \frac{1}{10} = -0.5304 + 0.6562 = 0.1258 \text{ kJ/kg K}$$

Thus $\Delta a = -535 - T_0(s_2 - s_1) = -535 - 293 \times 0.1258 = -571.9 \text{ kJ/kg}$

(c) The change of availability of the surroundings is equal to the work done, hence

$$\Delta a_{\text{surroundings}} = 535 \text{ kJ/kg}$$

(d) The irreversibility is the change of availability of the universe, which is the sum of the changes of availability of the system and its surroundings, i.e.

$$\Delta a_{\text{universe}} = \Delta a_{\text{system}} + \Delta a_{\text{surroundings}} = -571.9 + 535.0 = -36.9 \text{ kJ/kg}$$

This can also be calculated directly from an expression for irreversibility

$$\begin{aligned}I &= T_0 \Delta S \\ &= 293 \times 0.1258 = 36.86 \text{ kJ/kg}\end{aligned}$$

Note that the irreversibility is positive because it is defined as the *loss* of availability.

Example 4.5.2: an air compressor

A steady flow compressor for a gas turbine receives air at 1 bar and 15 °C, which it compresses to 7 bar with an efficiency of 83%. Based on surroundings at 5 °C, determine (a) the change of availability and the work for isentropic compression. For the actual process, evaluate (b) the change of availability and work done, (c) the change of availability of the surroundings and (d) the irreversibility.

Treat the gas as an ideal one, with the specific heat at constant pressure, $c_p = 1.004 \text{ kJ/kg K}$ and the ratio of specific heats, $\kappa = 1.4$.

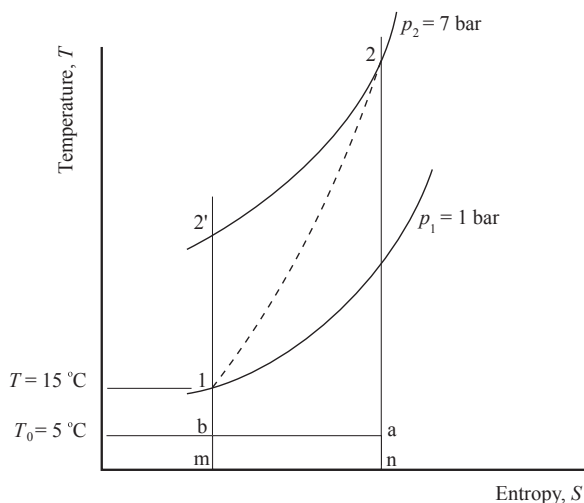


FIGURE 4.6

Compression process on T - s diagram.

Solution:

The processes are shown in Fig. 4.6.

(a) Isentropic compression

$$T_{2'} = T_1 \left(\frac{p_2}{p_1} \right)^{(\kappa-1)/\kappa} = 288 \times 7^{0.286} = 502.4 \text{ K.}$$

The work done can be calculated from the steady flow energy equation, giving

$$w_C|_{\text{isen}} = -\Delta h = -215.3 \text{ kJ/kg}$$

The change of availability is given by Eqn (4.13b) as

$$\Delta a_f = a_{f2'} - a_{f1} = h_{2'} - h_1 - T_0(s_{2'} - s_1) = \Delta h - T_0\Delta S.$$

If the process is isentropic, $\Delta S = 0$, and then

$$\Delta a_f = c_p(T_{2'} - T_1) = 1.004 \times (502.4 - 288) = 215.3 \text{ kJ/kg.}$$

(b) The actual work done

$$w_C = w_C|_{\text{isen}}/\eta_C = -215.3/0.83 = -259.4 \text{ kJ/kg}$$

Hence $h_2 = h_1 - w_C = 1.004 \times 288 - (-259.4) = 548.6 \text{ kJ/kg}$, and the temperature at 2, T_2 , is given by $T_2 = h_2/c_p = 546.4 \text{ K}$.

$$\Delta s_{12} = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1} = 0.6411 - 0.5565 = 0.08639 \text{ kJ/kg K.}$$

Hence

$$\begin{aligned} \Delta a_f &= a_{f2} - a_{f1} = \Delta h - T_0 \Delta s \\ &= 259.4 - 278 \times 0.08639 = 235.4 \text{ kJ/kg} \end{aligned}$$

There has been a *greater increase* in availability than in the case of reversible compression. This reflects the higher temperature achieved during irreversible compression.

- (c) The change of availability of the surroundings is equal to the enthalpy change of the system, i.e. $\Delta a_{\text{surr}} = -259.4 \text{ kJ/kg}$.
 (d) The process is an adiabatic one, i.e. there is no heat loss or addition. Hence the irreversibility of the process is given by

$$I = T_0 \Delta s = 278 \times 0.08639 = 24.02 \text{ kJ/kg}$$

This is the negative of the change of availability of the universe (system + surroundings) which is given by

$$\Delta a_{\text{univ}} = \Delta a_{\text{system}} + \Delta a_{\text{surr}} = 235.4 - 259.4 = -24.0 \text{ kJ/kg}$$

Hence, while the available energy in the fluid has been increased by the work done on it, the change is less than the work done. This means that, even if the energy in the gas after compression is passed through a *reversible* heat engine, it will not be possible to produce as much work as was required to compress the gas. Hence, the *quality of the energy in the universe has been reduced*; even though the quantity of energy has remained constant.

4.6 GRAPHICAL REPRESENTATION OF AVAILABLE ENERGY AND IRREVERSIBILITY

Consider the energy transfer from a high-temperature reservoir at T_H through a heat engine (not necessarily reversible), as shown in Fig. 4.7.

The available energy flow from the hot reservoir is

$$E_H = Q_H - T_0 \Delta S_H \quad (4.16)$$

The work done by the engine is

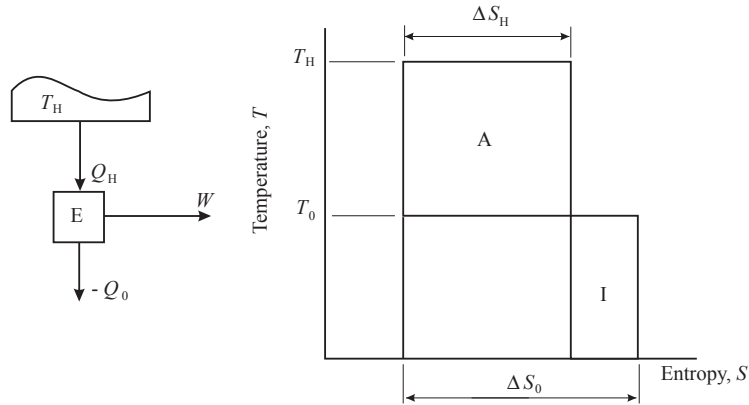
$$W = Q_H - Q_0$$

The total change of entropy of the universe is

$$\Sigma \Delta S = \Delta S_H + \Delta S_0 = \frac{Q_H}{T_H} - \frac{Q_0}{T_0} \quad (4.17)$$

Hence the energy which is unavailable due to irreversibility is defined by

$$\begin{aligned} E_{\text{irrev}} &= E_H - W = Q_H - T_0 \Delta S_H - W \\ &= Q_H - T_0 \Delta S_H - (Q_H - Q_0) = Q_0 - T_0 \Delta S_H \\ &= T_0 (\Delta S_0 - \Delta S_H) \end{aligned} \quad (4.18)$$

**FIGURE 4.7**

Representation of available energy and irreversibility.

In the case of a reversible engine, $\Sigma \Delta S = 0$ because entropy flow is conserved, i.e.

$$\frac{Q_H}{T_H} = \frac{Q_0}{T_0} \quad (4.19)$$

Hence the unavailable energy for a reversible engine is $T_0 \Delta S_H$ while the irreversibility is zero. However, for all other engines it is nonzero. The available energy is depicted on Fig. 4.7 by the area marked 'A', while the energy 'lost' due to irreversibility is denoted 'I' and is defined as

$$E_{\text{irrev}} = T_0(\Delta S_0 - \Delta S_H). \quad (4.20)$$

4.7 AVAILABILITY BALANCE FOR A CLOSED SYSTEM

The approaches derived previously, work very well when it is possible to define the changes occurring inside the system. However, it is not always possible to do this and it is useful to derive a method for evaluating the change of availability from 'external' parameters. This can be done in the following way for a closed system.

If a closed system goes from state 1 to state 2 by executing a process then the changes in that system are:

from the First Law:

$$U_2 - U_1 = \int_1^2 (\delta Q - \delta W) = \int_1^2 \delta Q - W \quad (4.21)$$

from the Second Law:

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + \sigma \quad (4.22)$$

where σ is the internal irreversibility of the system and T is the temperature at which the heat transfer interactions with the system occur (see Fig. 4.2(a)). Equations (4.21) and (4.22) can be written in terms of availability (see Eqn (4.10)), for a system which can change its volume during the process, as

$$A_2 - A_1 = U_2 - U_1 - T_0(S_2 - S_1) + p_0(V_2 - V_1) = \int_1^2 \delta Q - W + p_0(V_2 - V_1) - T_0 \int_1^2 \frac{\delta Q}{T} - T_0 \sigma \quad (4.23)$$

Equation (4.23) can be rearranged to give

$$A_2 - A_1 = \int_1^2 \left(1 - \frac{T_0}{T}\right) \delta Q - W + p_0(V_2 - V_1) - T_0 \sigma \quad (4.24)$$

The change in specific availability is given by

$$a_2 - a_1 = u_2 - u_1 - T_0(s_2 - s_1) + p_0(v_2 - v_1) = \int_1^2 \left(1 - \frac{T_0}{T}\right) \delta q - w + p_0(v_2 - v_1) - T_0 \sigma_m \quad (4.25)$$

where q , w and σ_m are the values of Q , W and σ per unit mass.

The significance of Eqn (4.24) can be examined by means of a couple of simple examples.

Example 4.7.1: change in availability for a closed system

A steel casting weighing 20 kg is removed from a furnace at a temperature of 800 °C and heat treated by quenching in a bath containing 500 kg water at 20 °C. Calculate the change in availability of the universe due to this operation. The specific heat of the water is 4.18 kJ/kg K, and that of steel is 0.42 kJ/kg K. Assume that the bath of water is rigid and perfectly insulated from the surroundings after the casting has been dropped in, and take the datum temperature and pressure as 20 °C and 1 bar respectively.

Solution:

The process can be considered to be a closed system if it is analysed after the casting has been introduced to the bath of water. Hence Eqn (4.24) can be applied.

$$A_2 - A_1 = U_2 - U_1 - T_0(S_2 - S_1) + p_0(V_2 - V_1) = \int_1^2 \left(1 - \frac{T_0}{T}\right) \delta Q - W + p_0(V_2 - V_1) - T_0 \sigma$$

In this case, if the combined system is considered, $\delta Q = 0$, $W = 0$, and $p_0(V_2 - V_1) = 0$ because the system is adiabatic and constant volume. Thus

$$A_2 - A_1 = -T_0 \sigma$$

The irreversibility can be calculated in the following manner:

- i. Final temperature of system

$$T_f = \frac{m_c c_c T_c + m_w c_w T_w}{m_c c_c + m_w c_w} = \frac{20 \times 0.42 \times 1073 + 500 \times 4.18 \times 293}{0.42 \times 20 + 500 \times 4.18} = 296.12 \text{ K}$$

ii. Change of entropy of casting

$$\delta S_c = \int_{T_s}^{T_f} \frac{\delta Q_R}{T} = \int_{T_s}^{T_f} \frac{m_c c_c dT}{T} = m_c c_c \ln \frac{T_f}{T_c} = 20 \times 0.42 \times \ln \frac{296.12}{1073} = -10.815 \text{ kJ/K}$$

iii. Change of entropy of water

$$\delta S_w = \int_{T_w}^{T_f} \frac{\delta Q_R}{T} = \int_{T_w}^{T_f} \frac{m_w c_w dT}{T} = m_w c_w \ln \frac{T_f}{T_w} = 500 \times 4.18 \times \ln \frac{296.12}{293} = 22.154 \text{ kJ/K}$$

iv. Change of entropy of system (and universe)

$$\delta S = \delta S_c + \delta S_w = -10.815 + 22.154 = 11.339 \text{ kJ/K}$$

v. Change of availability

$$A_2 - A_1 = -T_0 \sigma = -293 \times 11.34 = -3323 \text{ kJ}$$

This solution indicates that the universe is less able to do work after the quenching of the casting than it was before the casting was quenched. The loss of availability was analysed above by considering the irreversibility associated with the transfer of energy between the casting and the water. It could have been analysed in a different manner by taking explicit note of the work which could be achieved from each part of the composite system before and after the heat transfer had taken place. This will now be done.

i. Work available by transferring energy from the casting to the environment through a reversible heat engine before the process

$$\begin{aligned} W_c &= \int_{T_s}^{T_0} \left(1 - \frac{T_0}{T}\right) dQ = \int_{T_s}^{T_0} \left(1 - \frac{T_0}{T}\right) m_c c_c dT = m_c c_c \left[T - T_0 \ln T \right]_{T_c}^{T_0} \\ &= 20 \times 0.42 \times \left[(293 - 1073) - 293 \times \ln \left(\frac{293}{1073} \right) \right] = 3357.3 \text{ kJ} \end{aligned}$$

ii. Work available by transferring energy from the water bath to the environment through a reversible heat engine after the process

$$\begin{aligned} W_w &= \int_{T_f}^{T_0} \left(1 - \frac{T_0}{T}\right) dQ = \int_{T_f}^{T_0} \left(1 - \frac{T_0}{T}\right) m_w c_w dT = m_w c_w \left[T_f - T_0 \ln T \right]_{T_f}^{T_0} \\ &= 500 \times 4.18 \times \left[(293 - 296.12) - 293 \times \ln \left(\frac{293}{296.12} \right) \right] = -34.47 \text{ kJ} \end{aligned}$$

iii. Change of availability of universe is

$$A_2 - A_1 = -W = -(3357.3 - 34.47) = -3323 \text{ kJ}$$

This is the same solution as obtained by considering the irreversibility.

Equation (4.24) can be considered to be made up of a number of terms, as shown below.

$$\begin{aligned}
 A_2 - A_1 &= \underbrace{\int_1^2 \left(1 - \frac{T_0}{T}\right) \delta Q}_{\substack{\text{availability transfer} \\ \text{accompanying heat transfer}}} - \underbrace{W + p_0(V_2 - V_1)}_{\substack{\text{availability transfer} \\ \text{accompanying work}}} - \underbrace{T_0 \sigma}_{\substack{\text{availability destruction} \\ \text{due to irreversibilities}}} \\
 &= \underbrace{\int_1^2 \left(1 - \frac{T_0}{T}\right) \delta Q}_{\substack{\text{availability transfer} \\ \text{accompanying heat transfer}}} - \underbrace{W + p_0(V_2 - V_1)}_{\substack{\text{availability transfer} \\ \text{accompanying work}}} - \underbrace{I}_{\substack{\text{availability destruction} \\ \text{due to irreversibilities}}}
 \end{aligned} \tag{4.26}$$

It is also possible to write Eqn (4.26) in the form of a rate equation, in which case the rate of change of availability is

$$\begin{aligned}
 \frac{dA}{dt} &= \underbrace{\left(1 - \frac{T_0}{T}\right) \dot{Q}}_{\substack{\text{availability transfer} \\ \text{accompanying heat transfer}}} - \underbrace{\dot{W} + p_0 \frac{dV}{dt}}_{\substack{\text{availability transfer} \\ \text{accompanying work}}} - \underbrace{T_0 \dot{\sigma}}_{\substack{\text{availability destruction} \\ \text{due to irreversibilities}}} \\
 &= \underbrace{\left(1 - \frac{T_0}{T}\right) \dot{Q}}_{\substack{\text{availability transfer} \\ \text{accompanying heat transfer}}} - \underbrace{\dot{W} + p_0 \frac{dV}{dt}}_{\substack{\text{availability transfer} \\ \text{accompanying work}}} - \underbrace{i}_{\substack{\text{availability destruction} \\ \text{due to irreversibilities}}}
 \end{aligned} \tag{4.27}$$

Equations (4.26) and (4.27) can be written in terms of specific availability to give

$$a_2 - a_1 = \int_1^2 \left(1 - \frac{T_0}{T}\right) \delta q - w + p_0(v_2 - v_1) - T_0 \sigma_m = \int_1^2 \left(1 - \frac{T_0}{T}\right) \delta q - w + p_0(v_2 - v_1) - i \tag{4.28}$$

and

$$\frac{da}{dt} = \left(1 - \frac{T_0}{T}\right) \dot{q} - \dot{w} + p_0 \frac{dv}{dt} - T_0 \dot{\sigma}_m = \left(1 - \frac{T_0}{T}\right) \dot{q} - \dot{w} + p_0 \frac{dv}{dt} - i \tag{4.29}$$

Example 4.7.2: change of availability for a closed system in which the volume changes

An internal combustion engine operates on the Otto cycle (with combustion at constant volume) and has the parameters defined in Table 4.1; it is based on one in Heywood (1988).

Calculate the variation in availability of the gases in the cylinder throughout the cycle from start of compression to the end of expansion. Assume the compression and expansion processes are adiabatic.

Solution:

This example introduces two new concepts:

1. The effect of change of volume on the availability of the system and
2. The effect of ‘combustion’ on the availability of the system.

Equation (4.24) contains a term which takes into account the change of volume ($p_0(V_2 - V_1)$), but it does not contain a term for the change in availability which occurs due to ‘combustion’.

Equation (4.24) gives the change of availability of a system of constant composition as an extensive property. This can be modified to allow for combustion by the addition of a term for the availability of reaction. Chapter 10 contains a further discussion of the application of the energy equation to combustion processes, but it should be possible to understand this example without reading the whole of that chapter. This is defined as

$$\Delta A_R = \Delta F_R = U_P(T_s) - U_R(T_s) - T_0(S_R(T_s) - S_P(T_s)) \quad (4.30)$$

where F_R is the Helmholtz energy of reaction of the fuel at the standard temperature, T_s and T_s is the temperature at which the energies of reaction are evaluated. Hence,

$$\begin{aligned} \Delta A_R &= \Delta F_R = \Delta U_R - T_0(S_R(T_s) - S_P(T_s)) \\ &= (Q_v)_s - T_0(S_R(T_s) - S_P(T_s)) \end{aligned} \quad (4.31)$$

This term can be added into Eqn (4.24) to give

$$A_2 - A_1 = \Delta A_R + (U_2 - U_1) - T_0(S_2 - S_1) + p_0(V_2 - V_1) \quad (4.32)$$

Table 4.1 Operating Parameters for Otto Cycle

Compression ratio, r_c	12
Calorific value of fuel, Q'_v (kJ/kg)	44000
Ratio, $x_a = \Delta A_R/Q'_v$	1.0286
Pressure at start of compression, p_1 (bar)	1.0
Temperature at start of compression, T_1 (°C)	60
Air–fuel ratio, ϵ	15.39
Specific heat of air at constant volume, c_v (kJ/kg K)	0.946
Ratio of specific heats, κ	1.30
Temperature of surroundings, T_0 (K)	300
Pressure of surroundings, p_0 (bar)	1.0

Equation (4.24) can be generalised to give the value at state i relative to that at state 0, resulting in

$$\begin{aligned} A_i - A_0 &= \Delta A_R + (U_i - U_0) - T_0(S_i - S_0) + p_0(V_i - V_0) \\ &= m_f \Delta A_R + m[(u_i - u_0) - T_0(s_i - s_0) + p_0(v_i - v_0)] \end{aligned} \quad (4.33)$$

where

m_f = mass of fuel,

and

m = total mass of mixture = $m_f + m_{\text{air}}$

The specific availability, based on the total mass of mixture is

$$\begin{aligned} a_i - a_0 &= \frac{A_i - A_0}{m} = \frac{m_f}{m} \Delta A_R + [(u_i - u_0) - T_0(s_i - s_0) + p_0(v_i - v_0)] \\ &= \frac{\Delta A_R}{\varepsilon + 1} + [(u_i - u_0) - T_0(s_i - s_0) + p_0(v_i - v_0)] \end{aligned} \quad (4.34)$$

where ε = overall air–fuel ratio. Examples of the availability of reaction are given in Section 4.9.2. The availability of reaction can be related to the internal energy of reaction by

$$\Delta A_R = (Q_v)_s \left(1 - \frac{T_0(S_R(T_s) - S_P(T_s))}{(Q_v)_s} \right) = x_a (Q_v)_s, \quad (4.35)$$

which gives

$$a_i - a_0 = \frac{x_a (Q_v)_s}{\varepsilon + 1} + [(u_i - u_0) - T_0(s_i - s_0) + p_0(v_i - v_0)] \quad (4.36)$$

If the energy of reaction per unit mass of mixture is written as $q^* = \frac{(Q_v)_s}{\varepsilon + 1}$, then

$$\frac{a_i - a_0}{q^*} = \frac{1}{q^*} [(u_i - u_0) + x_a q^* - T_0(s_i - s_0) + p_0(v_i - v_0)] \quad (4.37)$$

Considering the individual terms in Eqn (4.37) gives

$$u_i - u_0 = c_v(T_i - T_0) = c_v T_0 \left(\frac{T_i}{T_0} - 1 \right) \quad (4.38)$$

$$p_0(v_i - v_0) = p_0 v_0 \left(\frac{v_i}{v_0} - 1 \right) = R T_0 \left(\frac{v_i}{v_0} - 1 \right) = (\kappa - 1) c_v T_0 \left(\frac{v_i}{v_0} - 1 \right) \quad (4.39)$$

$$T_0(s_i - s_0) = T_0 \left\{ c_p \ln \frac{T_i}{T_0} - R \ln \frac{p_i}{p_0} \right\} = c_v T_0 \left\{ \kappa \ln \frac{T_i}{T_0} - (\kappa - 1) \ln \frac{p_i}{p_0} \right\} \quad (4.40)$$

Hence

$$\frac{a_i - a_0}{q^*} = \frac{c_v T_0}{q^*} \left[\left(\frac{T_i}{T_0} - 1 \right) + \frac{x_a q^*}{c_v T_0} - \left\{ \kappa \ln \frac{T_i}{T_0} - (\kappa - 1) \ln \frac{p_i}{p_0} \right\} + (\kappa - 1) \left(\frac{v_i}{v_0} - 1 \right) \right] \quad (4.41)$$

Equation (4.41) can be applied around the cycle to evaluate the availability relative to that at the datum state. The values at the state points of the Otto cycle are shown in Tables 4.2 and 4.3, and the

Table 4.2 State Points Around Otto Cycle

State	v/v_0	p (bar)	T (K)	a/q^*	$\delta a/q^*$
0	1	1	300	1.0286	
1	1.11	1	333	1.029375	0.000775
2	0.0925	25.28923	701.7762	1.127041	0.097666
3	0.0925	127.5691	3540.043	0.955991	-0.17105
4	1.11	5.044404	1679.787	0.332836	-0.62316

Table 4.3 Terms in Eqn (4.41) Evaluated Around Cycle

State	$\left(\frac{T_i}{T_0} - 1\right)$	$\frac{x_a q^*}{c_v T_0}$	$(\kappa - 1) \left(\frac{v_i}{v_0} - 1\right)$	$\kappa \ln \frac{T_i}{T_0} - (\kappa - 1) \ln \frac{p_i}{p_0}$	$\frac{a_i}{q^*}$	$\frac{\delta a_{i,i-1}}{q^*}$
0	0	9.731469	0	0	1.0286	
1	0.11	9.731469	0.033	0.135668	1.029375	0.000775
2	1.339254	9.731469	-0.27225	0.135668	1.127041	0.097666
3	10.80014	9.731469	-0.27225	1.753948	0.955991	-0.17105
4	4.599289	9.731469	0.033	1.753948	0.332836	-0.62316

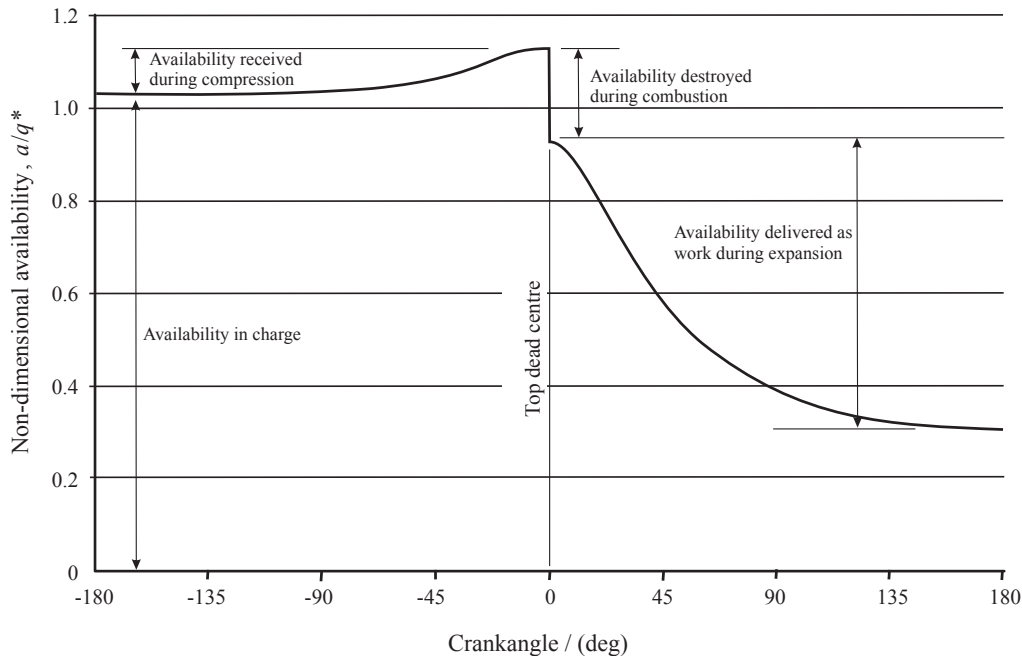
variation of availability as a function of crankangle and volume during the cycle (calculated by applying Eqn (4.41) in a step-by-step manner) is shown in Figs 4.8 and 4.9, respectively.

The value of availability of the charge at state 0 is based on the ratio of the availability of combustion of octane to the heat of reaction of octane, and this is calculated in Section 4.9.2. The calculation of most of the other points on the cycle is straightforward, but it is worthwhile considering what happens during the combustion process. In the Otto cycle, combustion takes place instantaneously at top dead centre (tdc), and the volume remains constant. This means that when Eqn (4.41) is used to consider the effect of adiabatic, constant volume combustion occurring between points 2 and 3 this gives

$$\frac{a_3 - a_0}{q^*} - \frac{a_2 - a_0}{q^*} = \frac{c_v T_0}{q^*} \left[\underbrace{\left(\frac{T_3}{T_0} - 1 \right) - \left\{ \left(\frac{T_2}{T_0} - 1 \right) + \frac{x_a q^*}{c_v T_0} \right\}}_{\text{change of availability due to combustion as fuel changes from reactants to products, = 0}} - \underbrace{\left\{ \kappa \ln \frac{T_3}{T_2} - (\kappa - 1) \ln \frac{p_3}{p_2} \right\}}_{\text{change of availability of gases due to change of entropy of gases}} \right] \quad (4.42)$$

Hence, the availability at point 3 is

$$\frac{a_3 - a_0}{q^*} = \frac{a_2 - a_0}{q^*} + \frac{c_v T_0}{q^*} \left[- \left\{ \kappa \ln \frac{T_3}{T_2} - (\kappa - 1) \ln \frac{p_3}{p_2} \right\} \right] \quad (4.43)$$

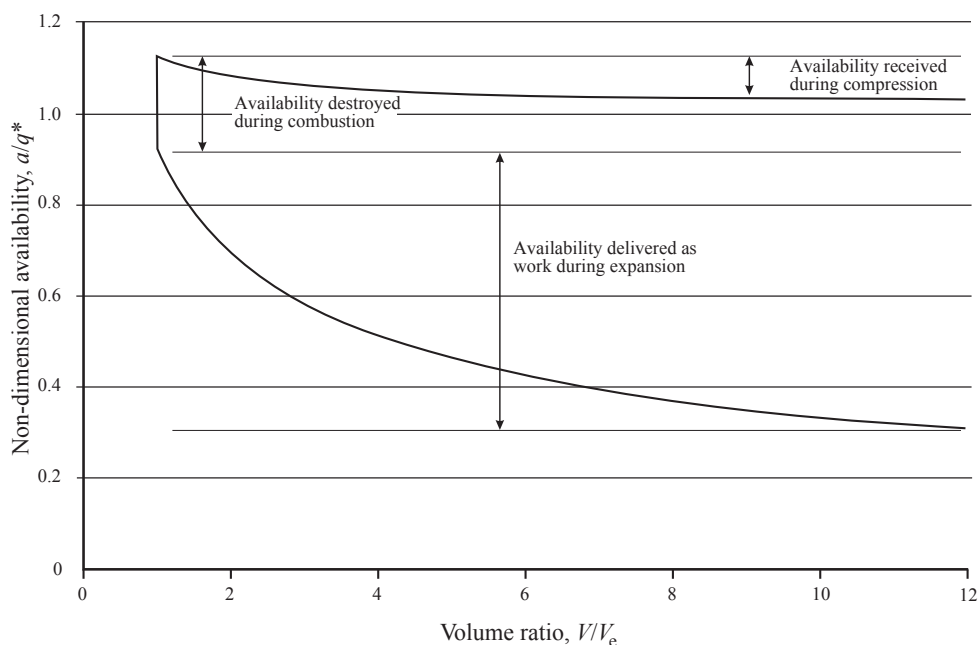
**FIGURE 4.8**

Variation of the nondimensional availability with crankangle for an Otto cycle.

Equation (4.43) is the change in entropy of the working fluid which is brought about by combustion, and since the entropy of the gases increases due to combustion this term reduces the availability of the gas.

Figures 4.8 and 4.9 show how the nondimensional availability of the charge varies around the cycle. This example is based on a cycle with a premixed charge, i.e. the fuel and air are induced into the engine through the inlet valve and the availability of the charge is greater at the beginning of the cycle than the end because the fuel contains availability which is released during the chemical reaction. This is similar to the energy contained in the reactants in a simple combustion process and released as the internal energy (or enthalpy) of reaction of the fuel. Considering Fig. 4.8, it can be seen that the availability of the charge increases during the compression stroke (-180° crankangle to 0° crankangle) because of the work done by the piston (which is isentropic in this ideal cycle case). The ‘combustion’ process takes place instantaneously at 0° crankangle and the availability contained in the fuel in the form of the chemical bonds (see Chapter 11) is released and converted, at constant volume, to thermal energy. The effect of this is to introduce an irreversibility defined by the change of entropy of the gas (Eqn (4.42)), and this causes a loss of availability. The expansion process (which is again isentropic for this ideal cycle) causes a conversion of availability in the charge as it is converted into expansion work.

The availability of the working fluid at the end of the cycle, 4, is a measure of the work that could be obtained from the charge after the cycle in the cylinder has been completed. This availability can

**FIGURE 4.9**

Variation of nondimensional availability with volume for an Otto cycle.

be obtained if the working fluid is taken down to the dead state by reversible processes. Turbochargers are used to convert part of this availability into work but cannot convert it all because it can only take the state of the fluid down to the pressure of the dead state, p_0 . If the full availability is to be converted, it is necessary to use a turbine (e.g. a turbocharger) and then a ‘bottoming’ cycle (e.g. a Rankine cycle based on a suitable working fluid) to take the exhaust gas down to the dead-state temperature, T_0 .

The nondimensional availability, a/q^* , is a measure of the work that can be obtained from the cycle. Hence, the total ‘nondimensional work’ that can be achieved is

$$\underbrace{\frac{\delta a_1}{q^*} - \frac{\delta a_4}{q^*}}_{\text{net work from availability}} + \underbrace{\frac{\delta a_{23}}{q^*}}_{\text{availability generated}} = 1.029375 - 0.332836 - 0.17105 = 0.5255$$

This is the ratio of the net work output to the energy supplied (q^*), and is equal to the thermal efficiency of the engine cycle. The thermal efficiency of this Otto cycle, with a compression ratio of 12:1, is

$$\eta_{\text{Otto}} = 1 - \frac{1}{r^{(\kappa-1)}} = 0.5255$$

Thus, the availability approach has given the same result as the basic equation. Where the availability approach shows its strength is in analysing the effects of finite combustion rates and heat transfer in real cycles; this has been discussed by Patterson and Van Wylen (1964).

4.8 AVAILABILITY BALANCE FOR AN OPEN SYSTEM

The availability balance of a closed system was derived in Section 4.7. A similar approach can be used to evaluate the change of availability in an open system. The *Unsteady Flow Energy Equation* (see Chapter 1, Eqn (1.30)) is

$$\sum_j \dot{Q} - \dot{W} = \left(\frac{dE}{dt} \right)_{cv} + \sum_e \dot{m}_e (h_e + V_e^2/2 + gz_e) - \sum_i \dot{m}_i (h_i + V_i^2/2 + gz_i) \quad (4.44)$$

where $\sum_j \dot{Q}$ is the sum of heat transfers to the control volume over the total number of heat transfer processes, j , and the summations of the inflows and outflows take into account all the inflows and outflows. If the changes in kinetic and potential energies are small, then this equation can be reduced to

$$\sum_j \dot{Q} - \dot{W} = \left(\frac{dE}{dt} \right)_{cv} + \sum_e \dot{m}_e h_e - \sum_i \dot{m}_i h_i \quad (4.45)$$

It is also possible to relate the rate of change of entropy to the heat transfers from the system and the irreversibilities in the system as

$$\dot{S} = \frac{dS_{cv}}{dt} = \sum_j \frac{\dot{Q}}{T} + \dot{\sigma}_{cv} - \sum_e \dot{m}_e s_e + \sum_i \dot{m}_i s_i \quad (4.46)$$

If the kinetic and potential energies of the control volume do not change then the internal energy in the control volume, $(E)_{cv}$, can be replaced by the intrinsic internal energy of the control volume, $(U)_{cv}$. The availability of the control volume is defined by Eqn (4.10), and hence

$$\frac{dA_{cv}}{dt} = \frac{dU_{cv}}{dt} + p_0 \frac{dV_{cv}}{dt} - T_0 \frac{dS_{cv}}{dt} \quad (4.47)$$

Substituting Eqns (4.46) and (4.47) into Eqn (4.45) gives

$$\frac{dA_{cv}}{dt} = \sum_j \left(1 - \frac{T_0}{T} \right) \dot{Q} - \left(\dot{W} - p_0 \frac{dV}{dt} \right) + \sum_i \dot{m}_i (h_i - T_0 s_i) - \sum_e \dot{m}_e (h_e - T_0 s_e) - T_0 \dot{\sigma}_{cv} \quad (4.48)$$

The terms $h - T_0 s$ are the flow availability, a_f , and hence Eqn (4.48) becomes

$$\begin{aligned} \frac{dA_{cv}}{dt} &= \sum_j \left(1 - \frac{T_0}{T} \right) \dot{Q} - \left(\dot{W} - p_0 \frac{dV}{dt} \right) + \sum_i \dot{m}_i a_{f_i} - \sum_e \dot{m}_e a_{f_e} - T_0 \dot{\sigma}_{cv} \\ &= \sum_j \left(1 - \frac{T_0}{T} \right) \dot{Q} - \left(\dot{W} - p_0 \frac{dV}{dt} \right) + \sum_i \dot{m}_i a_{f_i} - \sum_e \dot{m}_e a_{f_e} - \dot{I}_{cv} \end{aligned} \quad (4.49)$$

where $\dot{I}_{cv}$ is the irreversibility in the control volume.

Equation (4.49) is the *unsteady flow availability equation* that is the availability equivalent of the unsteady flow energy equation. Many of the processes considered in engineering are steady state ones, which means that the conditions in the control volume do not change with time. This means that $dA_{cv}/dt = 0$ and $dV/dt = 0$, and then Eqn (4.49) can be simplified to

$$\begin{aligned} 0 &= \sum_j \left(1 - \frac{T_0}{T}\right) \dot{Q} - \dot{W} + \sum_i \dot{m}_i a_{f_i} - \sum_e \dot{m}_e a_{f_e} - T_0 \dot{\sigma}_{cv} \\ &= \sum_j \left(1 - \frac{T_0}{T}\right) \dot{Q} - \dot{W} + \sum_i \dot{m}_i a_{f_i} - \sum_e \dot{m}_e a_{f_e} - \dot{I}_{cv} \end{aligned} \quad (4.50)$$

Example 4.8.1: steady flow availability

Superheated steam at 30 bar and 250 °C flows through a throttle with a downstream pressure of 5 bar. Calculate the change in flow availability across the throttle, neglecting the kinetic and potential terms, if the dead-state condition is $T_0 = 25$ °C and $p_0 = 1$ bar.

A throttle does not produce any work, and it can be assumed that the process is adiabatic (see Chapter 1, Section 1.5.8.3), i.e. $\dot{Q} = 0$, $\dot{W} = 0$.

Hence, Eqn (4.50) becomes, taking into account there is only one inlet and outlet

$$0 = \dot{m}_i a_{f_i} - \dot{m}_e a_{f_e} - \dot{I}_{cv}$$

The conditions at inlet, i, are

$$h_i = 2858 \text{ kJ/kg}; \quad s_i = 6.289 \text{ kJ/kg K},$$

and the conditions at exhaust, e, are

$$h_e = 2858 \text{ kJ/kg}; \quad s_e = 7.0650 \text{ kJ/kg K}.$$

Hence the irreversibility per unit mass is

$$\begin{aligned} \dot{I}_{cv} = \frac{\dot{I}_{cv}}{\dot{m}} &= (h_i - T_0 s_i) - (h_e - T_0 s_e) = (2858 - 298 \times 6.289) - (2858 - 298 \times 7.0650) \\ &= 231.28 \text{ kJ/kg} \end{aligned}$$

The significance of this result is that although energy is conserved in the flow through the throttle the ability of the fluid to do work is reduced by the irreversibility. In this case, because the enthalpy does not change across the throttle, the irreversibility could have been evaluated by

$$T_0(s_2 - s_1) = 298 \times (7.065 - 6.289) = 231.28 \text{ kJ/kg}.$$

4.9 EXERGY

Exergy is basically the available energy based on datum conditions at a dead state; it was introduced in Example 4.3.3. An obvious datum to be used in most calculations is the ambient condition, say p_0 , T_0 . This datum condition can be referred to as the *dead state* and the system reaches this when it is in thermal and mechanical equilibrium with it. A state of thermal and mechanical equilibrium is reached

when both the temperature and pressure of the system are equal to those of the dead state. The term exergy was proposed by Rant (1956), and similar functions had previously been defined by Gibbs (1928) and Keenan (1963).

Exergy will be given the symbol B (sometimes it is given the symbol Ξ) and specific exergy will be denoted by b (or ξ). The exergy of a system at state 1 is defined by

$$B_1 = A_1 - A_0 \quad (4.51)$$

where

A_1 is the available energy at state 1 and
 A_0 is the available energy at the dead state.

If a system undergoes a process between states 1 and 2 the maximum useful work, or available energy, that may be obtained from it is given by

$$W = A_1 - A_2 = (A_1 - A_0) - (A_2 - A_0) = B_1 - B_2 \quad (4.52)$$

Hence the maximum work, or heat transfer, that can be obtained as a system changes between two states is defined as the difference in exergy of those two states.

Exergy is very similar to available energy and is a quasi-, or pseudo-property. This is because it is not defined solely by the state of the system but also by the datum, or dead, state that is used.

A number of examples of the use of exergy will be given.

4.9.1 HEAT TRANSFER

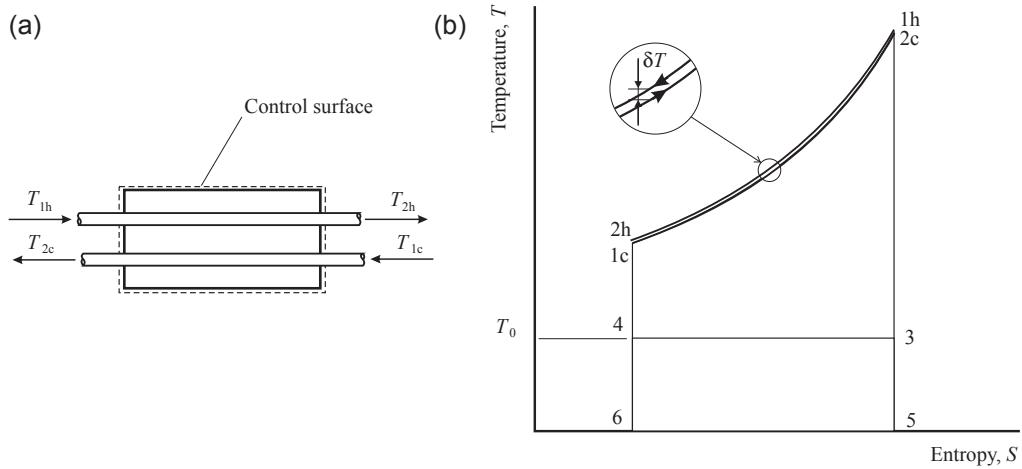
It is possible for energy to be transferred from one body to another without any loss of available energy. This occurs when the heat or energy transfer is ideal or reversible. No real heat transfer process will exhibit such perfection and exergy can be used to show the best way of optimising the effectiveness of such an energy transfer. All actual heat transfer processes are irreversible and the irreversibility results in a loss of exergy.

It should be noted in this section that even though the heat transfer processes for each of the systems are internally reversible, they might also be externally irreversible.

4.9.1.1 Ideal, reversible heat transfer

Ideal reversible heat transfer can be approached in a counterflow heat exchanger. In this type of device, the temperature difference between the two streams is kept to a minimum, because the hot 'source' fluid on entering the heat exchanger is in closest contact to the 'sink' fluid which is leaving the device, and vice versa. The processes involved are depicted by two almost coincident lines from 1 to 2 in Fig. 4.10.

In this ideal process, it will be assumed that, at all times, the fluid receiving the heat is at temperature, T , while the temperature of the source of heat is at all times at temperature, $T + \delta T$, i.e. T_{1c} is δT less than T_{2h} etc. From the First Law of Thermodynamics it is obvious that, if the boundaries of the control volume are insulated from the surroundings, the energy transferred from the hot stream must be equal to the energy received by the cold stream. This means that the areas under the curves in Fig. 4.10 must be equal; in this case they are identical. The exergy change of the hot stream is then given by

**FIGURE 4.10**

Reversible heat transfer in a counterflow heat exchanger. (a) Schematic diagram of heat exchanger; (b) Processes shown on T - s diagram.

$$\begin{aligned}
 \Delta B_h &= B_{2h} - B_{1h} = (A_{2h} - A_0) - (A_{1h} - A_0) \\
 &= A_{2h} - A_{1h} = (U + p_0 V - T_0 S)_{2h} - (U + p_0 V - T_0 S)_{1h} \\
 &= (U_{2h} - U_{1h}) - T_0(S_{2h} - S_{1h}) + p_0(V_{2h} - V_{1h})
 \end{aligned} \tag{4.53}$$

if it is assumed that $V_{1h} = V_{2h}$, then

$$\Delta B_h = (U_{2h} - U_{1h}) - T_0(S_{2h} - S_{1h}) \tag{4.54}$$

In Eqn (4.54), $U_{2h} - U_{1h}$ is the heat transferred from the hot stream, and $S_{2h} - S_{1h}$ is the change of entropy of the hot stream. In Fig. 4.10, $U_{2h} - U_{1h}$ is the area 1h-2h-6-5-1h and $T_0(S_{2h} - S_{1h})$ is the area 3-4-6-5-3. In the case of the hot stream, the change of energy and the change of entropy will both be negative, and because $(U_{2h} - U_{1h}) > T_0(S_{2h} - S_{1h})$ the change of exergy will also be negative.

A similar analysis can be done for the cold stream, and this gives

$$\begin{aligned}
 \Delta B_c &= B_{2c} - B_{1c} = (A_{2c} - A_0) - (A_{1c} - A_0) \\
 &= (U_{2c} - U_{1c}) - T_0(S_{2c} - S_{1c})
 \end{aligned} \tag{4.55}$$

In this case, $U_{2c} - U_{1c}$ is the heat transferred to the cold stream (area 1c-2c-5-6-1c) and this will be positive. The term $T_0(S_{2c} - S_{1c})$ is the unavailable energy of the cold stream (area 4-3-5-6-4), and this will also be positive because of the increase of entropy of the cold stream. Figure 4.10 shows that the heating and cooling processes are effectively identical on the T - s diagram and only differ in their direction. Hence, the change of energy of the hot and cold streams is equal (and opposite), and also the unavailable energies are equal (and opposite) for both streams. This means that for an ideal counterflow heat exchanger, in which the heat transfer takes place across an infinitesimal temperature difference (i.e. reversible heat transfer) the loss of exergy of the hot stream is equal to the gain of exergy of the cold stream. The change of exergy of the universe is zero, and the process is reversible.

If the heat exchanger in Fig. 4.10 were not reversible, i.e. there is a significant temperature difference between the hot and cold streams then the T - s diagram would be like that shown in Fig. 4.11. Figure 4.11(a) shows the processes for both the hot and cold streams on the same T - s diagram, while Figs 4.11(b) and 4.11(c) show individual T - s diagrams for the hot and cold streams respectively. The first point to recognise is that the energy transferred between two streams (areas 1h-2h-5h-6h-1h and 1c-2c-5c-6c-1c) are equal (and opposite). The change of exergy for the hot stream is denoted by the area 1h-2h-3h-4h-1h, while the unavailable energy is given by 3h-5h-6h-4h-3h. Similar quantities for the cold stream are 1c-2c-3c-4c-1c and 3c-5c-6c-4c-3c. It is obvious from Fig. 4.11(a) that the unavailable energy of the cold stream is greater than that for the hot stream because $T_0(S_{2c} - S_{1c}) > T_0(S_{1h} - S_{2h})$. This means that the exergy gained by the cold stream is less than that lost by the hot stream. For the hot stream

$$\Delta B_h = (U_{2h} - U_{1h}) - T_0(S_{2h} - S_{1h}), \quad (4.56)$$

while for the cold stream

$$\Delta B_c = (U_{2c} - U_{1c}) - T_0(S_{2c} - S_{1c}) \quad (4.57)$$

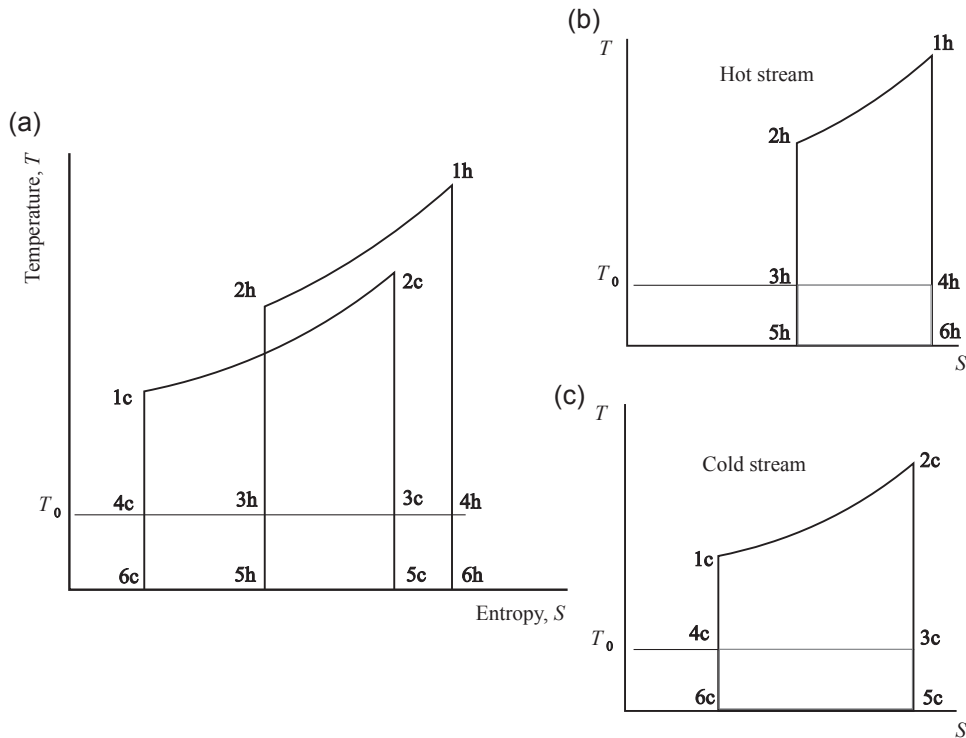


FIGURE 4.11

T - s diagrams for a counterflow heat exchanger with finite temperature difference between the streams.

The change of exergy of the universe is given by

$$\begin{aligned}\Delta B_{\text{univ}} &= \Delta B_h + \Delta B_c = (U_{2h} - U_{1h}) - T_0(S_{2h} - S_{1h}) + (U_{2c} - U_{1c}) - T_0(S_{2c} - S_{1c}) \\ &= -T_0(S_{2h} - S_{1h} + S_{2c} - S_{1c})\end{aligned}\quad (4.58)$$

The value of $\Delta B_{\text{univ}} < 0$ because the entropy change of the cold stream is greater than that of the hot stream. Hence, in this irreversible heat transfer device there has been a loss of exergy in the universe and energy has been degraded. This means that the maximum useful work available from the cold stream is less than that available from the hot stream, even though the energy contents of the two streams is the same.

This result has a further significance, which is that, to obtain the maximum transference of exergy, it is important to reduce the value of $T_0(S_1 - S_2)$. If the total amount of energy being transferred is kept constant then the loss of exergy can be minimised by increasing the temperature at which the heat is transferred. This is effectively shown in Fig. 4.11, where the high-temperature stream can be equivalent to a high-temperature source of heat, while the low-temperature stream is equivalent to a low-temperature source of heat. The quality of the heat (energy) in the high-temperature source is better than that in the low-temperature one.

4.9.1.2 Irreversible heat transfer

The processes depicted in Fig. 4.12 are those of an infinite heat source transferring energy to a finite sink. The temperature of the source remains constant at T_1 but that of the sink changes from T_5 to T_6 . The energy received by the sink will be equal to that lost by the source if the two systems are isolated from the surroundings. The process undergone by the source is one of *decreasing entropy* while that for

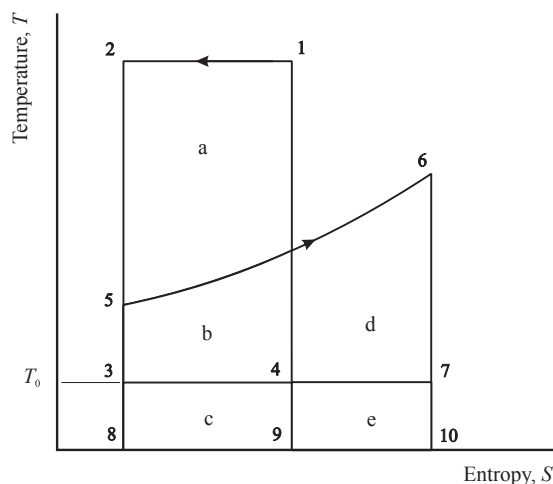


FIGURE 4.12

Irreversible heat transfer from an infinite reservoir to a finite sink.

the sink is one of increasing entropy. Hence, in Fig. 4.12, the areas 1-2-8-9-1 and 5-6-10-8-5 are equal. This means that areas

$$(a + b + c) = (b + c + d + e).$$

By definition the exergy change of the source is given by:

$$\Delta B_{\text{source}} = B_2 - B_1 = (U_2 - U_1) - T_0(S_2 - S_1) \quad (4.59)$$

This equation assumes that the heat transfer takes place at constant volume. In a similar way the exergy change of the sink is given by:

$$\Delta B_{\text{sink}} = B_6 - B_5 = (U_6 - U_5) - T_0(S_6 - S_5) \quad (4.60)$$

Since the source and sink are isolated from the surroundings (the remainder of the universe), then the entropy change of the universe is

$$\begin{aligned} \Delta B_{\text{univ}} &= \Delta B_{\text{source}} + \Delta B_{\text{sink}} \\ &= (U_2 - U_1) - T_0(S_2 - S_1) + [(U_6 - U_5) - T_0(S_6 - S_5)] \\ &= T_0(S_1 - S_6) \end{aligned} \quad (4.61)$$

The term $T_0(S_1 - S_6)$ is depicted by the area marked **e** on Fig. 4.12. Since S_6 is greater than S_1 , then the exergy of the universe (that is its ability to do work) has decreased by this amount. Thus whilst the energy of the universe has remained constant the quality of that energy has declined. This is true of all processes which take place irreversibly; that is all real processes.

4.9.2 EXERGY APPLIED TO COMBUSTION PROCESSES

Combustion processes are good examples of irreversible change: these are discussed in more detail in Chapter 10 *et seq.* In a combustion process the fuel, usually a hydrocarbon, is oxidised using an oxidant, usually air. The structure of the hydrocarbon is broken down as the bonds between the carbon and hydrogen atoms are broken and new bonds are formed to create carbon dioxide, carbon monoxide and water vapour (see Chapter 11). These processes are basically irreversible because they cannot be made to go in the opposite direction by the addition of a very small amount of energy. This seems to suggest that exergy of the universe is decreased by the combustion of hydrocarbon fuels. The following section describes how combustion can be considered using an exergy approach.

Consider a constant pressure combustion process. When the system is in equilibrium with its surroundings the exergy of component, i , is

$$b_i = (h_i - h_0) - T_0(s_i - s_0) \quad (4.62)$$

4.9.2.1 Exergy of reaction of water

Applying this to the simple reaction



$$\Delta B = B_2 - B_1 = B_P - B_R = \Sigma(b_i)_P - \Sigma(b_i)_R \quad (4.64)$$

where suffix R indicates reactants and suffix P indicates products.

Thus

$$\Delta B = \left(h_f^0\right)_{\text{H}_2\text{O}} - T_0(s_{\text{H}_2\text{O}} - s_{\text{H}_2} - 0.5s_{\text{O}_2}) \quad (4.65)$$

(Note: h_f^0 is the enthalpy of formation of a compound and $(h_f^0)_{\text{H}_2\text{O}} = -241820 \text{ kJ/kg}$ at 25°C .)

Substituting values gives, for $t_0 = 25^\circ\text{C}$ which is also the standard temperature for evaluating the enthalpy of reaction. Then

$$\begin{aligned} \Delta B &= -241820 - 298 \times (188.71 - 130.57 - 0.5 \times 205.04) \\ &= -228594.76 \text{ kJ/kmol K.} \end{aligned} \quad (4.66)$$

This means that the ability of the fuel to do work is 5.5% less than the original enthalpy of formation of the 'fuel', and hence 94.5% of the energy defined by the enthalpy of formation is the maximum energy that can be obtained from it.

4.9.2.2 Exergy of reaction of methane (CH_4)

The equation for combustion of methane is



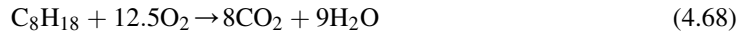
Hence,

$$\begin{aligned} \Delta B &= \Sigma(b_i)_P - \Sigma(b_i)_R = (\Delta H_R)_{\text{CH}_4} - T_0(s_{\text{CO}_2} + 2s_{\text{H}_2\text{O}} - s_{\text{CH}_4} - 2s_{\text{O}_2}) \\ &= -804.6 \times 10^3 - 298 \times (214.07 + 2 \times 188.16 - 182.73 - 2 \times 204.65) \\ &= -804.1 \times 10^3 \text{ kJ/kmol} \end{aligned}$$

In this case the exergy of reaction is almost equal to the enthalpy of reaction; this occurs because the entropy of the reactants and products are almost equal.

4.9.2.3 Exergy of reaction of octane (C_8H_{18})

The equation for combustion of octane is



Assume that the enthalpy of reaction of octane (ΔH_R) is $-5074.6 \times 10^3 \text{ kJ/kmol}$, and that the entropy of octane at 298 K is 360 kJ/kmol K. Then the exergy of reaction is

$$\begin{aligned} \Delta B &= \Sigma(b_i)_P - \Sigma(b_i)_R = (\Delta H_R)_{\text{C}_8\text{H}_{18}} - T_0(8s_{\text{CO}_2} + 9s_{\text{H}_2\text{O}} - s_{\text{C}_8\text{H}_{18}} - 12.5s_{\text{O}_2}) \\ &= -5074.6 \times 10^3 - 298 \times (8 \times 214.07 + 9 \times 188.16 - 360 - 12.5 \times 204.65) \\ &= -5219.9 \times 10^3 \text{ kJ/kmol} \end{aligned}$$

In this case the exergy of reaction is greater than the enthalpy of reaction by 2.86%: this is because the entropy of the products is greater than that of the reactants.

4.10 THE VARIATION OF FLOW EXERGY FOR A PERFECT GAS

This derivation is based on Haywood (1980).

The definition of exergy is, from Eqn (4.51)

$$B_1 = A_1 - A_0$$

while that for the exergy of a flowing gas is, by comparison with Eqn (4.13b) for the availability of a flowing gas,

$$B_{f1} = A_{f1} - A_{f0} = (H_1 - T_0 S_1) - (H_0 - T_0 S_0) \quad (4.69)$$

Equation (4.69) can be expanded to give the specific flow exergy as

$$b_{f1} = a_{f1} - a_{f0} = (h_1 - T_0 s_1) - (h_0 - T_0 s_0) \quad (4.70)$$

Now, for a perfect gas,

$$h = c_p T \quad (4.71)$$

and the change of entropy

$$s_1 - s_0 = c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} \quad (4.72)$$

Hence, the flow exergy for a perfect gas can be written as

$$b_{f1} = (h_1 - h_0) - T_0 \left(c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} \right) = c_p (T - T_0) - T_0 \left(c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} \right) \quad (4.73)$$

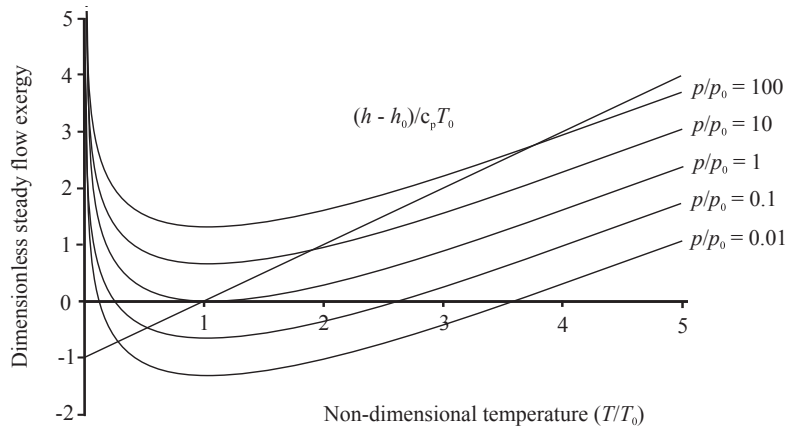
The flow exergy can be nondimensionalised by dividing by the enthalpy at the dead-state temperature, T_0 , to give

$$\frac{b_{f1}}{c_p T_0} = \left(\frac{T}{T_0} - 1 \right) - \ln \frac{T}{T_0} - \frac{\kappa - 1}{\kappa} \ln \frac{p}{p_0} \quad (4.74)$$

Equation (4.74) has been evaluated for a range of temperature ratios and pressure ratios, and the variation of exergy is shown in Fig. 4.13.

Also shown in Fig. 4.13, as a straight line, is the variation of enthalpy for the parameters shown. It can be seen that the exergy is sometimes bigger than the enthalpy, and vice versa. This is because the enthalpy is purely a measure of the thermodynamic energy of the gas relative to the datum temperature. When the dimensionless temperature, $T/T_0 < 1.0$ the enthalpy is negative, and when $T/T_0 > 1.0$ the enthalpy is positive. This simply means that the thermodynamic energy can be greater than or less than the datum value. While the enthalpy varies monotonically with the nondimensional temperature, the exergy does not. The reason for this is that the exergy term, say at $p/p_0 = 1.0$, is given by

$$\frac{b_{f1}}{c_p T_0} = \left(\frac{T}{T_0} - 1 \right) - \ln \frac{T}{T_0} \quad (4.75)$$

**FIGURE 4.13**

Variation of exergy with temperature and pressure for a perfect gas.

$$\text{For } \frac{T}{T_0} > 1, \quad \left(\frac{T}{T_0} - 1 \right) - \ln \frac{T}{T_0} > 1$$

$$\text{and also for } \frac{T}{T_0} < 1, \quad \left(\frac{T}{T_0} - 1 \right) - \ln \frac{T}{T_0} > 1$$

The physical significance of this is that the system can produce work output as long as there is a temperature difference between the system and the dead state; the sign of the temperature difference does not matter.

4.11 CONCLUDING REMARKS

This chapter has introduced the concept of the ‘quality’ of energy through the quasi-properties availability and exergy. It has been shown that energy available at a high temperature has better quality than that at a low temperature. The effect of irreversibilities on the quality of energy has been considered, and while the energy of the universe might be considered to remain constant, the quality of that energy will tend to decrease. Furthermore, this chapter shows graphically the concept of ‘external irreversibility’ – an important factor affecting a heat engine operating on an internally reversible Carnot cycle while producing power output. This is returned to in Chapter 6.

It was also shown that the irreversibility of processes can be calculated, and it is this area that should be tackled by engineers to improve the efficiency of energy utilisation in the world.

4.12 PROBLEMS

P4.1 A piston-cylinder assembly contains 3 kg of air at 15 bar and 620 K. The environment is at a pressure of 1 bar and 300 K. The air is expanded in a fully reversible adiabatic process to a pressure of 5.5 bar. Calculate the useful work which can be obtained from this process. Also calculate the maximum useful work which can be obtained from the gas in (a) the initial state and (b) the final state.

Assume that the specific heats for the gas are $c_p = 1.005 \text{ kJ/kg K}$ and $c_v = 0.718 \text{ kJ/kg K}$.
[295.5 kJ; 509.6 kJ; 214.1 kJ]

- P4.2** Air passes slowly through a rigid control volume A, as shown in Fig. P4.2(a), in a hypothetical, *fully reversible*, steady-flow process between specified stable end states 1 and 2 in the presence of an environment at temperature T_0 and pressure p_0 . States 1 and 2, and also the values of T_0 and p_0 , are defined below.

$$T_1 = 550 \text{ K} \quad \text{and} \quad p_1 = 2 \text{ bar.}$$

$$T_2 = T_0 = 300 \text{ K} \quad \text{and} \quad p_2 = p_0 = 1 \text{ bar.}$$

The air may be treated as a perfect gas, with $c_p = 1.005 \text{ kJ/kg K}$ and $c_v = 0.718 \text{ kJ/kg K}$.

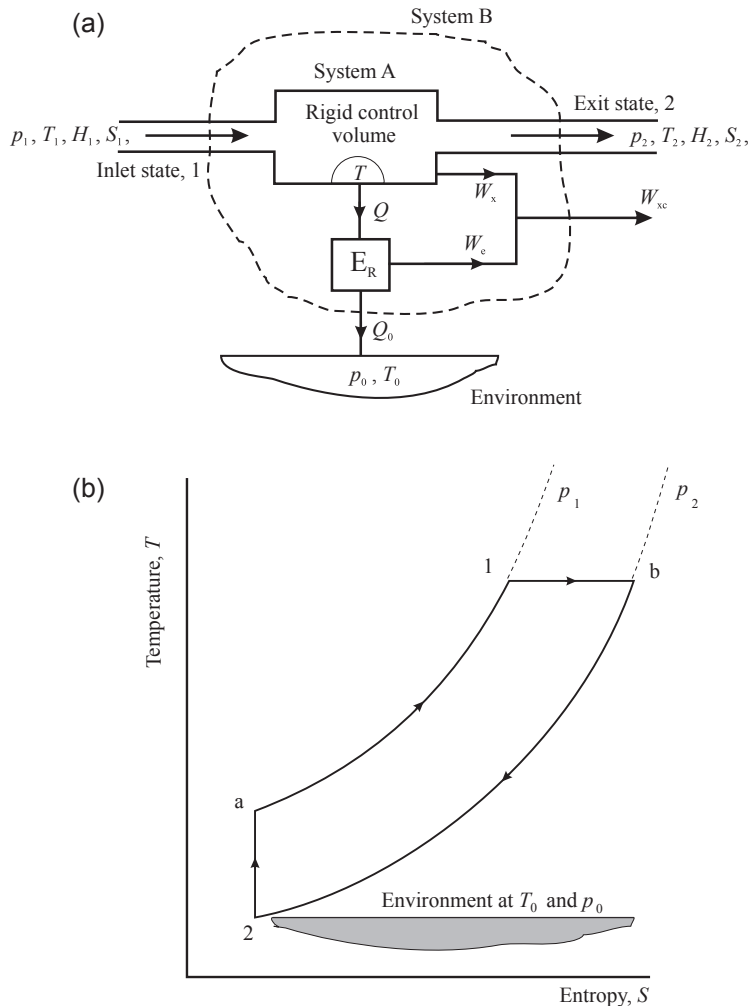


FIGURE P4.2

(a) Schematic diagram of system (b) T - s diagram of processes.

- (a) When the air follows path 1-a-2, see Fig. P4.2(b), calculate the following work *output* quantities in each of the subprocesses 1-a and a-2.
- (i) The *direct shaft work*, W_{x_A} , coming from the control volume as the air passes through the given subprocess.
 - (ii) The *external work*, W_e , produced by any auxiliary cyclic devices required to ensure external reversibility in that exchange with the environment during the given subprocess.
 - (iii) The gross work, W_g .
 - (iv) The total useful shaft work, W_x .

[66.03; 62.2; 128.23; 128.23 (kJ/kg)]

- (b) Calculate the above work output quantities for each of the subprocesses 1-b and b-2 when the air follows the alternative path 1-b-2.

[109.41; 18.77; 128.18; 128.18 (kJ/kg)]

P4.3 Confirm that item (iv) in P4.2 is equal to $(b_1 - b_2)$, where $b = h - T_0s$, the specific *steady-flow availability function*. (Note that, since $T_2 = T_0$ and $p_2 = p_0$, state 2 is the *dead state*, so that item (iv) is in this case equal to the *steady-flow exergy* of unit mass of air in state 1 for an environment at $T_0 = 300$ K and $p_0 = 1$ bar.)

[128.2 kJ/kg]

P4.4 A mass of 0.008 kg of helium is contained in a piston-cylinder unit at 4 bar and 235 °C. The piston is pushed in by a force, F , until the cylinder volume is halved, and a cooling coil is used to maintain the pressure constant. If the dead-state conditions are 1.013 bar and 22 °C, determine:

- (i) The work done on the gas by the force, F ;
- (ii) The change in availability;
- (iii) The heat transfer from the gas and
- (iv) The irreversibility.

Show the heat transfer process defined in part (iii) and the unavailable energy on a T - s diagram, and the work terms on a p - V diagram.

The following data may be used for helium, which can be assumed to behave as a perfect gas:

Ratio of specific heats, $\kappa = c_p/c_v = 1.667$

Molecular weight, $m_w = 4$

Universal gas constant, $\Re = 8.3143$ kJ/kmol K.

[−3.154 kJ; 1.0967 kJ; −10.556 kJ; 2.0573 kJ]

P4.5 A system at constant pressure consists of 10 kg of air at a temperature of 1000 K. Calculate the maximum amount of work which can be obtained from the system if the dead-state temperature is 300 K, and the dead-state pressure is equal to the pressure in the system. Take the specific heat at constant pressure of air, c_p , as 0.98 kJ/kg K (see P2.8, Chapter 2).

[3320.3 kJ]

P4.6 A thermally isolated system at constant pressure consists of 10 kg of air at a temperature of 1000 K and 10 kg of water at 300 K, connected together by a reversible heat engine. What is the maximum work that can be obtained from the system as the temperatures equalise? (See P2.9, Chapter 2.)

Assume

$$\text{for water : } c_v = 4.2 \text{ kJ/kg K;}$$

$$\kappa = c_p/c_v = 1.0;$$

$$\text{for air : } c_v = 0.7 \text{ kJ/kg K;}$$

$$\kappa = c_p/c_v = 1.4.$$

[2884.2 kJ]

- P4.7** An amount of pure substance equal to 1 kmol undergoes an *irreversible* cycle. Neglecting the effects of electricity, magnetism and gravity, state whether each of the following relationships is true or false, giving reasons for your assertion.

(i) $\oint \delta Q = \oint (du_m + pdv_m);$

(ii) $\oint \frac{du_m + pdv_m}{T} > 0;$

(iii) $\oint \delta W < \oint pdv_m;$

where the suffix *m* indicates that the quantities are in molar terms.

[False; false; true]

- P4.8** A gas turbine operates between an inlet pressure of 15 bar and an exhaust pressure of 1.2 bar. The inlet temperature to the turbine is 1500 K and the turbine has an isentropic efficiency of 90%. The surroundings are at a pressure of 1 bar and a temperature of 300 K. Calculate, for the turbine alone:

- The specific power output;
- The exhaust gas temperature;
- The exergy change in the gas passing through the turbine and
- The irreversibility or lost work.

Assume the working substance is an ideal gas with a specific heat at constant pressure of $c_p = 1.005 \text{ kJ/kg K}$ and the specific gas constant, $R = 0.287 \text{ kJ/kg K}$.

[697.5 kJ/kg; 806 K; 727.7 kJ/kg; 343.6 kJ/kg]

- P4.9** It is proposed to improve the energy utilisation of a steel works by transferring the heat from the gases leaving the blast furnace at 600 °C to those entering the furnace at 50 °C (before the heat exchanger is fitted). The minimum temperature of the flue gases is limited to 150 °C to avoid condensation of sulfurous acid in the pipework at exit pressure of 1 bar.

Draw a simple schematic diagram of the heat exchanger you would design, showing the hot and cold gas streams. Explain with the aid of *T-s* diagrams, why a counterflow heat exchanger is the most efficient. If the minimum temperature difference between the hot and cold streams is 10 °C, calculate the minimum loss of exergy for both types of heat exchanger, based on dead-state conditions of 1 bar and 20 °C.

[−72.33 kJ/kg; −45.09 kJ/kg]

- P4.10** Find the maximum and maximum useful, specific work (kJ/kg) that could be derived from combustion products that are (a) stationary and (b) flowing in an environment under the following conditions.

	<i>p</i> (bar)	<i>T</i> (K)	<i>v</i> (m ³ /kg)	<i>u</i> (kJ/kg)	<i>s</i> (kJ/kg K)
Products (1)	7	1000	0.41	760.0	7.4
Environment (0)	1	298.15	0.83	289.0	6.7

[262.3; 220.3; 466.3; 424.3]

RATIONAL EFFICIENCY OF POWER PLANT

5.1 THE INFLUENCE OF FUEL PROPERTIES ON THERMAL EFFICIENCY

The thermal efficiency of a cycle has been defined previously, in terms of specific quantities, as

$$\eta_{th} = \frac{w_{net}}{q_{in}} \quad (5.1)$$

where

w_{net} = net work output from the cycle per unit mass of fluid

and

q_{in} = energy addition to the cycle per unit mass of fluid.

In this case q_{in} is the energy transfer to the working fluid, and does not take into account any losses (irreversibilities) in the boiler or heat transfer device. Equation (5.1) can be rewritten for the whole power plant, including the boiler or heat transfer mechanism, as

$$\eta_0 = \eta_B \eta_{th} = \frac{\omega_{net}}{-\Delta h_0} \quad (5.2)$$

where

η_0 = overall efficiency of power plant,

η_B = efficiency of boiler,

η_{th} = thermal efficiency of cycle,

ω_{net} = net work output from the cycle per *unit mass of fuel* and

Δh_0 = specific enthalpy of reaction of fuel.

This might be considered to be an unfair, and possibly misleading, method of defining the efficiency because the energy addition cannot all be turned into work, as was shown when considering exergy and availability (Chapter 4). Another definition of efficiency can be derived based on the Second Law, and this relates the work output from the cycle to the maximum work output obtainable.

The efficiency of the power plant has been related, in Eqn (5.2), to the amount of energy that has been added to the cycle by the combustion of the fuel. In the past this has been based on the enthalpy of reaction of the fuel, or usually its calorific value, Q'_p . It was shown previously (Chapter 4) that this is not the energy available for the production of work, and that the maximum available work that can be

obtained from the fuel is based on the change of its *exergy* at the dead-state conditions. Hence, the maximum available work *from unit mass of fuel* is

$$-\Delta g_0 = g_{R_0} - g_{P_0} \quad (5.3)$$

This is related to the enthalpy of formation by the equation

$$\Delta g_0 = \Delta h_0 - T_0(s_{R_0} - s_{P_0}) \quad (5.4)$$

It was shown in [Section 4.9.2](#) that $|\Delta g_0|$ could be greater than, or less than, $|\Delta h_0|$, and the difference was dependent on the structure of the fuel and the composition of the exhaust products. The efficiency of the power plant can then be redefined as

$$\eta_0 = \frac{\omega_{\text{net}}}{-\Delta g_0} \quad (5.5)$$

where

ω_{net} = actual net work output from the cycle per *unit mass of fuel* and

Δg_0 = change of Gibbs energy caused by combustion

= maximum net work obtainable from unit mass of fuel.

[Equation \(5.5\)](#) is often referred to as the *Second Law Efficiency*, because the work output is related to the available energy in the fuel, rather than its enthalpy change. The actual effect on thermal efficiency of using the change of Gibbs energy instead of the enthalpy of reaction is usually small (a few percent).

5.2 RATIONAL EFFICIENCY

When the efficiencies defined in [Eqns \(5.2\) and \(5.5\)](#) are evaluated they contain terms which relate to the ‘efficiency’ of the energy transfer device (boiler) in transferring energy from the combustion gases to the working fluid. These effects are usually neglected when considering cycles, and the energy added is related to the change in enthalpy of the working fluid as it passes through the boiler, superheater, etc. Actual engine cycles will be considered later. First, a general heat engine will be considered, see [Fig 5.1](#). For convenience, the values will all be taken as specific values per unit mass flow of working fluid.

The engine shown in [Fig 5.1](#) could be either a wholly reversible (i.e. internally and externally) one or an irreversible one. If it were internally reversible then it would follow the Carnot cycle 1-2-3s-4-1. If it were irreversible then it would follow the cycle 1-2-3-4-1. Consider first the reversible cycle. The efficiency of this cycle is

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{(T_1 - T_{3s})(s_2 - s_1)}{T_1(s_2 - s_1)} = \frac{(T'_H - T'_L)(s_2 - s_1)}{T'_H(s_2 - s_1)} \quad (5.6)$$

which is the efficiency of an internally reversible engine operating between the temperature limits T'_H and T'_L . This efficiency will always be less than unity unless $T'_L = 0$. However, the Second Law states that it is never possible to convert the full energy content of the energy supplied into work, and the maximum net work that can be achieved is

$$\hat{w}_{\text{net}} = b_2 - b_1 = h_2 - h_1 - T_0(s_2 - s_1) \quad (5.7)$$

where T_0 is the temperature of the dead state.

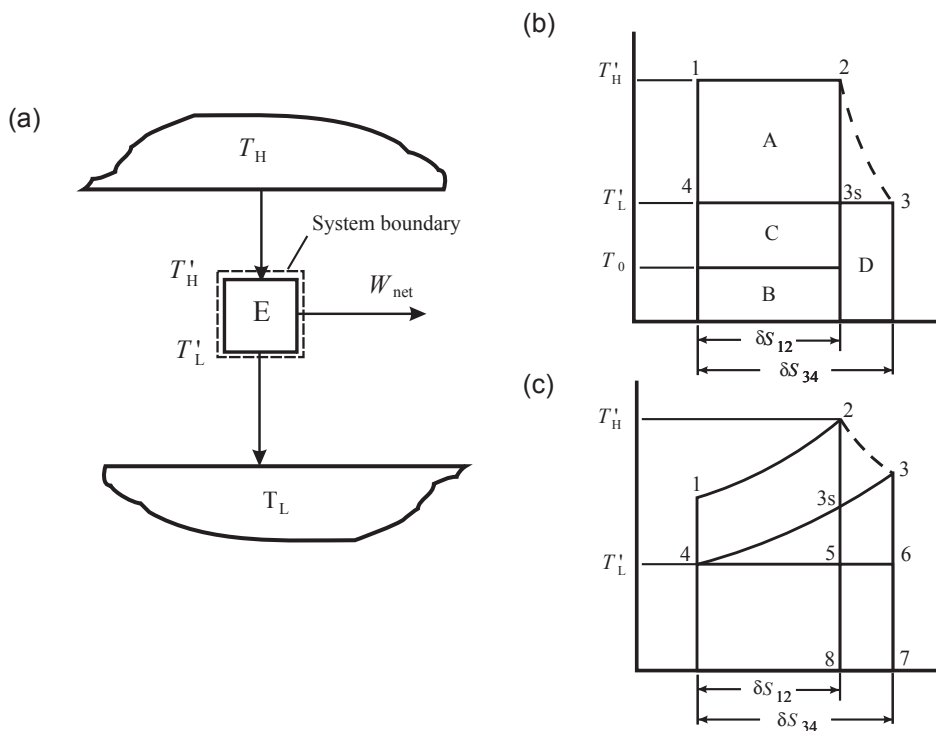


FIGURE 5.1

A heat engine operating between two reservoirs. (a) Schematic diagram of engine, (b) T - s diagram for engine which receives and rejects energy isothermally, (c) T - s diagram for engine which receives and rejects energy non-isothermally.

Hence, the Second Law efficiency of the heat engine is

$$\begin{aligned}
 \eta_{2,\text{th}} &= \frac{w_{\text{net}}}{\hat{w}_{\text{net}}} = \frac{(T_1 - T_{3s})(s_2 - s_1)}{h_2 - h_1 - T_0(s_2 - s_1)} = \frac{T_1(s_2 - s_1) - T_{3s}(s_2 - s_1)}{h_2 - h_1 - T_0(s_2 - s_1)} = \frac{h_2 - h_1 - T_{3s}(s_2 - s_1)}{h_2 - h_1 - T_0(s_2 - s_1)} \\
 &= \frac{h_2 - h_1 - T_0(s_2 - s_1) - (T_{3s} - T_0)(s_2 - s_1)}{h_2 - h_1 - T_0(s_2 - s_1)} = 1 - \frac{(T_{3s} - T_0)(s_2 - s_1)}{h_2 - h_1 - T_0(s_2 - s_1)}
 \end{aligned} \tag{5.8}$$

where $\eta_{2,\text{th}}$ is called the Second Law efficiency, or the *rational efficiency*, η_R . This result can be interpreted on Fig 5.1(b) in the following way. Examination of Eqn (5.8) shows that if the $T_{3s} = T_0$ then $\eta_R = 1.0$. This because when $T_{3s} = T_0$ then area C is zero (i.e. the line at $T'_L = T_0$ is coincident with that at T_{3s}). Then the difference in the enthalpies, $h_2 - h_1$, is depicted by areas A + B, and the unavailable energy, $T_0(s_2 - s_1)$ by area B, and hence the energy available to produce work is area A. This shows that the cycle is as efficient as an internally reversible cycle operating between the

same two temperature limits (T_{3s} and T_1). If T_0 is not equal to T_3 , but is equal to a lower temperature, T'_L , then the rational efficiency will be less than unity because energy which has the capacity to do work is being rejected. This is depicted by area C in Fig 5.1(b), and the rational efficiency becomes

$$\eta_R = \frac{\text{Areas (A + B + C)} - \text{Areas (B + C)}}{\text{Areas (A + B + C)} - \text{Area (B)}} = \frac{\text{Area A}}{\text{Areas (A + C)}} < 1 \quad (5.9)$$

Consideration of Eqn (5.8) shows that it is made up of a number of different components which can be categorised as available energy and unavailable energy. This is similar to exergy, as shown below

$$b = a - a_0 = \underbrace{h - h_0}_{\text{available energy}} - \underbrace{T_0(s - s_0)}_{\text{unavailable energy}} = \underbrace{E}_{\text{available energy}} - \underbrace{\Phi}_{\text{unavailable energy}} \quad (5.10)$$

Thus Eqn (5.7) may be rewritten

$$\hat{w}_{\text{net}} = b_2 - b_1 = h_2 - h_1 - T_0(s_2 - s_1) = \delta E_{12} - \delta \Phi_{12}, \quad (5.11)$$

giving Eqn (5.8) as

$$\eta_R = \eta_{2,\text{th}} = \frac{w_{\text{net}}}{\hat{w}_{\text{net}}} = \frac{h_2 - h_1 - T_{3s}(s_2 - s_1)}{h_2 - h_1 - T_0(s_2 - s_1)} = \frac{\delta E_{12} - \delta \Phi_{12} - (T_{3s} - T_0)(s_2 - s_1)}{\delta E_{12} - \delta \Phi_{12}} \quad (5.12)$$

which can be written as

$$\eta_R = \eta_{2,\text{th}} = 1 - \frac{(T_{3s} - T)(s_2 - s_1)}{\delta E_{12} - \delta \Phi_{12}}. \quad (5.13)$$

If $T_0 = T_{3s}$ then the rational efficiency, $\eta_R = 1.0$. If $T_0 < T_{3s}$, as would be the case if there were external irreversibilities, then $\eta_R < 1.0$ because the working fluid leaving the engine still contains the capacity to do work.

If the engine is not internally reversible then the T - s diagram becomes 1-2-3-4-1, as depicted in Fig 5.1(b). The effect of the internal irreversibility is to cause the entropy at 3 to be bigger than that at $3s$, and hence the entropy difference, $\delta S_{34} > \delta S_{12}$. The effect of this is that the net work becomes

$$\begin{aligned} w_{\text{net}} &= (h_2 - h_1) - (h_3 - h_4) = T_1(s_2 - s_1) - T_3(s_3 - s_4) \\ &= T_1(s_2 - s_1) - T_3(s_{3s} - s_4) - T_3(s_3 - s_{3s}) \\ &= h_2 - h_1 - T_0(s_2 - s_1) - (T_3 - T_0)(s_2 - s_1) - T_3(s_3 - s_{3s}) \\ &= \delta E_{12} - \delta \Phi_{12} - (T_3 - T_0)(s_2 - s_1) - T_3(s_3 - s_{3s}) \end{aligned} \quad (5.14)$$

Hence, from Eqn (5.14)

$$\eta_R = \eta_{2,\text{th}} = 1 - \frac{(T_3 - T_0)(s_2 - s_1) + T_3(s_3 - s_{3s})}{\delta E_{12} - \delta \Phi_{12}}. \quad (5.15)$$

In the case of the irreversible engine even if $T_0 = T_3$ the rational efficiency is still less than unity because of the increase in entropy caused by the irreversible expansion from 2 to 3. The loss of available energy, in this irreversibility, is depicted by area D in Fig 5.1(b). In the case of $T_0 = T_3$,

$$\eta_R = 1 - \frac{T_3(s_3 - s_{3s})}{\delta E_{12} - \delta \Phi_{12}}. \quad (5.16)$$

If the dead-state temperature is less than T_3 then the rational efficiency is even lower because of the loss of available energy shown as area C on Fig 5.1(b).

Up till now it has been assumed that the cycle is similar to a Carnot cycle, with isothermal heat supply and rejection. Such a cycle is typical of one in which the working fluid is a vapour which can change phase. However, many cycles use air as a working fluid (e.g. Otto, Diesel, Joule cycles, etc. – see Chapter 3), and in this case it is not possible to supply and reject heat at constant temperature. A general cycle of this type is shown in Fig 5.1(c), and it can be seen that the heat is supplied over a range of temperatures from T_1 to T_2 , and rejected over a range of temperatures from T_3 to T_4 . If only the heat engine is considered then it is possible to neglect the temperature difference of the heat supply: this is an *external* irreversibility.

However, it is not possible to neglect the varying temperature of heat rejection, because the engine is rejecting available energy to the surroundings. If the cycle is reversible, i.e. 1-2-3_s-4-1, then the rational efficiency of the cycle is

$$\eta_R = \frac{w_{\text{net}}}{b_2 - b_1} \quad (5.17)$$

If the cycle shown is a Joule (gas turbine) cycle (see Chapter 3) then

$$\begin{aligned} w_{\text{net}} &= h_2 - h_1 - (h_{3s} - h_4) = b_2 - b_1 + T_0(s_2 - s_1) - \{b_{3s} - b_4 + T_0(s_{3s} - s_4)\} \\ &= b_2 - b_1 - \{b_{3s} - b_4\} \end{aligned} \quad (5.18)$$

Hence, the net work is made up of the maximum net work supplied and the maximum net work rejected, i.e.

$$w_{\text{net}} = [\hat{w}_{\text{net}}]_{\text{supplied}} - [\hat{w}_{\text{net}}]_{\text{rejected}} \quad (5.19)$$

These terms are defined by areas 1-2-3_s-5-1 and 4-3_s-5-4 respectively in Fig 5.1(c). Thus the rational efficiency of an engine operating on a Joule cycle is

$$\eta_R = \frac{b_2 - b_1 - (b_{3s} - b_4)}{b_2 - b_1} = 1 - \frac{b_{3s} - b_4}{b_2 - b_1} \quad (5.20)$$

Equation (5.20) shows that it is never possible for an engine operating on a cycle in which the temperature of energy rejection varies to achieve a rational efficiency of 100%. This is simply because there will always be energy available to produce work in the rejected heat.

If the cycle is not reversible, e.g. if the expansion is irreversible, then the cycle is defined by 1-2-3-4-1, and there is an increase in entropy from 2 to 3. Eqn (5.18) then becomes

$$\begin{aligned} w_{\text{net}} &= h_2 - h_1 - (h_3 - h_4) = b_2 - b_1 + T_0(s_2 - s_1) - \{b_3 - b_4 + T_0(s_3 - s_4)\} \\ &= \underbrace{b_2 - b_1}_{\text{area 1-2-3s-5-4-1}} - \underbrace{(b_3 - b_4)}_{\text{area 4-3-6-4}} - \underbrace{T_0(s_3 - s_{3s})}_{\text{area 5-6-7-8-5}} \end{aligned} \quad (5.21)$$

Equation (5.21) shows that the irreversibility of the expansion process reduces the net work significantly by (1) increasing the amount of exergy rejected and (2) increasing the irreversibility of the cycle. The rational efficiency of this cycle is

$$\eta_R = 1 - \frac{(b_3 - b_4) - T_0(s_3 - s_{3s})}{b_2 - b_3} \quad (5.22)$$

The irreversible cycle can be seen to be less efficient than the reversible one by comparing Eqns (5.20) and (5.22). In the case shown $b_2 - b_1$ is the same for both cycles, but $b_3 - b_4 > b_{3s} - b_4$, and in addition the irreversibility $T_0(s_3 - s_{3s})$ has been introduced.

5.3 RANKINE CYCLE

It was stated above that the efficiency of a cycle is often evaluated neglecting the irreversibility of the heat transfer to the system. Such a situation can be seen on the steam plant shown in Fig 5.2(a), which can be represented by the simplified diagram shown in Fig 5.2(b), which shows the heat engine contained in system B.

Now, consider the passage of the working fluid through system A. It enters system A with a state defined by 3 on the Rankine cycle (see Fig 5.3), and leaves system A with a state defined by 2. The usual definition of thermal efficiency given in Eqn (5.1) results in

$$\eta_{th} = \frac{w_{net}}{h_3 - h_2} \quad (5.23)$$

where

w_{net} = specific net work output from the cycle.

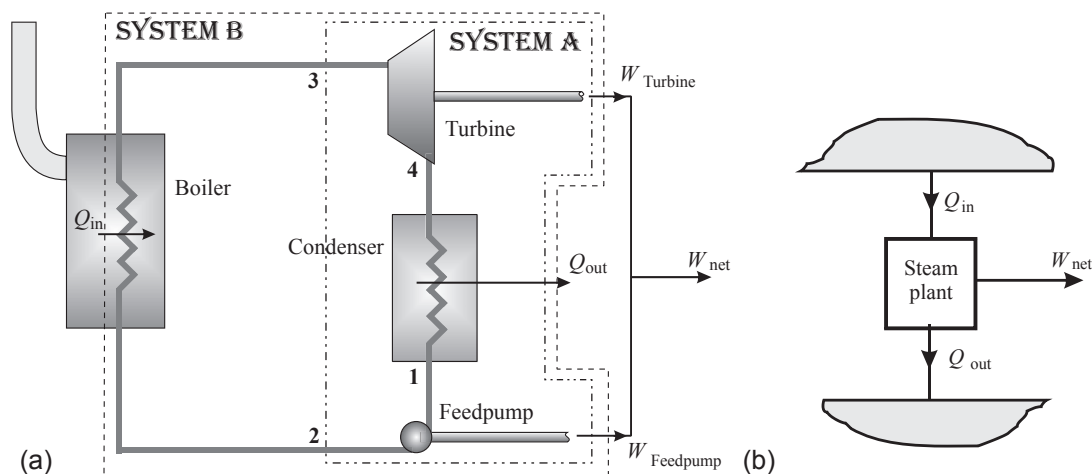
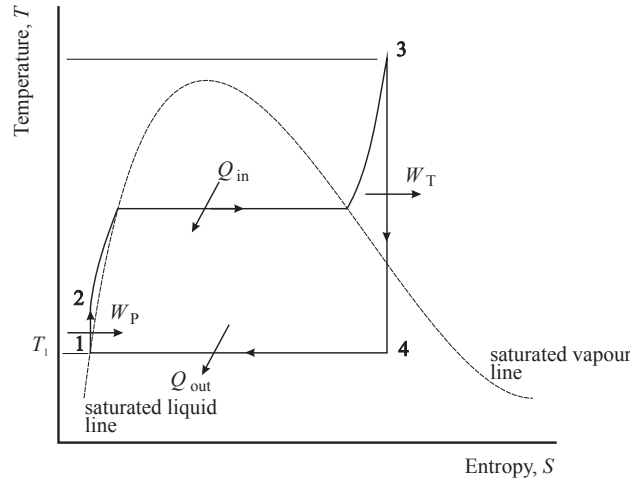


FIGURE 5.2

Steam turbine power plant. (a) Schematic diagram of plant; (b) plant shown as 'heat engine'.

**FIGURE 5.3**

Rankine cycle for steam turbine plant.

However, from the definition of exergy, the maximum work (per unit mass of steam) that is obtainable from the fluid is

$$\hat{w}_{\text{net}} = b_3 - b_2 = (h_3 - h_2) - T_0(s_3 - s_2) \quad (5.7)$$

Examination of Eqn (5.7) shows that it consists of two terms: a difference of the enthalpies between states 3 and 2, and the product of the dead-state temperature, T_0 , and the difference of the entropies between states 3 and 2. The first term is obviously equal to the energy added between states 2 and 3, and is q_{in} . Considering the other term, the energy rejected to the cold reservoir is

$$q_{\text{out}} = h_4 - h_1 = T_1(s_4 - s_1) \quad (5.24)$$

If the condenser were of infinite size then the temperature at 1 could be equal to the environmental temperature, T_0 . Also, if the feed pump and the turbine were both reversible then processes 3-4 and 1-2 would be isentropic and Eqn (5.24) could be reduced to

$$q_{\text{out}} = h_4 - h_1 = T_0(s_3 - s_2) \quad (5.25)$$

Hence, for an internally reversible engine the maximum net work output is the sum of the heat supplied and the heat rejected, as shown previously simply from considerations of energy. If the cycle was not reversible due to inefficiencies in the turbine and feed pump, then the difference between the entropies at states 4 and 1 would be greater than the differences at states 2 and 3, and q_{out} would be greater than in the ideal case. Hence, the cycle would be less efficient.

The thermal efficiency of an ideal Rankine cycle (i.e. one in which the turbine and feed pump are both isentropic) is given by

$$\eta_{\text{Rankine}} = \frac{\hat{w}_{\text{net}}}{h_3 - h_2} = \frac{b_3 - b_2}{h_3 - h_2} \quad (5.26)$$

If the turbine and feed pump of the cycle are not isentropic then the work output will be less than that of the ideal Rankine cycle and it is possible to define the *efficiency ratio* as

$$\text{Efficiency ratio} = \frac{\eta_{\text{cycle}}}{\eta_{\text{Rankine}}} \quad (5.27)$$

Substituting from Eqns (5.23) and (5.26) gives

$$\begin{aligned} \text{Efficiency ratio} &= \frac{w_{\text{net}}}{h_3 - h_2} \cdot \frac{h_3 - h_2}{b_3 - b_2} = \frac{w_{\text{net}}}{b_3 - b_2} \\ &= \text{rational efficiency, } \eta_R \end{aligned} \quad (5.28)$$

This means that a steam turbine which operates on a *reversible* Rankine cycle will have a rational efficiency of 100% because the condenser temperature is T_0 . If there are any irreversibilities then the rational efficiency will be less than 100%. Rational efficiency shows the scope for improving the device within the constraints of, say, peak pressure and temperature. If the rational efficiency is low then the efficiency can be improved significantly, whereas if it is high then not much improvement is possible.

It has to be remembered that these definitions of rational efficiency for a steam plant cycle are based on the dead-state temperature being made equal to the condenser temperature. If another temperature is chosen then the rational efficiency will be reduced as shown in Eqn (5.22). It will be shown that this results in a rational efficiency of unity for an ideal (internally reversible) Rankine cycle, and such an approach can be used to indicate how far an actual (irreversible) steam plant cycle falls short of the yardstick set by the reversible one. However, this approach also masks the ‘cost’ of external irreversibilities between the working fluid in the condenser and the true dead state of environmental conditions. These effects are discussed in the examples.

When the term rational efficiency is applied to an air-standard cycle it is never possible to achieve a value of unity because the temperature at which energy is rejected is not constant. This will also be considered in the examples by reference to the Joule cycle for a gas turbine.

5.4 EXAMPLES

5.4.1 STEAM TURBINE CYCLES

- Q1.** A steam turbine operates on a basic Rankine cycle with a maximum pressure of 20 bar and a condenser pressure of 0.5 bar. Evaluate the thermal efficiency of the plant. Calculate the maximum net work available from the cycle, and evaluate the rational efficiency of the cycle.

Solution

The T - s diagram for the Rankine cycle is shown in Fig 5.4. The parameters for the state points on cycle 1-2-3-4-6-1 will now be evaluated.

Conditions at 4

$$\begin{aligned} p_4 &= 20 \text{ bar}; \quad x_4 = 1 \\ t_s &= 212.4^\circ\text{C}; \quad h_g = 2799 \text{ kJ/kg}; \quad s_g = 6.340 \text{ kJ/kg K} \end{aligned}$$

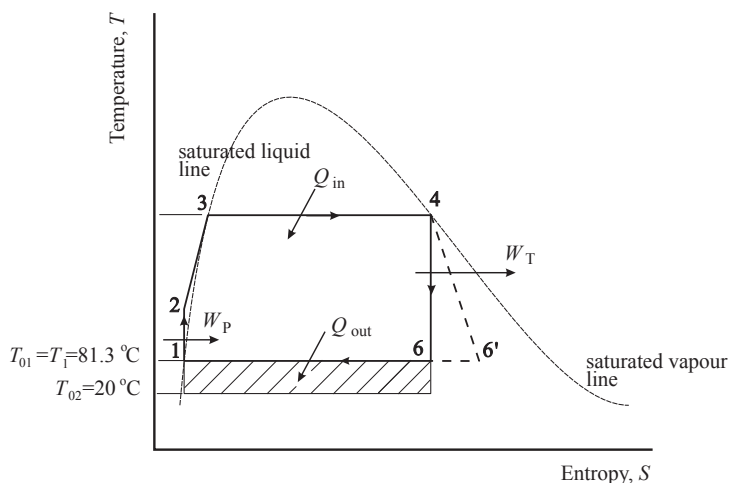


FIGURE 5.4

Temperature–entropy diagram for basic Rankine cycle.

Conditions at 6

$$p_6 = 0.5 \text{ bar}; \quad s_6 = 6.340 \text{ kJ/kg K}.$$

$$t_s = 81.3 \text{ °C}; \quad h_g = 2645 \text{ kJ/kg}; \quad h_f = 340 \text{ kJ/kg}; \quad s_g = 7.593 \text{ kJ/kg K}; \quad s_f = 1.091 \text{ kJ/kg K}.$$

thus

$$x_6 = \frac{6.340 - 1.091}{7.593 - 1.091} = 0.8073$$

$$h_6 = x_6 h_g + (1 - x_6) h_f = 0.8073 \times 2645 + (1 - 0.8073) \times 340 = 2200.8 \text{ kJ/kg}$$

Conditions at 1

$$p_1 = 0.5 \text{ bar}; \quad s_1 = 1.091 \text{ kJ/kg K}; \quad h_1 = 340 \text{ kJ/kg}.$$

$$v_1 = v_f = 0.001029 \text{ m}^3/\text{kg}.$$

Conditions at 2

$$p_2 = 20 \text{ bar}; \quad s_2 = 1.091 \text{ kJ/kg K}.$$

$$v_2 = 0.001029 + 0.2 \times (-0.0006 \times 10^{-2}) = 0.001028 \text{ kJ/kg K}.$$

Hence feed pump work,

$$w_P = w_{12} = -v dp = -dh_{12}.$$

$$= -(0.001029 + 0.001028)/2 \times 19.5 \times 100 = -2.005 \text{ kJ/kg}.$$

$$h_2 = h_1 + dh_{12} = 340 + 2.005 = 342.0 \text{ kJ/kg}.$$

Work done by turbine,

$$w_T = h_4 - h_6 = 2799 - 2200.8 = 598.2 \text{ kJ/kg K.}$$

$$\text{Thermal efficiency of the cycle is } \eta_{th} = \frac{w_{net}}{q_{in}} = \frac{w_T + w_P}{h_4 - h_2} = \frac{598.2 - 2.0}{2799 - 342.0} = 0.243$$

The maximum net work available can be evaluated from the change of exergy between state points 4 and 2. Hence,

$$\hat{w}_{net} = b_4 - b_2.$$

It is necessary to define a dead-state condition. This is arbitrary, and in this case will be taken as the condition at 1. Hence, $p_0 = 0.5 \text{ bar}$; $T_0 = 81.3 + 273 = 354.3 \text{ K}$.

Thus,

$$b_4 = h_4 - T_0 s_4 - (h_0 - T_0 s_0) = 2799 - 354.3 \times 6.340 - a_0 = 552.7 - a_0 \text{ kJ/kg};$$

$$b_2 = h_2 - T_0 s_2 - (h_0 - T_0 s_0) = 342.0 - 354.3 \times 1.091 - a_0 = -44.5 - a_0 \text{ kJ/kg}.$$

Hence,

$$\hat{w}_{net} = 552.7 - (-44.5) = 597.2 \text{ kJ/kg}.$$

Thus, the rational efficiency is

$$\eta_R = \frac{w_{net}}{b_4 - b_2} = \frac{w_{net}}{\hat{w}_{net}} = \frac{598.2 - 2.0}{597.2} = 1.00.$$

In this case the rational efficiency is equal to unity because the turbine and feed pump have isentropic efficiencies of 100%, and it was assumed that the temperature of the working fluid in the condenser was equal to the dead-state (ambient) temperature. Hence, although the cycle is not very efficient, at 24.3%, there is no scope for improving it *unless* the operating conditions are changed.

It is possible to evaluate the rational efficiency of a steam plant operating on a Rankine cycle in which the condenser temperature is above the ambient temperature. If the dead-state temperature in the previous example was taken as 20 °C, rather than 81.3 °C then the following values would be obtained.

$$b_4 = h_4 - T_0 s_4 - a_0 = 2799 - 293 \times 6.340 - a_0 = 941.4 - a_0 \text{ kJ/kg};$$

$$b_2 = h_2 - T_0 s_2 - a_0 = 342.1 - 293 \times 1.091 - a_0 = 22.4 - a_0 \text{ kJ/kg}.$$

Hence,

$$\hat{w}_{net} = 941.4 - 22.4 = 919.0 \text{ kJ/kg}.$$

Thus, the rational efficiency is

$$\eta_R = \frac{w_{net}}{b_4 - b_2} = \frac{w_{net}}{\hat{w}_{net}} = \frac{598.2 - 2.0}{919.0} = 0.649$$

This result shows that irreversibilities in the condenser producing a temperature drop of 81.3–20 °C would reduce the potential efficiency of the power plant significantly. Basically this irreversibility is equivalent to a loss of potential work equal to the area of the T – s diagram bounded by the initial dead-state temperature of 81.3 °C and the final one of 20 °C and the entropy difference, as shown in Fig 5.4, i.e. $(T_{01} - T_{02})(s_4 - s_2)$, which is equal to $(354.3 - 293) \times (6.340 - 1.091) = 321.8 \text{ kJ/kg}$.

- Q2.** Re-evaluate the parameters for the steam plant in Q1 based on $t_0 = 81.3^\circ\text{C}$ if (a) The isentropic efficiency of the turbine is 80%; (b) The isentropic efficiency of the feed pump is 70%; (c) If the efficiency of the components is the combination of those given in (a) and (b).

Solution

(a) Turbine efficiency, $\eta_T = 80\%$.

If the turbine efficiency is 80% then the work output of the turbine becomes

$$w_T = \eta_T (w_T)_{\text{isen}} = 0.80 \times 598.2 = 478.6 \text{ kJ/kg.}$$

Hence, the thermal efficiency of the cycle is $\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_T + w_P}{h_4 - h_2} = \frac{478.6 - 2.0}{2799 - 342.0} = 0.194$
The rational efficiency is

$$\eta_R = \frac{[w_{\text{net}}]_{\text{actual}}}{b_4 - b_2} = \frac{[w_{\text{net}}]_{\text{actual}}}{\hat{w}_{\text{net}}} = \frac{478.6 - 2.0}{597.2} = 0.798.$$

The rational efficiency has been significantly reduced by the inefficiency of the turbine, and the rational efficiency is approximately equal to the isentropic efficiency of the turbine.

(b) Feed pump efficiency, $\eta_P = 70\%$.

The feed pump work becomes

$$w_P = \frac{(w_P)_{\text{isen}}}{\eta_P} = \frac{2.0}{0.7} = -2.864 \text{ kJ/kg.}$$

$$h_{2'} = h_1 + dh_{12'} = 340 + 2.864 = 342.9 \text{ kJ/kg.}$$

The thermal efficiency of the cycle becomes $\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_T + w_P}{h_4 - h_{2'}} = \frac{598.2 - 2.864}{2799 - 342.9} = 0.242.$

The exergy at $2'$ may be evaluated approximately by assuming that the entropy does not change significantly over the pumping process, i.e. $s_{2'} = s_1$.

Hence

$$b_{2'} = h_{2'} - T_0 s_{2'} - a_0 = 342.9 - 354.3 \times 1.091 - a_0 = -43.6 - a_0 \text{ kJ/kg.}$$

The rational efficiency is

$$\eta_R = \frac{[w_{\text{net}}]_{\text{actual}}}{b_4 - b_{2'}} = \frac{[w_{\text{net}}]_{\text{actual}}}{\hat{w}_{\text{net}}} = \frac{598.2 - 2.86}{597.2} = 0.997$$

The reduction in thermal efficiency is small and the rational efficiency is almost 1. Hence, the Rankine cycle is not much affected by inefficiencies in the feed pump.

(c) Turbine efficiency, $\eta_T = 80\%$; feed pump efficiency, $\eta_P = 70\%$.

The thermal efficiency is $\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_T + w_P}{h_4 - h_{2'}} = \frac{478.6 - 2.86}{2799 - 342.9} = 0.194$

The rational efficiency is $\eta_R = \frac{[w_{\text{net}}]_{\text{actual}}}{b_4 - b_{2'}} = \frac{[w_{\text{net}}]_{\text{actual}}}{\hat{w}_{\text{net}}} = \frac{478.6 - 2.86}{597.2} = 0.797$

Q3. Steam turbine cycles

The steam plant in question Q2 is modified so that the steam is superheated before entering the turbine so that the exit conditions from the turbine of the ideal cycle are dry saturated. Evaluate the

parameters for the steam plant if (a) the isentropic efficiency of the turbine is 80%; (b) the isentropic efficiency of the feed pump is 70%; (c) if the efficiency of the components is the combination of those given in (a) and (b). Assume that $t_0 = 81.3^\circ\text{C}$.

Solution

This cycle is shown in Fig 5.5.

Conditions at 6

$$p_6 = 0.5 \text{ bar;}$$

$$t_s = 81.3^\circ\text{C; } h_g = 2645 \text{ kJ/kg; } h_f = 340 \text{ kJ/kg; } s_g = 7.593 \text{ kJ/kg K; } s_f = 1.091 \text{ kJ/kg K.}$$

$$h_6 = 2645 \text{ kJ/kg; } s_6 = 7.593 \text{ kJ/kg K.}$$

Conditions at 5

$$p_5 = 20 \text{ bar; } s_5 = s_6 = 7.593 \text{ kJ/kg K.}$$

$$\text{Hence, } t_5 = 500 + \frac{7.593 - 7.431}{7.701 - 7.431} \times 100 = 560^\circ\text{C;}$$

$$h_5 = 3467 + 0.6 \times (3690 - 3467) = 3601 \text{ kJ/kg.}$$

Work done by turbine,

$$w_T = h_5 - h_6 = 3601 - 2645 = 956 \text{ kJ/kg K.}$$

$$\text{Thermal efficiency of the cycle is } \eta_{th} = \frac{w_{net}}{q_{in}} = \frac{w_T + w_P}{h_5 - h_2} = \frac{956 - 2.0}{3601 - 342.0} = 0.292$$

$$b_5 = h_5 - T_0 s_5 - a_0 = 3601 - 354.3 \times 7.593 - a_0 = 910.8 - a_0 \text{ kJ/kg;}$$

$$b_2 = h_2 - T_0 s_2 - a_0 = 342.1 - 354.3 \times 1.091 - a_0 = -44.4 - a_0 \text{ kJ/kg.}$$

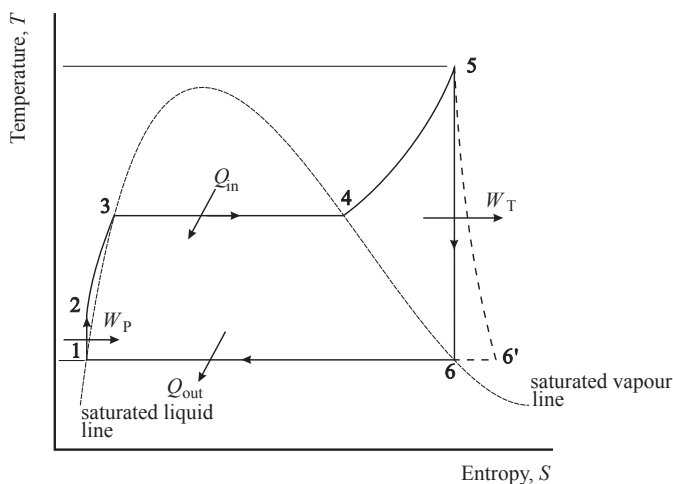


FIGURE 5.5

Temperature–entropy diagram for Rankine cycle with superheat.

The rational efficiency is

$$\eta_R = \frac{[w_{\text{net}}]_{\text{actual}}}{b_4 - b_2} = \frac{[w_{\text{net}}]_{\text{actual}}}{\hat{w}_{\text{net}}} = \frac{956 - 2.11}{955.2} \cong 1.00$$

(a) Turbine efficiency, $\eta_T = 80\%$.

$$w_T = \eta_T (w_T)_{\text{isen}} = 0.80 \times 956 = 764.8 \text{ kJ/kg.}$$

Hence, the thermal efficiency of the cycle is $\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_T + w_P}{h_4 - h_2} = \frac{764.8 - 2.0}{3601 - 342.0} = 0.234$
The rational efficiency is

$$\eta_R = \frac{[w_{\text{net}}]_{\text{actual}}}{b_5 - b_2} = \frac{[w_{\text{net}}]_{\text{actual}}}{\hat{w}_{\text{net}}} = \frac{764.8 - 2.0}{955.2} = 0.799.$$

Hence, again, the effect of the turbine efficiency is to reduce the rational efficiency by an amount almost equal to its isentropic efficiency.

(b) Feed pump efficiency, $\eta_P = 70\%$.

The effect on the feed pump work is the same as above, and the thermal efficiency of the cycle becomes

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_T + w_P}{h_4 - h_{2'}} = \frac{956 - 2.86}{3601 - 342.8} = 0.293.$$

The rational efficiency is

$$\eta_R = \frac{[w_{\text{net}}]_{\text{actual}}}{b_5 - b_{2'}} = \frac{[w_{\text{net}}]_{\text{actual}}}{\hat{w}_{\text{net}}} = \frac{956 - 2.86}{910.8 - (-43.7)} = 0.998$$

Again, the reduction in thermal efficiency is small and the rational efficiency is almost 1.

(c) Turbine efficiency, $\eta_T = 80\%$; feed pump efficiency, $\eta_P = 70\%$.

The thermal efficiency is $\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_T + w_P}{h_5 - h_{2'}} = \frac{764.8 - 2.86}{3601 - 342.8} = 0.234$

The rational efficiency is $\eta_R = \frac{[w_{\text{net}}]_{\text{actual}}}{b_5 - b_{2'}} = \frac{[w_{\text{net}}]_{\text{actual}}}{\hat{w}_{\text{net}}} = \frac{764.8 - 2.86}{955.2} = 0.798$

It can be seen that both the basic and superheated Rankine cycles are equally affected by inefficiencies in the individual components. The rational efficiency is an estimate of how close the cycle comes to the internally reversible cycle.

Q4. Gas turbine cycle

A gas turbine operating on an ideal Joule cycle, has a pressure ratio of 20:1, and a peak temperature of 1200 K. Calculate the net work output, the maximum work output, the thermal efficiency and the rational efficiency of the cycle. Assume that the working fluid is air with a value of $\kappa = 1.4$ and a specific gas constant $R = 0.287 \text{ kJ/kg K}$. The inlet conditions at 1 are 1 bar and 300 K, and these should be taken as the dead-state conditions also.

Solution

The ideal Joule cycle is depicted by 1-2s-3-4s-1 on Fig 5.6(a). The relationship between entropy and the primitive properties for an ideal gas is

$$s - s_0 = c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0}.$$

From the parameters given, $c_p = \frac{\kappa R}{\kappa - 1} = \frac{1.4 \times 0.287}{0.4} = 1.0045 \text{ kJ/kg K}$.

The compression process from 1 to 2s is isentropic, and hence $T_{2s} = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} = 300 \times 20^{\frac{0.4}{1.4}} = 706.1 \text{ K}$

The isentropic work done in the compressor is

$$w_{C_{\text{isen}}} = -dh_{12s} = c_p(T_1 - T_{2s}) = -1.0045 \times (706.1 - 300) = -407.9 \text{ kJ/kg}.$$

The energy added to the cycle is

$$q_{2s3} = c_p(T_3 - T_{2s}) = 1.0045 \times (1200 - 706.1) = 496.1 \text{ kJ/kg}.$$

For an isentropic expansion from 3 to 4s

$$T_{4s} = T_3 \left(\frac{p_{4s}}{p_3} \right)^{\frac{\kappa-1}{\kappa}} = 1200 \times \left(\frac{1}{20} \right)^{\frac{0.4}{1.4}} = 509.9 \text{ K}$$

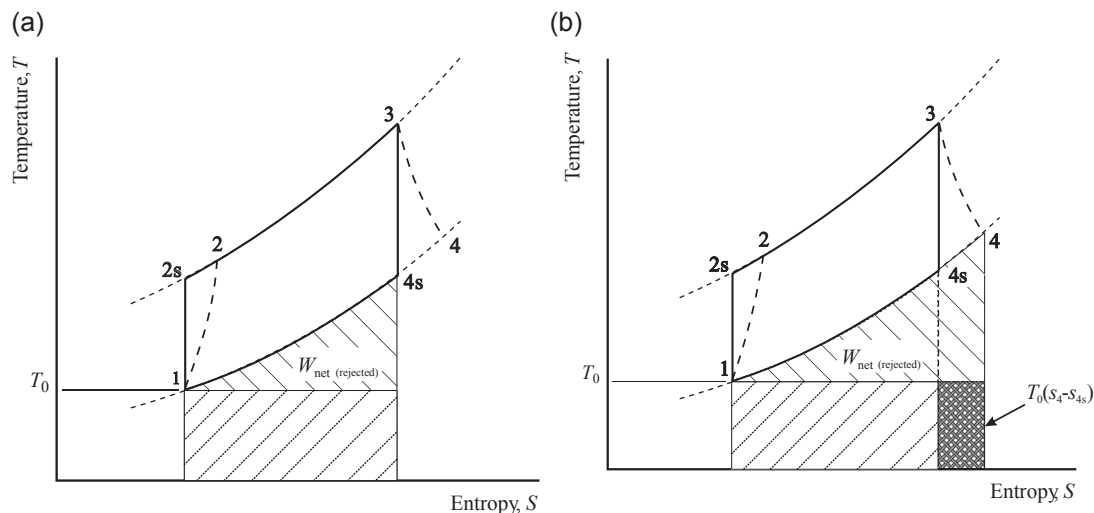


FIGURE 5.6

(a) Temperature–entropy diagram for Joule cycle. (b) Temperature–entropy diagram for Joule cycle with irreversible compression and expansion.

Hence the isentropic turbine work is

$$w_{T_{\text{isen}}} = c_p(T_3 - T_{4s}) = 1.0045 \times (1200 - 509.9) = 693.2 \text{ kJ/kg}.$$

The net work from the cycle is $w_{\text{net}} = w_T + w_C = 693.2 + (-407.9) = 285.3 \text{ kJ/kg}$ and the thermal efficiency is $\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{2s3}} = \frac{285.3}{496.1} = 0.575$.

This value is equal to the standard expression for the efficiency of a Joule cycle, defined as $\eta_{\text{th}} = 1 - \frac{1}{r_p^{\frac{\kappa-1}{\kappa}}}$, see Chapter 3.

The maximum net work output is defined by

$$\hat{w}_{\text{net}} = b_3 - b_2.$$

Now, the values of exergy are defined, for a perfect gas as

$$b = (h - T_0 s) - (h_0 - T_0 s_0) = (h - h_0) - T_0(s - s_0) = c_p \left\{ (T - T_0) - T_0 \left(\ln \frac{T}{T_0} - \frac{\kappa - 1}{\kappa} \ln \frac{p}{p_0} \right) \right\}.$$

Thus, along an isobar,

$$b = c_p \left\{ (T - T_0) - T_0 \ln \frac{T}{T_0} \right\}.$$

Since both 2s and 3 are at the same pressure

$$b_3 - b_{2s} = c_p \left\{ (T_3 - T_0) - T_0 \ln \frac{T_3}{T_0} - \left[(T_2 - T_0) - T_0 \ln \frac{T_2}{T_0} \right] \right\} = c_p \left\{ (T_3 - T_2) - T_0 \ln \frac{T_3}{T_2} \right\}$$

Thus

$$\hat{w}_{\text{net}} = 1.0045 \times \left\{ (1200 - 706.1) - 300 \ln \frac{1200}{706.1} \right\} = 336.3 \text{ kJ/kg}.$$

The rational efficiency of the cycle based on these dead state conditions is

$$\eta_R = \frac{w_{\text{net}}}{\hat{w}_{\text{net}}} = \frac{285.3}{336.3} = 0.848.$$

This means that the ideal Joule cycle is only capable of extracting 84.8% of the maximum net work from the working fluid, whereas under similar conditions (with the dead-state temperature defined as the minimum cycle temperature) the Rankine cycle had a rational efficiency of 100%. The reason for this is that the energy rejected by the Joule cycle, from 4s to 1, still has the potential to do work. The maximum net work obtainable from the rejected energy is $b_{4s} - b_1$. This is equal to

$$\begin{aligned} [\hat{w}_{\text{net}}]_{\text{rejected}} &= b_{4s} - b_1 = c_p \left\{ (T_{4s} - T_1) - T_0 \ln \frac{T_{4s}}{T_1} \right\} \\ &= 1.0045 \times \left\{ (509.9 - 300) - 300 \ln \frac{509.9}{300} \right\} = 50.99 \text{ kJ/kg}. \end{aligned}$$

This term is shown on Fig 5.6(a), and is energy which is unavailable for the production of work.

If the efficiencies of the turbine and compressor are not 100% then the T - s diagram is shown in Fig 5.6(b). It can be seen that the rejected energy is larger in this case.

Q5. Gas turbine cycles

For the gas turbine cycle defined in Q4, calculate the effect of (a) a turbine isentropic efficiency of 80%; (b) a compressor isentropic efficiency of 80% and (c) the combined effect of both inefficiencies.

Solution

(a) Turbine isentropic efficiency, $\eta_T = 80\%$.

This will affect the work output of the turbine in the following way

$$w_T = \eta_T w_{T_{\text{isen}}} = 0.8 \times 693.2 = 554.6 \text{ kJ/kg.}$$

Hence

$$w_{\text{net}} = w_T + w_C = 554.6 + (-407.9) = 146.7 \text{ kJ/kg,}$$

and

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{2s3}} = \frac{146.7}{496.1} = 0.296.$$

The temperature after the turbine is $T_4 = T_3 - \eta_T \Delta T_{\text{isen}} = 1200 - 0.8 \times 690.1 = 647.9 \text{ K}$ and the entropy at 4, related to 1, is $s_4 - s_1 = c_p \ln \frac{T_4}{T_1} - R \ln \frac{p_4}{p_1} = 1.0045 \ln \frac{647.9}{300} = 0.7734 \text{ kJ/kg K.}$

Hence, the rejected maximum net work is

$$\begin{aligned} \hat{w}_{\text{net, rejected}} &= b_4 - b_1 = c_p \left\{ (T_4 - T_1) - T_0 \ln \frac{T_4}{T_1} \right\} = 1.0045 \times \left\{ (647.9 - 300) - 300 \ln \frac{647.9}{300} \right\} \\ &= 117.4 \text{ kJ/kg.} \end{aligned}$$

This is a significant increase over the rejected potential work for the ideal Joule cycle. However, in addition to the inefficiency of the turbine increasing the maximum net work rejected, it also increases the unavailable energy by the irreversibility, $T_0 (s_4 - s_{4s})$, as shown in Fig 5.6(b). This is equal to

$$T_0 (s_4 - s_{4s}) = 300 \times (0.7734 - 0.5328) = 72.2 \text{ kJ/kg}$$

Since the maximum net work is the same for this case as the ideal one then the net work is given by

$$w_{\text{net}} = \hat{w}_{\text{net}} - [\hat{w}_{\text{net}}]_{\text{rejected}} - T_0 (s_4 - s_{4s}) = 336.3 - 117.4 - 72.2 = 146.7 \text{ kJ/kg.}$$

This is the same value as found from the more basic calculation.

The rational efficiency of this cycle is $\eta_R = \frac{w_{\text{net}}}{\hat{w}_{\text{net}}} = \frac{146.7}{336.3} = 0.436.$

(b) Compressor isentropic efficiency, $\eta_C = 80\%$.

The work done in the compressor is

$$w_C = \frac{w_{C_{\text{isen}}}}{\eta_C} = -509.9 \text{ kJ/kg}$$

Temperature after compressor, at 2 is

$$T_2 = T_1 - \frac{w_C}{c_p} = 300 - \frac{(-509.9)}{1.0045} = 807.6 \text{ K}$$

The energy added to the cycle is

$$q_{23} = c_p(T_3 - T_2) = 1.0045 \times (1200 - 807.6) = 394.2 \text{ kJ/kg.}$$

The net work from the cycle is $w_{\text{net}} = w_T + w_C = 693.2 + (-509.9) = 183.3 \text{ kJ/kg}$ and the thermal efficiency is $\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{23}} = \frac{183.3}{394.2} = 0.465$.

The maximum net work output is defined by

$$\hat{w}_{\text{net}} = b_3 - b_2.$$

Since both 2 and 3 are at the same pressure

$$b_3 - b_2 = c_p \left\{ (T_3 - T_2) - T_0 \ln \frac{T_3}{T_2} \right\}$$

Thus

$$\hat{w}_{\text{net}} = 1.0045 \times \left\{ (1200 - 807.6) - 300 \ln \frac{1200}{807.6} \right\} = 273.6 \text{ kJ/kg.}$$

The rational efficiency of the cycle based on these dead-state conditions is

$$\eta_R = \frac{w_{\text{net}}}{\hat{w}_{\text{net}}} = \frac{183.3}{273.6} = 0.670.$$

The net work output of the device is made up of

$$w_{\text{net}} = \hat{w}_{\text{net}} - [\hat{w}_{\text{net}}]_{\text{rejected}} - T_0(s_2 - s_{2s}) = 273.6 - 50.9 - 40.2 = 182.5 \text{ kJ/kg.}$$

In this case, the inefficiency of the compressor has introduced a quantity of unavailable energy $T_0(s_2 - s_{2s})$, which is depicted on Fig 5.7.

(c) Compressor isentropic efficiency, $\eta_C = 80\%$ and turbine isentropic efficiency, $\eta_T = 80\%$.

This cycle combines the two inefficiencies considered above. Hence, the net work output of the cycle is

$$w_{\text{net}} = w_T + w_C = 554.6 + (-509.9) = 44.7 \text{ kJ/kg.}$$

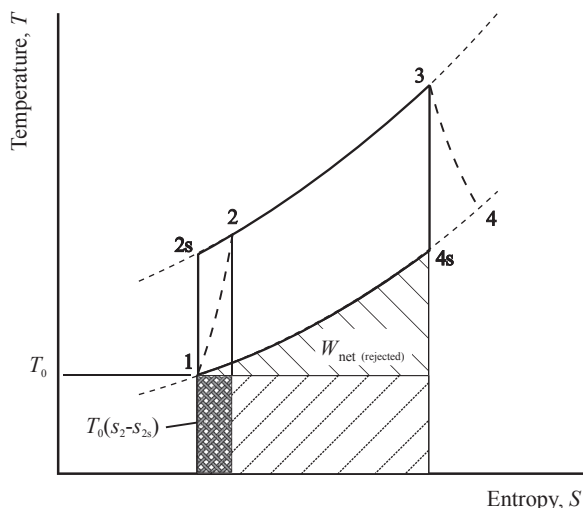
Net heat addition $q_{23} = 394.2 \text{ kJ/kg.}$

Hence, thermal efficiency is

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{23}} = \frac{44.7}{394.2} = 0.113.$$

The net work output of this cycle is made up in the following way

$$\begin{aligned} w_{\text{net}} &= \hat{w}_{\text{net}} - [\hat{w}_{\text{net}}]_{\text{rejected}} - T_0(s_4 - s_{4s}) - T_0(s_2 - s_{2s}) \\ &= 273.6 - 117.4 - 72.2 - 40.2 = 43.8 \text{ kJ/kg} \end{aligned}$$

**FIGURE 5.7**

The effect of inefficiency in the compressor.

This equation shows how the inefficiencies reduce the net work obtainable from the cycle. However, an additional quantity of net work has been lost which is not evident from the equation, and that is the reduction in maximum net work caused by the inefficiency of the compressor. The latter causes the temperature after compression to be higher than the isentropic value, and hence less fuel is necessary to reach the maximum cycle temperature.

5.5 CONCLUDING REMARKS

The concept of the Second Law, or Rational Efficiency, has been introduced. This provides a better measure of how closely a particular power-producing plant approaches its maximum achievable efficiency than does the conventional 'First Law' thermal efficiency.

It has been shown that devices in which the working fluid changes phase (e.g. steam plant) can achieve rational efficiencies of 100%, whereas those which rely on a single phase fluid (e.g. gas turbines) can never approach such a high value. The effect of irreversibility on rational efficiency has also been shown.

5.6 PROBLEMS

P5.1 In a test of a steam power plant (Fig. P5.1), the measured rate of steam supply was 7.1 kg/s when the net rate of work output was 5000 kW. The condensate left the condenser as saturated liquid at 38 °C and the superheated steam leaving the boiler was at 10 bar and 300 °C.

Neglecting the change in state of the feed water in passing through the feed pump, and taking the environment temperature as being equal to the saturation temperature of the

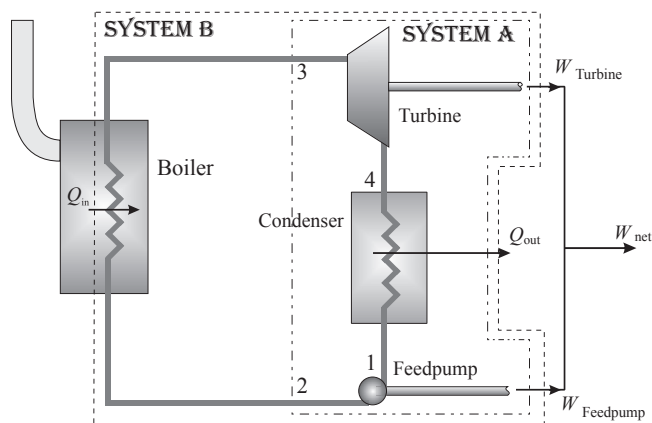


FIGURE P5.1

Steam turbine powerplant.

- condensate in the condenser, calculate the *rational efficiency* of the work-producing steam circuit (system A). Also calculate the *thermal efficiency* of the cyclic plant.
[83.3%; 24.3%]
- P5.2** Again neglecting the change in state of the feed water in passing through the feed pump, calculate the *thermal efficiency* of an ideal Rankine cycle in which the conditions of the fluid at inlet to and exit from the boiler are the same as those of the plant in P5.1. Thence confirm that the *efficiency ratio* of that plant is equal to the rational efficiency of the work-producing steam circuit calculated in P5.1.
[29.2%; 83.3%]
- P5.3** Neglecting the temperature rise of the feed water in passing through the feed pump, calculate the *mean temperature of heat reception* in the ideal Rankine cycle of P5.1. Thence make a second, alternative calculation of the *thermal efficiency* of this ideal Rankine cycle.
[440 K; 29.2%]
- P5.4** Air enters the compressor of a simple gas turbine at a pressure of 1 bar and a temperature of 25 °C. The compressor has a pressure ratio of 15, and an isentropic efficiency of 85%, and delivers air to a combustion chamber which is supplied with methane (CH_4) at 25 °C. The products of combustion leave the chamber at 1450 K and suffer a pressure loss of 5% in passing through it. They are then expanded in a turbine with an isentropic efficiency of 90% to a pressure of 1.05 bar. Calculate (a) the air–fuel ratio of the engine, (b) the power output per unit mass flow of air and (c) the rational efficiency of the engine. What is the maximum work per unit mass of exhaust gas that could be obtained if the ambient conditions are 1 bar and 25 °C?
The enthalpy of reaction based on 25 °C is $-50,000$ kJ/kg and the Gibbs energy of reaction is $-51,000$ kJ/kg. The products of combustion can be treated as a perfect gas with $c_p = 1.2$ kJ/kg K and $\kappa = 1.35$.
[0.02; 372.9 kJ/kg; 36.6%; 260.4 kJ/kg]

P5.5 A steam turbine operates on a superheated Rankine cycle. The pressure and temperature of the steam leaving the boiler are 10 bar and 350 °C respectively. The specific steam consumption of the plant is 4.55 kg/kWh. The pressure in the condenser is 0.05 bar.

If the feed pump work may be neglected, calculate the thermal efficiency of the plant, the turbine isentropic efficiency and evaluate the rational efficiency. Also calculate the mean temperature of reception of heat in the boiler and use this in conjunction with the condenser temperature to evaluate the thermal efficiency. Explain why the value calculated by this method is higher than that obtained previously.

[26.5%; 86%; 84.84%; 30.85%]

P5.6 Fig P5.6 depicts a closed cycle gas turbine operating on the Joule cycle (i.e. constant pressure heat addition and rejection, and isentropic compression and expansion). Energy is added to the working fluid (air) by a heat exchanger maintained at 1250 K, and rejected to another heat exchanger maintained at 300 K. The maximum temperature of the working fluid is 1150 K and its minimum temperature is 400 K. The pressure ratio of the compressor is 5:1. Evaluate the irreversibilities introduced by the heat transfer processes and calculate

(a) the First Law efficiency $\eta_I = \frac{\text{work output}}{\text{energy addition}};$

(b) the Second Law efficiency $\eta_{II} = \frac{\text{work output}}{\text{availability of energy addition}}.$

Assume $c_p = 1.005 \text{ kJ/kg K}$, $\kappa = 1.4$, and the specific gas constant, $R = 0.287 \text{ kJ/kg K}$.

Calculate the maximum efficiency that could be achieved from this system by modification of the heat exchangers.

[36.9%; 48.5%]

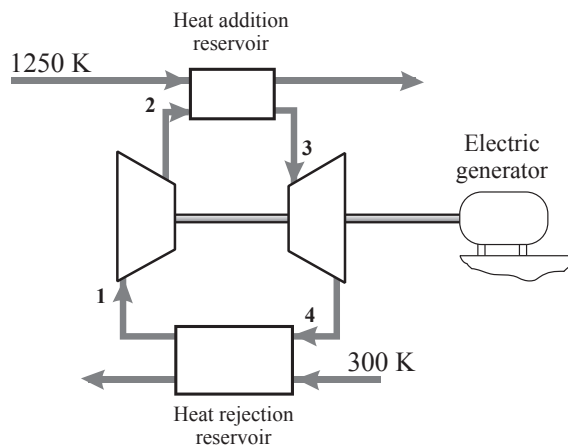


FIGURE P5.6

Closed cycle gas turbine operating on ideal Joule cycle.

FINITE TIME (OR ENDOREVERSIBLE) THERMODYNAMICS

6.1 GENERAL CONSIDERATIONS

The thermal efficiency of a Carnot cycle operating between high-temperature (T_H) and low-temperature (T_C) reservoirs is given by

$$\eta_{th} = 1 - \frac{T_C}{T_H} \quad (6.1)$$

This cycle is extremely idealised. It requires an ideal, reversible heat engine (internally reversible) but in addition the heat transfer from the reservoirs is also reversible (externally reversible). To achieve external reversibility it is necessary that the temperature difference between the reservoirs and the engine is infinitesimal (see Chapter 4, Section 4.9.1.1), which means that the heat exchanger surface area must be very large or the time to transfer heat must be long. The former is limited by size and cost factors whilst the latter will limit the actual power output achieved for the engine. It is possible to evaluate the **maximum power output** achievable from an internally reversible (endoreversible) heat engine receiving heat irreversibly from two reservoirs at T_H and T_C . This will now be done, following an approach used by Bejan (1988).

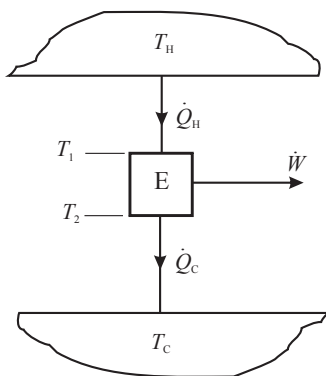
This analysis is referred to as finite time thermodynamics (FTT) because it considers the rates at which energy can be transferred through the systems involved. It was stated in Chapter 2 that the Carnot cycle was internally and externally reversible. It is possible to conceive of internal reversibility because this relies on the processes inside the heat engine being reversible, e.g. the isentropic efficiency of the devices is 100%, and there are no heat or pressure losses in the system; such an engine is referred to as endoreversible. However, external reversibility requires that the heat transfer takes place across an infinitesimal temperature difference – which will result in a very slow rate of heat transfer. In FTT, the requirement of external reversibility is removed and the heat transfer takes place across a significant temperature drop – the rate of heat transfer can then be calculated.

Assume that the engine is an endoreversible one operating at steady state, and therefore steady flow (e.g. like a steam turbine or closed cycle gas turbine); a similar analysis is possible for an intermittent device (e.g. like a Stirling engine). A schematic of such an engine is shown in Fig. 6.1.

The reservoir at T_H transfers heat to the engine across a resistance and it is received by the engine at temperature T_1 . In a similar manner, the engine rejects energy at T_2 but the cold reservoir is at T_C .

It can be assumed that the engine itself is reversible and acts as a Carnot cycle device with

$$\eta_{th} = 1 - \frac{T_2}{T_1}. \quad (6.2)$$

**FIGURE 6.1**

Internally reversible heat engine operating between reservoirs at T_H and T_C .

This thermal efficiency is less than the maximum achievable value given by Eqn (6.1) because $T_2/T_1 > T_C/T_H$. The value can only approach that of Eqn (6.1) if the temperature drops between the reservoirs and the engine approach zero.

The heat transfer from the hot reservoir can be defined as

$$\dot{Q}_H = U_H A_H (T_H - T_1), \quad (6.3)$$

where

U_H = heat transfer coefficient of hot reservoir (e.g. kW/m²K)

A_H = area of heat transfer surface of hot reservoir (e.g. m²) and

$\dot{Q}_H$ = rate of heat transfer (e.g. kW).

The heat transfer to the cold reservoir is similarly

$$\dot{Q}_C = U_C A_C (T_2 - T_1). \quad (6.4)$$

By the First Law

$$\dot{W} = \dot{Q}_H - \dot{Q}_C. \quad (6.5)$$

Now, the heat engine is internally reversible and hence the entropy entering and leaving it must be equal;

i.e.

$$\frac{\dot{Q}_H}{T_1} = \frac{\dot{Q}_C}{T_2}. \quad (6.6)$$

This means that

$$\dot{W} = \dot{Q}_H \left(1 - \frac{\dot{Q}_C}{\dot{Q}_H} \right) = \dot{Q}_H \left(1 - \frac{T_2}{T_1} \right). \quad (6.7)$$

It is possible to manipulate these equations to give $\dot{W}$ in terms of T_H , T_C , $U_H A_H$ and the ratio $T_2/T_1 = \tau$.

From Eqn (6.4),

$$T_2 = \frac{\dot{Q}_C}{U_C A_C} + T_C \quad (6.8)$$

and, from Eqn (6.6),

$$\begin{aligned} T_1 &= \frac{\dot{Q}_H}{\dot{Q}_C} T_2 = \frac{\dot{Q}_H}{\dot{Q}_C} \left\{ \frac{\dot{Q}_C}{U_C A_C} + T_C \right\}, \\ &= \frac{1}{\tau} \left\{ \frac{\dot{Q}_C}{U_C A_C} + T_C \right\}. \end{aligned} \quad (6.9)$$

Hence,

$$\dot{Q}_H = U_H A_H T_H - \frac{U_H A_H}{\tau} \left\{ \frac{\dot{Q}_C}{U_C A_C} + T_C \right\} = U_H A_H T_H - \frac{U_H A_H \dot{Q}_H}{U_C A_C} - \frac{U_H A_H T_C}{\tau}.$$

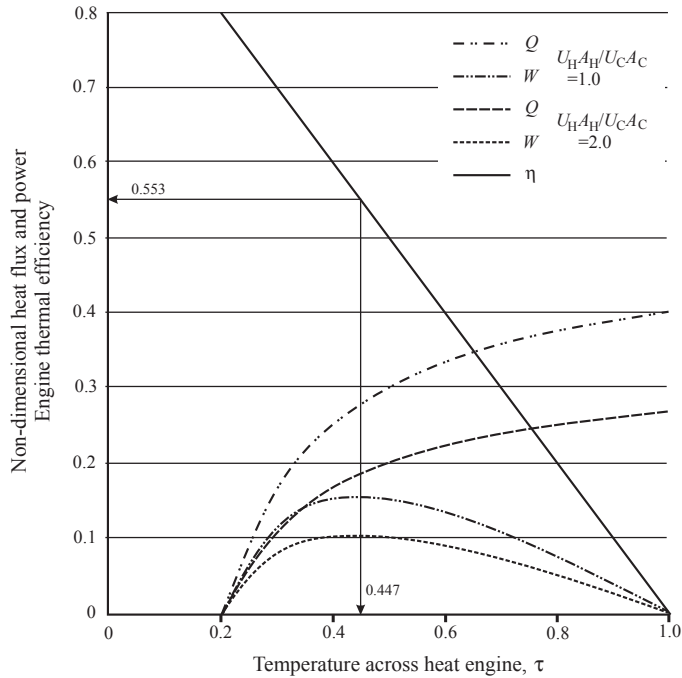
Rearranging gives

$$\frac{\dot{Q}_H}{U_H A_H T_H} = \left\{ \frac{1 - \frac{T_C}{T_H} \frac{1}{\tau}}{1 + \frac{U_H A_H}{U_C A_C}} \right\} = \frac{\left(\tau - \frac{T_C}{T_H} \right)}{\tau \left(1 + \frac{U_H A_H}{U_C A_C} \right)}, \quad (6.10)$$

and hence,

$$\frac{\dot{W}}{U_H A_H T_H} = \frac{\left(\tau - \frac{T_C}{T_H} \right)}{\tau \left(1 + \frac{U_H A_H}{U_C A_C} \right)} (1 - \tau). \quad (6.11)$$

The nondimensional heat addition from the hot reservoir, $\dot{Q}_H/U_H A_H T_H$, and the nondimensional power output, $\dot{W}/U_H A_H T_H$, can both be calculated as a function of τ for given values of T_C/T_H and $U_H A_H/U_C A_C$. The thermal efficiency, η , of the heat engine can also be evaluated as $\dot{W}/\dot{Q}$. Figure 6.2 shows how these parameters vary for $T_H/T_C = 5.0$, and two values of $U_H A_H/U_C A_C = 1.0$ and 2.0 . It can be readily seen that the actual power output reaches a maximum value for a particular value of τ . Also shown is that the efficiency of the engine, which is the same for both values of $U_H A_H/U_C A_C$, decreases from the Carnot efficiency of 80% at $\tau = T_C/T_H$ to 0 at $\tau = 0$. The efficiency at maximum power is 55.3% and this occurs at a value of $\tau = 0.447$. This graph confirms that a Carnot cycle has the highest achievable efficiency but produces zero power output, because when $\tau = T_C/T_H$ this means that the heat transfer is externally reversible, but infinitesimally slow. It would be interesting to evaluate the efficiency of the engine when it produces its maximum power output, and this will be done below.

**FIGURE 6.2**

Variation of heat flux, power output and thermal efficiency for an endoreversible engine operating with $T_H/T_C = 5.0$.

6.2 EFFICIENCY AT MAXIMUM POWER

It is shown in Fig. 6.2 that the rate of work output (power) is a function of the ratio of temperatures of the hot and cold reservoirs, the ratio of temperatures across the engine and the thermal resistances. The optimum temperature ratio across the engine (τ) to give maximum power output is obtained when

$$\frac{\partial \dot{W}}{\partial \tau} = 0.$$

Differentiating Eqn (6.11) with respect to τ gives.

$$\begin{aligned} \frac{\partial \dot{W}}{\partial \tau} &= \left(\frac{1}{1 + \frac{U_H A_H}{U_C A_C}} \right) \left\{ \frac{(1 - \tau)}{\tau} - \frac{(\tau - T_C/T_H)}{\tau} - \frac{(\tau - T_C/T_H)(1 - \tau)}{\tau^2} \right\} \\ &= \frac{1}{\tau} \left(\frac{1}{1 + \frac{U_H A_H}{U_C A_C}} \right) \left\{ -\tau + \frac{1}{\tau} \frac{T_C}{T_H} \right\}. \end{aligned} \quad (6.12)$$

Hence, $\frac{\partial \dot{W}}{\partial \tau} = 0$ when $\tau = \infty$ or $\tau^2 = \frac{T_C}{T_H}$.

Considering only the nontrivial case, **for maximum work output**

$$\frac{T_2}{T_1} = \left(\frac{T_C}{T_H} \right)^{1/2}. \quad (6.13)$$

This result has the effect of maximising the energy flow through the engine while maintaining the thermal efficiency ($\eta_{th} = 1 - T_2/T_1$) at a reasonable level. It compromises between the high efficiency ($\eta_{th} = 1 - T_C/T_H$) of the Carnot cycle (which produces zero energy flow rate) and the zero efficiency engine in which $T_2 = T_1$ (which produces high energy flow rates but no power).

Hence the efficiency of an internally reversible, ideal heat engine operating at maximum power output is

$$\eta_{th} = 1 - \left(\frac{T_C}{T_H} \right)^{1/2}. \quad (6.14)$$

Applying this result to the example given in Fig. 6.2, we obtain $\eta = 0.5528$, as shown above.

An example will be used to show the significance of this result.

EXAMPLE

Consider a heat engine connected to a hot reservoir at 1600 K and a cold one at 400 K. The heat transfer conductances (UA) are the same on both the hot and cold sides. Evaluate the high and low temperatures of the working fluid of the internally reversible heat engine for maximum power output; also calculate the maximum power.

Equation (6.11) gives the work rate (power) as

$$\frac{\dot{W}}{U_H A_H T_H} = \frac{\left(\tau - \frac{T_C}{T_H} \right)}{\tau \left(1 + \frac{U_H A_H}{U_C A_C} \right)} (1 - \tau).$$

For maximum power output, $\tau = (T_C/T_H)^{1/2} = (400/1600)^{1/2}$.

Then,

$$\frac{\dot{W}}{U_H A_H} = 1600 \frac{\left(\frac{1}{2} - \frac{1}{4} \right)}{\frac{1}{2}(1 + 1)} \left(1 - \frac{1}{2} \right) = \frac{1600}{8} = 200 \text{ units}$$

and, from Eqn (6.10),

$$\frac{\dot{Q}_H}{U_H A_H} = \frac{\dot{W}}{U_H A_H (1 - \tau)} = 400 \text{ units}$$

Then,

$$\frac{\dot{Q}_C}{U_H A_H} = \frac{\dot{Q}_C}{U_C A_C} = \frac{1}{U_H A_H} (\dot{Q}_H - \dot{W}) = 200 \text{ units.}$$

Thus

$$T_1 = \frac{1}{\tau} \left\{ \frac{\dot{Q}_C}{U_{CA}C} + T_C \right\} = 2 \times (200 + 400) = 1200 \text{ K},$$

and

$$T_2 = \frac{1200}{2} = 600 \text{ K}.$$

This results in the temperature values shown in Fig. 6.3 for the engine and reservoirs.

The efficiency of the Carnot cycle operating between the reservoirs would have been $\eta_{th} = 1 - 400/1600 = 0.75$ but the efficiency of this engine is $\eta_{th} = 1 - 600/1200 = 0.50$. Thus the engine which delivers maximum power is significantly less efficient than the Carnot engine.

It is possible to derive relationships for the intermediate temperatures. Equation (6.9) gives

$$T_1 = \frac{1}{\tau} \left\{ \frac{\dot{Q}_C}{U_{CA}C} + T_C \right\}, \quad (6.9)$$

and Eqn (6.8) defines T_2 as

$$T_2 = \frac{\dot{Q}_C}{U_{CA}C} + T_C. \quad (6.8)$$

Also $\dot{Q}_C = \dot{Q}_H - \dot{W}$, and then,

$$\frac{\dot{Q}_C}{U_{HA}A_H T_H} = \frac{\dot{Q}_H}{U_{HA}A_H T_H} - \frac{\dot{W}}{U_{HA}A_H T_H}.$$

Substituting from Eqns (6.10) and (6.11) gives

$$\frac{\dot{Q}_C}{U_{HA}A_H T_H} = \frac{(\tau - T_C/T_H)}{\left(1 + \frac{U_{HA}A_H}{U_{CA}C}\right)}. \quad (6.15)$$

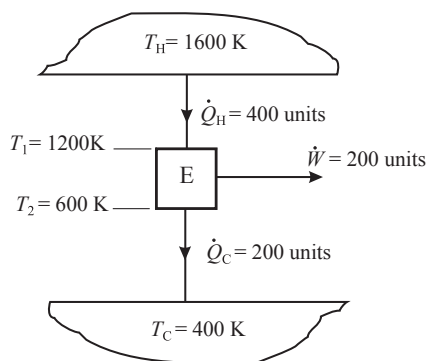


FIGURE 6.3

Example of internally reversible heat engine operating between reservoirs at $T_H = 1600 \text{ K}$ and $T_C = 400 \text{ K}$ with $U_{HA}A_H/U_{CA}C = 1$.

Substituting in Eqn (6.8) gives

$$\begin{aligned}
 T_2 &= \frac{U_H A_H T_H (\tau - T_C/T_H)}{U_C A_C \left(1 + \frac{U_H A_H}{U_C A_C}\right)} + T_C, \\
 &= \frac{U_H A_H T_H (\tau - \tau^2)}{(U_C A_C + U_H A_H)} + T_C, \\
 &= T_C^{1/2} \left\{ \frac{U_H A_H T_H^{1/2} + U_C A_C T_C^{1/2}}{U_H A_H + U_C A_C} \right\}
 \end{aligned} \tag{6.16}$$

Similarly,

$$T_1 = T_H^{1/2} \left\{ \frac{U_H A_H T_H^{1/2} + U_C A_C T_C^{1/2}}{U_H A_H + U_C A_C} \right\}. \tag{6.17}$$

To be able to compare the effect of varying the resistances, it is necessary to maintain the total resistance to heat transfer the same. For example, let

$$U_H A_H + U_C A_C = 2.$$

Then, if $\frac{U_H A_H}{U_C A_C} = 1$ (as in the previous example), $U_H A_H = 1$.

Consider the effect of having a high resistance to the high temperature reservoir, e.g. $U_H A_H / U_C A_C = 1/2$.

This gives

$$U_H A_H = \frac{2}{1 + \frac{U_C A_C}{U_H A_H}} = \frac{2}{3}.$$

Then,

$$\frac{\dot{W}}{U_H A_H} = 1600 \frac{(1/2 - 1/4)}{(1 + 1/2)/2} (1 - 1/2) = 267 \text{ units, giving } \dot{W} = 177.8 \text{ units.}$$

$$\frac{\dot{Q}_H}{U_H A_H} = \frac{\dot{W}}{U_H A_H (1 - \tau)} = 534 \text{ units and } \dot{Q}_H = 355.6 \text{ units.}$$

Then,

$$\frac{\dot{Q}_C}{U_C A_C} = \frac{\dot{Q}_H}{U_H A_H} \cdot \frac{1}{2} = \frac{1}{2 U_H A_H} (\dot{Q}_H - \dot{W}) = 133.5 \text{ units, giving } \dot{Q}_C = 177.8 \text{ units}$$

Hence,

$$T_1 = \frac{1}{\tau} (133.5 + 400) = 2 \times 533.5 = 1067 \text{ K, and } T_2 = 533.5 \text{ K.}$$

If the resistance to the low-temperature reservoir is high, i.e. $U_H A_H / U_C A_C = 2$, the situation changes, as shown below.

First,

$$U_H A_H = \frac{2}{1 + 1/2} = \frac{2}{3/2} = \frac{4}{3}$$

giving

$$\frac{\dot{W}}{U_H A_H} = 1600 \frac{(1/2 - 1/4)(1 - 1/2)}{(1 + 2)/2} = 133 \text{ units, which results in } \dot{W} = 177.8 \text{ kW,}$$

and

$$\frac{\dot{Q}_H}{U_H A_H} = 267 \text{ units, or } \dot{Q} = 355.6 \text{ kW}$$

Then,

$$\frac{\dot{Q}_C}{U_C A_C} = \frac{2\dot{Q}_C}{U_H A_H} = \frac{2}{U_H A_H} (\dot{Q}_H - \dot{W}) = 267 \text{ units, giving } \dot{Q}_C = 177.8 \text{ kW.}$$

Hence,

$$T_1 = \frac{1}{\tau} \left\{ \frac{\dot{Q}_C}{U_C A_C} + T_C \right\} = 2(267 + 400) = 1334 \text{ K, and } T_2 = 667 \text{ K.}$$

These results are shown graphically in Fig. 6.4.

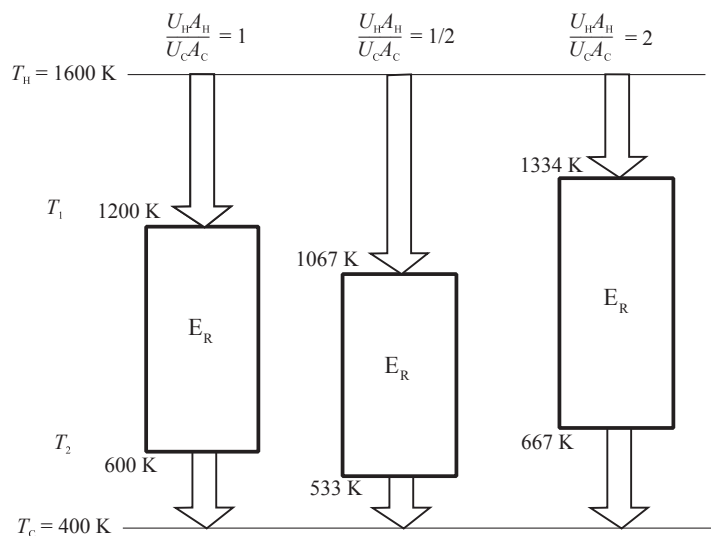


FIGURE 6.4

The effect of heat transfer parameters on engine temperatures for a heat engine operating between reservoirs at $T_H = 1600 \text{ K}$ and $T_C = 400 \text{ K}$.

Comparing the power outputs based on the same total resistance, i.e. $U_H A_H + U_C A_C = 2$ gives the following table.

$U_H A_H / U_C A_C$	$\dot{Q}_H$	$\dot{W}$	$\dot{Q}_C$
1	400	200	200
1/2	355.6	177.7	177.7
2	355.6	177.7	177.7

It can be seen that the optimum system is one in which the high- and low-temperature resistances are equal. In this case the entropy generation (per unit of work) of the universe is minimised, as shown in the table below.

$\frac{U_H A_H}{U_C A_C}$	$\frac{\dot{Q}_H}{T_H}$	$\frac{\dot{Q}_H}{T_1}$	$\frac{\Delta S_H}{W}$	$\frac{\dot{Q}_C}{T_2}$	$\frac{\dot{Q}_C}{T_C}$	$\frac{\Delta S_C}{W}$	$\sum \frac{\Delta S}{W}$
1	-0.25	+0.333	$+4.17 \times 10^{-4}$	-0.333	+0.5	$+4.17 \times 10^{-4}$	$+8.34 \times 10^{-4}$
1/2	-0.225	+0.333	$+6.23 \times 10^{-4}$	-0.333	0.4443	$+6.24 \times 10^{-4}$	+0.00125
2	-0.225	+0.266	$+2.48 \times 10^{-4}$	-0.266	0.4443	$+10.00 \times 10^{-4}$	+0.00125

6.3 EFFICIENCY OF COMBINED CYCLE INTERNALLY REVERSIBLE HEAT ENGINES WHEN PRODUCING MAXIMUM POWER OUTPUT

One way of improving the overall efficiency of power production between two reservoirs is to use two engines. For example, a gas turbine and steam turbine can be used in series to make the most effective use of the available temperature drop. Such a power plant is referred to as a combined cycle gas turbine, and this type of generating system will be introduced in Section 17.1 in connection with gas turbine cycles. These plants can be examined in the following way, based on the two heat engines in series shown in Fig. 6.5.

In this case the product UA will be replaced by a ‘conductivity’ C to simplify the notation. Then,

$$\dot{Q}_H = C_H(T_H - T_1) \quad (6.18)$$

$$\dot{Q}_2 = C_2(T_2 - T_3) \quad (6.19)$$

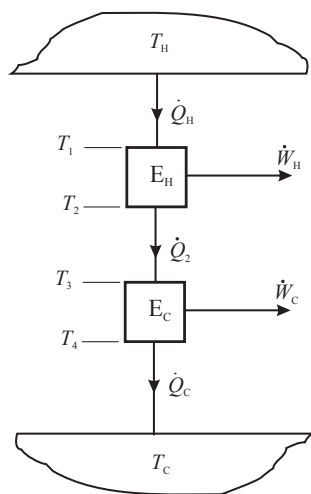
$$\dot{Q}_C = C_C(T_4 - T_C) \quad (6.20)$$

Also, for E_H

$$\frac{\dot{Q}_H}{T_1} = \frac{\dot{Q}_2}{T_2} \quad (6.21)$$

and for E_C

$$\frac{\dot{Q}_2}{T_3} = \frac{\dot{Q}_C}{T_4} \quad (6.22)$$

**FIGURE 6.5**

Two internally reversible engines in series forming a combined cycle device operating between two reservoirs at T_H and T_C .

Let $\tau_1 = T_2/T_1$ and $\tau_2 = T_4/T_3$, then rearranging [Eqns \(6.18\)–\(6.20\)](#) gives

$$T_1 = T_H - \dot{Q}_H/C_H, \quad (6.23)$$

$$T_2 = \dot{Q}_2/C_2 + T_3, \quad (6.24)$$

and

$$T_4 = \dot{Q}_C/C_C + T_C. \quad (6.25)$$

Also

$$T_3 = \frac{\dot{Q}_2}{\dot{Q}_C} T_4 = \frac{\dot{Q}_2}{\dot{Q}_C} \left\{ \frac{\dot{Q}_C}{C_C} + T_C \right\} = \frac{1}{\tau_2} \left\{ \frac{\dot{Q}_C}{C_C} + T_C \right\}, \quad (6.26)$$

and

$$T_2 = \frac{\dot{Q}_2}{C_2} + \frac{1}{\tau_2} \left\{ \frac{\dot{Q}_C}{C_C} + T_C \right\}. \quad (6.27)$$

Similarly,

$$T_1 = \frac{\dot{Q}_H}{\dot{Q}_2} T_2 = \frac{1}{\tau_1} \left[\frac{\dot{Q}_2}{C_2} + \frac{1}{\tau_2} \left\{ \frac{\dot{Q}_C}{C_C} + T_C \right\} \right]. \quad (6.28)$$

From Eqns (6.18) and (6.28),

$$\dot{Q}_H = C_H \left[T_H - \frac{1}{\tau_1} \left(\frac{\dot{Q}_2}{C_2} + \frac{1}{\tau_2} \left\{ \frac{\dot{Q}_C}{T_C} + T_C \right\} \right) \right] \quad (6.29)$$

Rearranging Eqn (6.29) gives,

$$\frac{\dot{Q}_H}{C_H T_H} = \left(1 - \frac{\dot{Q}_H}{C_2 T_H} - \frac{\dot{Q}_H}{C_C T_H} - \frac{1}{\tau_1 \tau_2} \frac{T_C}{T_H} \right), \quad (6.30)$$

which can be written as

$$\frac{\dot{Q}_H}{C_H T_H} = \frac{(\tau_1 \tau_2 - T_C/T_H)}{\tau_1 \tau_2 \left(1 + \frac{C_H}{C_2} + \frac{C_H}{C_C} \right)}. \quad (6.31)$$

The power output of engine E_H can be obtained from Eqn (6.31) as

$$\frac{\dot{W}_H}{C_H T_H} = \frac{\dot{Q}_H}{C_H T_H} (1 - \tau_1) = \frac{(\tau_1 \tau_2 - T_C/T_H)}{\tau_1 \tau_2 \left(1 + \frac{C_H}{C_2} + \frac{C_H}{C_C} \right)} (1 - \tau_1). \quad (6.32)$$

In a similar manner $\dot{W}_C/C_H T_H$ can also be evaluated as

$$\frac{\dot{W}_C}{C_H T_H} = \frac{\dot{Q}_H}{C_H T_H} \tau_1 (1 - \tau_2) = \frac{(\tau_1 \tau_2 - T_C/T_H)(1 - \tau_2)\tau_1}{\tau_1 \tau_2 \left(1 + \frac{C_H}{C_2} + \frac{C_H}{C_C} \right)}, \quad (6.33)$$

$$= \tau_1 \frac{\dot{W}_H}{C_H T_H} \frac{(1 - \tau_2)}{(1 - \tau_1)}. \quad (6.34)$$

It can be seen from Eqns (6.32) and (6.34) that it is possible to split the power output of the two engines in an arbitrary manner, dependent on the temperature drops across each engine. The ratio of work output of the two engines is

$$\frac{\dot{W}_H}{\dot{W}_C} = \frac{1}{\tau_1} \frac{(1 - \tau_1)}{(1 - \tau_2)}. \quad (6.35)$$

This shows that if the temperature ratios across the high-temperature and the low-temperature engines are equal (i.e. $\tau_1 = \tau_2$), the work output of the low-temperature engine will be

$$\dot{W}_C = \tau_1 \dot{W}_H \quad (6.36)$$

Hence the work output of the low-temperature engine will be lower than that of the high-temperature engine *for the same temperature ratio*. The reason comes directly from Eqns (6.32) and (6.33), which show that the work output of an engine is directly proportional to the temperature of the 'heat' at entry.

The power output of a combined cycle power plant is the sum of the power of the individual engines, hence,

$$\frac{\dot{W}_{CC}}{C_H T_H} = \frac{1}{C_H T_H} (\dot{W}_H + \dot{W}_C) = \frac{(\tau_1 \tau_2 - T_C/T_H)}{\tau_1 \tau_2 \left(1 + \frac{C_H}{C_2} + \frac{C_H}{C_C}\right)} [(1 - \tau_1) + (1 - \tau_2)\tau_1].$$

This may be reduced to

$$\frac{\dot{W}_{CC}}{C_H T_H} = \frac{(\tau_1 \tau_2 - T_C/T_H)}{\tau_1 \tau_2 \left(1 + \frac{C_H}{C_2} + \frac{C_H}{C_C}\right)} [1 - \tau_1 \tau_2]. \quad (6.37)$$

The efficiency of the combined cycle is defined by

$$\eta_{th} = \frac{\dot{W}_{CC}}{\dot{Q}_H} = 1 - \tau_1 \tau_2 \quad (6.38)$$

Equation (6.38) shows that the expression for the efficiency of the combined cycle engine at maximum power output is similar to that for the efficiency of a single heat engine, except that in this case the temperature ratio of the single engine is replaced by the product of the two temperature ratios. If the combined cycle device is considered to be two endoreversible heat engines connected by a perfect conductor (i.e. the resistance between the engines is zero; $C_2 = \infty$), then $T_3 = T_2$, and Eqn (6.38) becomes

$$\eta_{th} = \frac{\dot{W}_{CC}}{\dot{Q}_H} = 1 - \tau_1 \tau_2 = 1 - \frac{T_1}{T_2} \frac{T_3}{T_4} = 1 - \frac{T_1}{T_4} \quad (6.39)$$

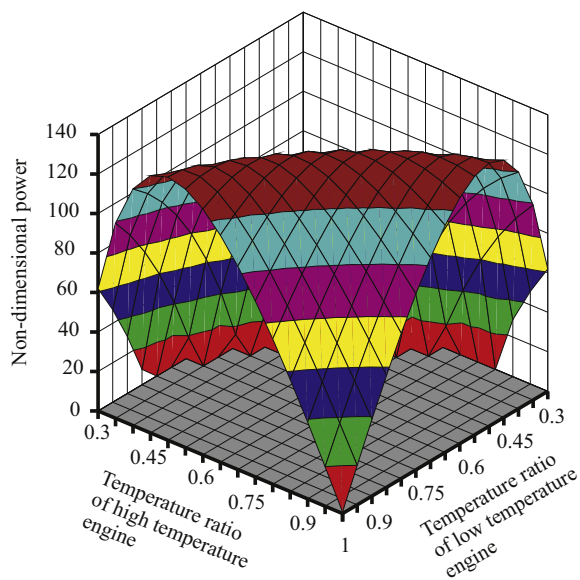
The efficiency given in Eqn (6.39) is the same efficiency as would be achieved by a single endoreversible heat engine operating between the same two temperature limits, and what would be expected if there was no resistance between the two engines in the combined cycle plant.

To determine the efficiency of the combined cycle plant, composed of endoreversible heat engines, producing maximum power output requires the evaluation of the maxima of the surface, $\dot{W}_{CC}$, plotted against the independent variables τ_1 and τ_2 . It is difficult to obtain a mathematical expression for this and so the maximum work will be evaluated for some arbitrary conditions to demonstrate the necessary conditions. This will be done based on the following assumptions:

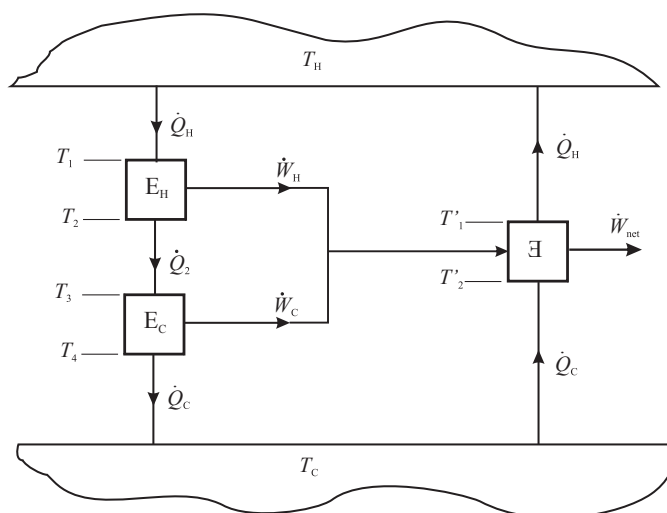
Temperatures: $T_H = 1600$ K; $T_C = 400$ K

Conductivities: $C_H = C_2 = C_C = 1$

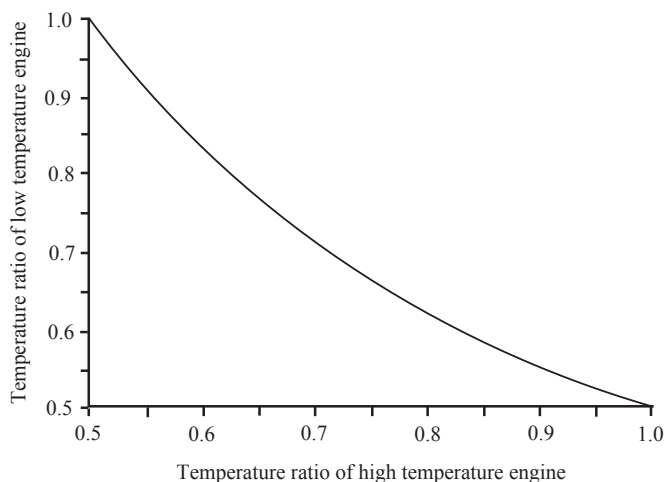
While these assumptions are arbitrary, it can be shown that the results obtained are logical and general. The variation of maximum power output with temperature ratios across the high- and low-temperature engines is shown in Fig. 6.6. It can be seen that the maximum power occurs along a ridge that goes across the base plane. Examination shows that, in this case, this obeys the equation $\tau_1 \tau_2 = 0.5 = \sqrt{T_C/T_H}$. Hence, the efficiency of a combined cycle heat engine operating at maximum power output is the same as the efficiency obtainable from a single heat engine operating between the two same reservoirs. This solution is quite logical, otherwise it would be possible to arrange heat engines as in Fig. 6.7, and produce net work output while transferring energy with a single reservoir.

**FIGURE 6.6**

Variation of maximum work output with temperature ratio across the two engines.

**FIGURE 6.7**

Combined cycle heat engine driving reversed heat engine.

**FIGURE 6.8**

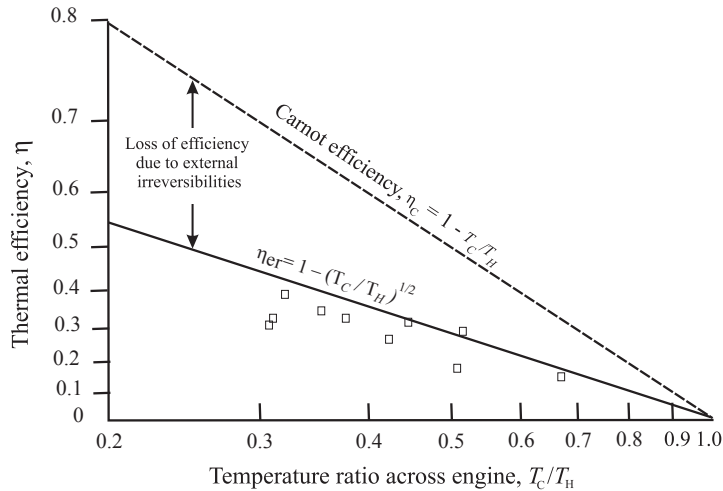
Variations in temperature ratio of high- and low-temperature heat engines that produce maximum power output.

Thus the variation of τ_1 with τ_2 to produce maximum power output is shown in Fig. 6.8; all of these combinations result in the product being 0.5.

6.4 PRACTICAL SITUATIONS

The ideas put forward in this chapter may seem to be rather esoteric, and without much connection to the real world. However, it is well known that ‘real’ engines never achieve the Carnot efficiency, and Bejan (1988) compared data from power stations to that which would be predicted using Eqn (6.14); this is shown in Fig. 6.9. It can be seen that the ‘best’ power stations lie on the line depicted by Eqn (6.14). Most of the data lie below that line, and this could be because the actual ‘heat engine’ (i.e. the plant excluding the heat transfers into and out of the system) is nowhere near reversible, or the operating condition is not at the maximum theoretical power. Either way, this approach goes some way to showing why there is such a big difference between the Carnot efficiency and that obtained in practice, and enables a more realistic assessment of the potential efficiency of a power plant.

It is also possible that some engines will achieve efficiencies that lie above the line, and these might be thought to show the analysis is incorrect. Gyftopoulos (1999), in a criticism of FTT, gives the example of a combined cycle power plant achieving an overall thermal efficiency of 60%, which he states would imply a temperature ratio, $T_H/T_C = 6.0$, and results in $T_H = 1800$ K – obviously an unreasonable value. However, by reference to Fig. 6.2, such an efficiency of 60% is achievable if the criterion of maximum power is relaxed. Calculations with $T_H/T_C = 4.0$ show that the loss of power operating at $T_1/T_2 = 2.5$, to achieve the 60% efficiency, rather than $T_1/T_2 = 2.0$, results in a 10% loss of power, but a 20% gain in efficiency. Hence, sometimes operators will choose to operate at a higher efficiency than achievable at maximum power; this particularly true when fuel prices are high.

**FIGURE 6.9**

Thermal efficiency of power plant compared with that of endoreversible cycle (each square depicts data from actual plant).

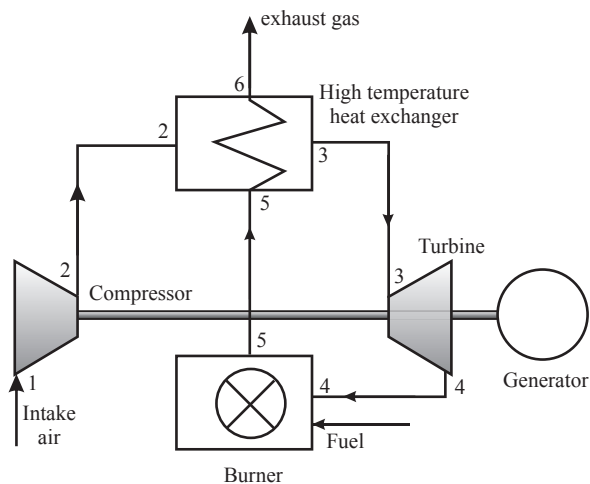
Data from Bejan (1988).

Such considerations can also be applied to other situations; whenever an attempt is made to produce power, the whole system should be considered. For example, if an electric motor is being driven by a battery, it is necessary to assess the effect of the current on the actual voltage achieved at the terminals of the battery, reduced by the internal resistance of the cell and then the voltage drops along the leads to the motor. Similarly, the ‘thermostatic’ efficiency of a fuel cell (see Chapter 21) can be evaluated by considering the open circuit potential difference of the cell, but this potential is reduced when drawing a significant current to achieve maximum power output. Hence, new concepts have been introduced that enable a broader view of systems operation to be achieved.

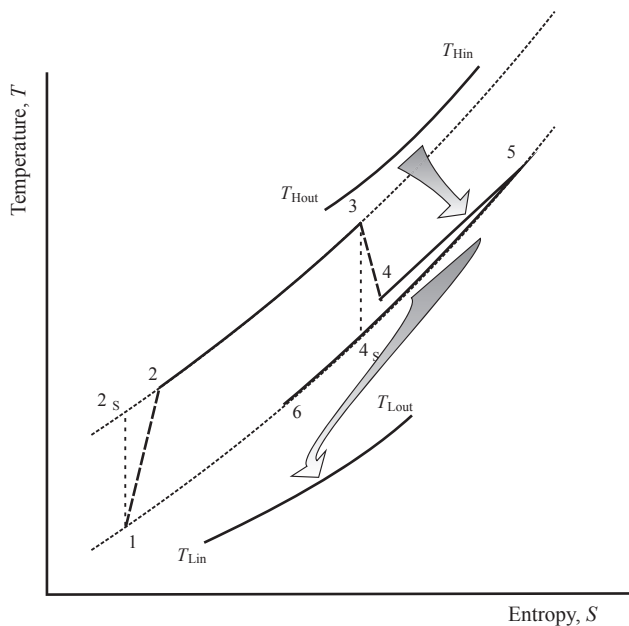
6.5 MORE COMPLEX EXAMPLE OF THE USE OF FTT

Ma and Turan (2010) describe an analysis of a class of indirectly fired gas turbine (IFGT) cycles using FTT. The system is shown in Fig. 6.10, which depicts a ‘closed cycle’ gas turbine indirectly fuelled using biogas. The reason for indirect fuelling is that the biogas might contain corrosive particles that could cause erosion of the turbine blades.

The operating cycle of the system is shown on a T - S diagram in Fig. 6.11. The basic components of this class of cycles are the compressor, high-temperature heat exchangers (HTHEs), combustion chamber and a gas turbine as shown in Fig. 6.10. The working fluid, air, enters the compressor at state 1 and is non-isentropically compressed to state 2. After state 2 (ideally to state 2s), the air leaving the compressor enters the HTHE and is heated to state 3 by the high temperature burnt biomass gas flow. The heated air then enters the turbine and expands non-isentropically to state 4 (ideally to state 4s). After leaving the turbine, the air that is still hot enters the combustion chamber and takes part in the

**FIGURE 6.10**

Arrangement for a gas turbine to use biofuel by indirect combustor.

**FIGURE 6.11**

Temperature-entropy diagram for the system shown in Fig. 6.10.

combustion process with biomass fuel to the highest temperature point of the cycle, i.e. state 5. The hot gas exits the combustion chamber and enters the HTHE, where it adds energy to the air by cooling to state 6 at constant pressure. In Fig. 6.11, the process 1-2s is an isentropic compression and the actual process 1-2 takes into account the non-isentropic nature of a real compressor; the process 3-4s is an

isentropic expansion while 3-4 signifies a real, non-isentropic, expansion in a real turbine. The real IFGT cycle 1-2-3-4-5-6-1 can now be analysed.

In order to perform the FTT analysis of the IFGT cycle under consideration, the following assumptions are employed.

1. The flow is one-dimensional steady flow, and conservation of energy can be applied to each component.
2. The working fluids (air and combustion gases) are ideal gases and possess constant specific heats. The working fluids flow through the system in a one-dimensional quasi-static fashion.
3. The compression process (1-2) and expansion process (4-5) are adiabatic, but irreversible (i.e. not isentropic). The deviations from isentropic processes are accounted for by the component isentropic efficiencies. The isentropic efficiency, η_T , of the turbine is the ratio of the power from the actual expansion process to its isentropic counterpart. The isentropic efficiency of the compressor, η_C , is the ratio of the power required during the isentropic compression to that of the actual compression. η_T and η_C have values between zero and unity – usually around 80–90%.

$$\eta_T = \frac{T_3 - T_4}{T_3 - T_{4s}} \quad (6.40)$$

$$\eta_C = \frac{T_{2s} - T_1}{T_2 - T_1} \quad (6.41)$$

4. The pressure ratio of the cycle is the ratio of the maximum pressure of the cycle, achieved at state 2, to the minimum pressure of the cycle at the turbine exit, assumed equal to that at compressor inlet (state 1), i.e.

$$\pi_C = \frac{p_2}{p_1} \quad (6.42)$$

5. The pressure drop in the pipes connecting the components is defined using a coefficient of total pressure recovery, i.e.

$$D = 1 - \frac{\Delta p}{p} \quad (6.43)$$

$$\frac{p_3}{p_4} = D \cdot \frac{p_2}{p_1} \quad (6.44)$$

The working fluid is assumed to be an ideal gas with a constant thermal capacitance rate, C_{wf} ($C_{wf} = \dot{m}c_p$). The high-temperature (hot-side) heat reservoir is assumed to have a finite thermal capacitance rate, C_H . The inlet and outlet temperatures of the heating fluid are T_{Hin} and T_{Hout} , respectively. The low-temperature (cold-side) heat reservoir is also assumed to have a finite thermal capacitance rate, C_L , and the inlet and outlet temperatures of the cooling fluid are T_{Lin} and T_{Lout} , respectively. All heat exchangers, including the two heat reservoirs and the HTHE, are assumed to be counterflow heat exchangers with constant heat conductances $U_H A_H$, $U_L A_L$ and $U_{HE} A_{HE}$, respectively.

The analytical formulae for the nondimensional power output and efficiency, as functions of the total pressure ratio, component effectiveness for the heat exchangers (HTHE $\{\varepsilon_{HE}\}$, hot- $\{\varepsilon_H\}$ and cold-side $\{\varepsilon_L\}$ heat exchangers), compressor and turbine efficiencies and the thermal capacity rates of the working fluid and the heat reservoirs, the pressure recovery coefficient, the heat reservoir inlet temperature ratio, are derived and analysed in Ma and Turan (2009). IFGT cycles are most efficient under low compression ratio ranges (2.0–5.0) and are ideal for micro gas turbine technology with their low power output. The optimal total pressure ratio, π_C , under maximum power output is always higher than that under maximum cycle thermal efficiency. When either of the heat transfer effectiveness of the hot or the cold-side heat exchanger, the pressure recovery coefficient, isentropic efficiencies of the gas turbine and the compressor and the heat reservoir inlet temperature ratio increases, the dimensionless power output, cycle efficiency and their corresponding optimal total pressure ratios increase. It must be noted that the optimal total pressure ratio, π_C , under the maximum cycle thermal efficiency decreases with the increase of heat transfer effectiveness of the HTHE. The model derived can be further used to optimise the operational parameters and forecast performance of practical IFGT configurations and choices.

Figure 6.12 gives the particular relationship between η_{IFGT} and $\bar{P}_{IFGT}$ with $\eta_C = 0.85$, $\eta_T = 0.85$, $D = 0.93$, $T_{Hin}/T_{Lin} = 4.0$ and $\varepsilon_H = \varepsilon_L = 0.90$, under several specific values of ε_{HE} with a varying total compression ratio of the compressor, π_C . Figure 6.12, which shows the variation of $\bar{P}_{IFGT}$ with η_{IFGT} , indicates that the relationship is a completely closed curve; this is much different from the parabolic curves of the Carnot cycle and the regenerated endoreversible closed Brayton cycle. It is apparent that the operating conditions for maximum power are not the same as those for maximum efficiency. Also Fig. 6.12 shows how important a high value of heat exchanger effectiveness, ε_{HE} , is if a high value of overall thermal efficiency or high power output are to be obtained.

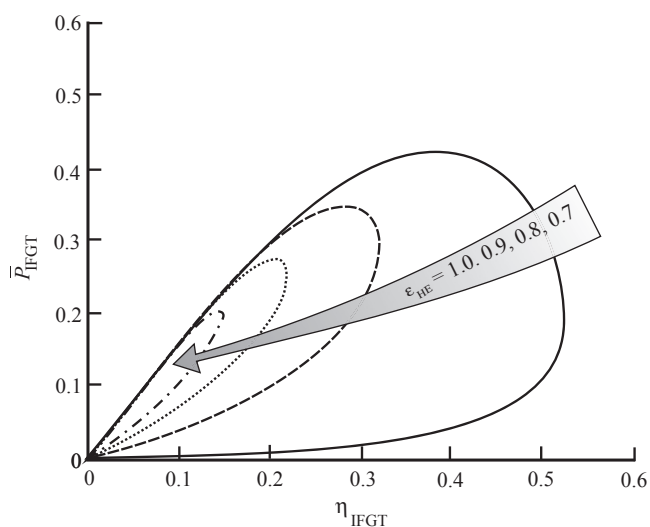


FIGURE 6.12

Variation of nondimensional power with thermal efficiency.

6.6 CONCLUDING REMARKS

A new method for assessing the potential thermal efficiency of heat engines has been introduced. This is based on the engine operating at its maximum power output, and it is shown that the thermal efficiency is significantly lower than that of a Carnot cycle between the same temperature limits. The loss of overall efficiency is due to the external irreversibilities that are present in all devices producing power output – even electrical devices. It has been shown that this approach approximates the thermal efficiency achieved by actual power plant.

It has been shown that a combined cycle power plant cannot operate at a higher thermal efficiency than a single cycle plant *between the same temperature limits*. However, the use of two cycles enables the temperature limits to be widened, and this is the reason better efficiencies are achieved.

Finally, an example was given of a nonreversible gas turbine with a heat exchanger, called an IFGT cycle.

The model derived could be used to optimise the operational parameters and forecast performance of practical IFGT configurations and choices. Furthermore, relevant equations can be used to optimise the performance of the particular IFGT cycles under a variety of constraints, including: (1) seeking the optimal pressure ratio to achieve either maximum power output or maximum efficiency, with all other parameters held constant; (2) finding the optimal set of values of the various thermal conductances under the constant total heat conductance criteria. The FTT approach shows that IFGT cycles are most efficient under low compression ratio ranges (2.0–5.0) and appropriate for integrating micro gas turbine technology for low power output applications. The optimal total pressure ratio, π_c , under maximum power output is always higher than that under maximum cycle thermal efficiency. The IFGT cycles share common characteristics with regenerated Brayton cycles and intercooled, regenerated Brayton cycles such that the dimensionless power output, efficiency and the corresponding optimal total pressure ratio are highest when the heat transfer effectiveness of the hot- or the cold-side heat exchanger, the pressure recovery coefficient, isentropic efficiencies of the gas turbine and the compressor and the heat reservoir inlet temperature ratio are high. It was also shown that the optimal total pressure ratio, π_c , under the maximum cycle thermal efficiency decreases with the increase of heat transfer effectiveness of the HTHE.

6.7 PROBLEMS

P6.1 Explain why the Carnot cycle efficiency is unrealistically high for a real engine. Introducing the concept of external irreversibility, evaluate the efficiency of an endoreversible engine at maximum power output.

Consider a heat engine connected to high-temperature reservoir at $T_H = 1200$ K and a low temperature one at $T_C = 300$ K. If the heat transfer conductance from the reservoirs to the engine are in the ratio $(UA)_H/(UA)_C = C_H/C_C = 2$, evaluate the following:

1. the maximum Carnot cycle efficiency;
2. the work output of the Carnot cycle;
3. the engine efficiency at maximum power output;
4. the maximum power output, $\dot{W}/C_H$ and
5. the maximum and minimum temperatures of the working fluid at maximum power output.

Derive all the necessary equations, but assume the Carnot efficiency, $\eta = 1 - T_C/T_H$.
[0.75; 0; 0.5; 100; 1000 K; 500 K]

- P6.2** A heat engine operates between two *finite* reservoirs, initially at 800 and 200 K, respectively. The temperature of the hot reservoir falls by 1 K for each 1 kJ extracted from it, while the temperature of the cold reservoir rises by 1 K for each 1 kJ added. What is the maximum work output from the engine as the reservoir temperatures equalise? Is the equalisation temperature for maximum work a higher or lower limit of the equalisation temperature?
[200 kJ; lower]

- P6.3** Closed cycle gas turbines operate on the *internally reversible* Joule cycle with an efficiency of

$$\eta_{\text{Joule}} = 1 - \frac{1}{r_p^{(\kappa-1)/\kappa}}$$

where r_p = pressure ratio of the turbine and κ = ratio of specific heats, $c_p/c_v = 1.4$.

This equation significantly overestimates the efficiency of the cycle when *external irreversibilities* are taken into account. Shown in Fig. P6.3 is a T - s diagram for a closed cycle gas turbine receiving energy from a high-temperature reservoir at $T_H = 1200$ K and rejecting energy to a low-temperature reservoir at $T_C = 400$ K.

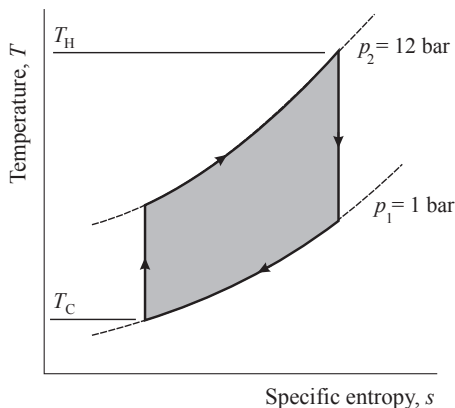


FIGURE P6.3

Temperature-entropy diagram for Joule cycle.

1. Evaluate the Carnot efficiency and compare this with the Joule efficiency; explain why the Joule efficiency is the lower.
2. Calculate the ratio of the gas turbine cycle work to the energy delivered from the high-temperature reservoir (Q_H for the Carnot cycle). This ratio is less than the Joule efficiency – explain why in terms of unavailable energy.
3. Calculate the external irreversibilities and describe how these may be reduced to enable the Joule efficiency to be achieved.
4. What are the mean temperatures of energy addition and rejection in the Joule cycle? What would be the thermal efficiency of a Carnot cycle based on these mean temperatures?
[0.667; 0.508; 0.4212; $I_H/c_p = 79.9$; 994 K; 489 K]

P6.4 Explain why the Carnot cycle overestimates the thermal efficiency achievable from an engine producing power output. Discuss why external irreversibility reduces the effective temperature ratio of an endoreversible engine.

Show that the thermal efficiency at maximum power output of an endoreversible engine executing an Otto cycle is

$$\eta_{\text{th}} = 1 - \left(\frac{T_C}{T_H} \right)^{1/2}$$

where T_H = maximum temperature of the cycle and T_C = minimum temperature of the cycle.

P6.5 The operating processes of a spark-ignition engine can be represented by the Otto cycle, which is *internally reversible* and gives a thermal efficiency of

$$\eta_{\text{Otto}} = 1 - \frac{1}{r^{(\kappa-1)}},$$

where r = volumetric compression ratio; κ = ratio of specific heats, c_p/c_v .

An Otto cycle is depicted in Fig. P6.5, and the temperatures of the two reservoirs associated with the cycle are shown as T_H and T_C . The thermal efficiency of a Carnot cycle operating between these two reservoirs is $\eta = 1 - T_C/T_H$. This value is significantly higher than that of the Otto cycle operating between the same reservoirs. Show the ratio of net work output for the Otto cycle to the energy transferred from the high-temperature reservoir for the Carnot cycle, Q_H , is

$$\eta = \left(1 - \frac{1}{r^{(\kappa-1)}} \right) \frac{T_3 - T_2}{T_3 \ln(T_3/T_2)},$$

where T_2 and T_3 are defined in Fig. P6.5.

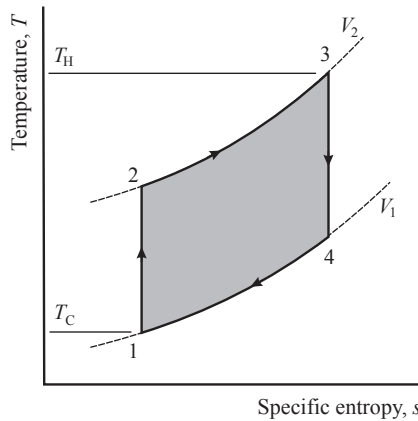


FIGURE 6.5

Temperature-entropy diagram for Otto cycle.

Explain why this value of η differs from that of the Otto cycle, and discuss the significance of the term $\frac{T_3 - T_2}{T_3 \ln(T_3/T_2)}$. Evaluate the entropy change required at the high-temperature reservoir to supply the Otto cycle in terms of the entropy span, $s_3 - s_2$, of the Otto cycle.

$$\left[\Delta s_H = c_v T_2 \left(e^{\Delta s/c_v} - 1 \right) / T_H \right]$$

P6.6 It is required to specify an ideal closed cycle gas turbine to produce electricity for a process plant. The first specification requires that the turbine produces the maximum work output possible between the peak temperature (1200 K) and the inlet temperature (300 K). The customer then feels that the efficiency of the turbine could be improved by

1. incorporating a heat exchanger;
2. introducing reheat to the turbine by splitting the turbine pressure ratio such that the pressure ratio of each stage is the square root of the compressor pressure ratio.

Evaluate the basic cycle efficiency, and then evaluate separately the effects of the heat exchanger and reheat. If these approaches have not increased the efficiency, propose another method by which the gas turbine performance might be improved (between the same temperature limits), without reducing the work output; evaluate the thermal efficiency of the proposed plant. The ratio of specific heats may be taken as $\kappa = 1.4$.

[0.5; 0.4233; 0.5731]

GENERAL THERMODYNAMIC RELATIONSHIPS: FOR SINGLE COMPONENT SYSTEMS OR SYSTEMS OF CONSTANT COMPOSITION

The relationships which follow are based on single component systems or systems of constant composition. These are a subset of the more general equations which can be derived, and which allow for changes in composition. It will be shown in Chapter 12 that if a change in composition occurs then another term called chemical potential, μ , which defines the effect of this change is required.

7.1 THE MAXWELL RELATIONSHIPS

The concept of functional relationships between properties was introduced previously. For example, the Second Law states that, for a reversible process, T , s , u , p and v are related in the following manner.

$$TdS = dU + pdV \quad (7.1)$$

or, in specific (or molar) terms

$$Tds = du + pdv \quad (7.1a)$$

Rearranging Eqn (7.1a) enables the change of internal energy, du , to be written as

$$du = Tds - pdv \quad (7.2)$$

i.e.

$$u = f(s, v) \quad (7.2a)$$

It will be shown that in Chapter 12, in the general case where the composition can change, Eqn (7.1) should be written as

$$TdS = du + pdV - \sum_i \mu_i dn_i \quad (7.1b)$$

where,

μ_i = chemical potential of component i and

n_i = amount of component i .

The chemical potential terms will be omitted in the following analysis, although similar equations to those below can be derived by taking them into account.

It can be seen from Eqns (7.2) and (7.2a) that the specific internal energy can be represented by a three-dimensional surface based on the independent variables of entropy and specific volume. If this surface is *continuous* then the following relationships can be derived based on the mathematical properties of the surface. The restriction of a continuous surface means that it is 'smooth'. It can be seen from Fig. 2.5 that the p - v - T surface for water is continuous over most of the surface, but there are discontinuities at the saturated liquid and saturated vapour lines shown in Fig. 2.6. Hence, the following relationships apply over the major regions of the surface, *but not across the boundaries*. For a continuous surface,

$$z = z(x, y) \quad \text{where } z \text{ is a continuous function.}$$

Then,

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy. \quad (7.3)$$

Let

$$M = \left(\frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y} \right)_x. \quad (7.4)$$

Then,

$$dz = Mdx + Ndy. \quad (7.5)$$

For continuous functions the derivatives $\frac{\partial^2 z}{\partial x \partial y}$ and $\frac{\partial^2 z}{\partial y \partial x}$ are equal, and hence $\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$. Consider also the expressions obtained when $z = z(x, y)$ and x and y are themselves related to additional variables u and v , such that $x = x(u, v)$ and $y = y(u, v)$. Then,

$$\left(\frac{\partial z}{\partial u} \right)_v = \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial u} \right)_v + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial u} \right)_v \quad (7.6)$$

Let $z = v$ and $u = x$, then $x = x(z)$ and

$$\left(\frac{\partial z}{\partial u} \right)_v = 0, \quad \text{and} \quad \left(\frac{\partial x}{\partial u} \right)_v = 1. \quad (7.7)$$

Hence

$$0 = \left(\frac{\partial z}{\partial x} \right)_y + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z \quad (7.8)$$

giving

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial x}{\partial y} \right)_z = -1. \quad (7.9)$$

These expressions will now be used to consider relationships derived previously. The following functional relationships have already been obtained.

$$du = Tds - pdv \quad (7.10)$$

$$dh = Tds + vdp \quad (7.11)$$

$$df = -pdv - sdT \quad (7.12)$$

$$dg = vdp - sdT \quad (7.13)$$

Consider the expression for du , given in Eqn (7.10) then, by analogy with Eqn (7.3),

$$T = \left(\frac{\partial u}{\partial s} \right)_v, -p = \left(\frac{\partial u}{\partial v} \right)_s \quad \text{and} \quad \left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial p}{\partial s} \right)_v \quad (7.14)$$

In a similar manner the following relationships can be obtained, *for constant composition or single component systems*:

$$T = \left(\frac{\partial h}{\partial s} \right)_p, v = \left(\frac{\partial h}{\partial p} \right)_s; \left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p \quad (7.15)$$

$$-p = \left(\frac{\partial f}{\partial v} \right)_T, -s = \left(\frac{\partial f}{\partial T} \right)_v; \left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T \quad (7.16)$$

$$v = \left(\frac{\partial g}{\partial p} \right)_T, -s = \left(\frac{\partial g}{\partial T} \right)_p, \left(\frac{\partial v}{\partial T} \right)_p = - \left(\frac{\partial s}{\partial p} \right)_T. \quad (7.17)$$

If the pairs of relationships for T are equated then,

$$\left(\frac{\partial u}{\partial s} \right)_v = \left(\frac{\partial h}{\partial s} \right)_p \quad (7.18a)$$

and, similarly

$$\left(\frac{\partial g}{\partial p} \right)_T = \left(\frac{\partial h}{\partial p} \right)_s \quad (7.18b)$$

$$\left(\frac{\partial u}{\partial v} \right)_s = \left(\frac{\partial f}{\partial v} \right)_T \quad (7.18c)$$

$$\left(\frac{\partial g}{\partial T} \right)_p = \left(\frac{\partial f}{\partial T} \right)_v \quad (7.18d)$$

In addition to these equivalences, Eqns (7.14)–(7.17) also show that

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial p}{\partial s} \right)_v \quad (7.19a)$$

$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p \quad (7.19b)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad (7.19c)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \quad (7.19d)$$

Equations (7.19) are called the *Maxwell relationships*.

7.1.1 GRAPHICAL INTERPRETATION OF MAXWELL RELATIONS

Let a system comprising a pure substance execute a small reversible cycle 1-2-3-4-1 consisting of two isochors separated by dV and two isentropes separated by ds ; these cycles are shown in Fig. 7.1 (a) and (b).

If the cycles are reversible the area on the T - s diagram must equal the area on the p - v diagram. Now the difference in pressure between lines 1 and 2 is given by $\left(\frac{\partial p}{\partial s}\right)_v ds$, and to the first order the difference in pressure between lines 3 and 4 is the same. Hence, the area on the p - v diagram is

$$\left(\frac{\partial p}{\partial s}\right)_v ds dv. \quad (7.20a)$$

Applying the same approach to the T - s diagram, the difference in temperature between lines 1 and 4 is $-\left(\frac{\partial T}{\partial v}\right)_s dv$, which is negative because the temperature decreases as the volume increases, and the area of the diagram is

$$-\left(\frac{\partial T}{\partial v}\right)_s dv ds. \quad (7.20b)$$

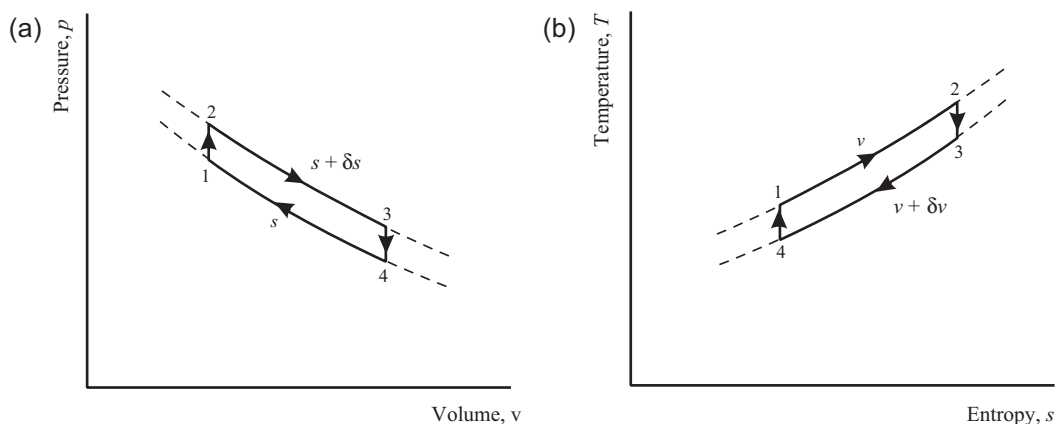


FIGURE 7.1

Elemental cycles illustrating the Maxwell relationships. (a) Pressure-volume diagram, (b) temperature-entropy diagram.

Thus, equating the two areas gives

$$-\left(\frac{\partial T}{\partial v}\right)_s dv ds = \left(\frac{\partial p}{\partial s}\right)_v ds dv. \quad (7.21)$$

and hence

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s. \quad (7.19a)$$

7.2 USES OF THE THERMODYNAMIC RELATIONSHIPS

When performing certain types of calculation it is useful to have data on the values of the specific heat capacities of the substance under consideration and also the variation of these specific heat capacities with the other properties. The specific heat capacities themselves are first derivatives of the internal energy (u) and the enthalpy (h), and hence the variations of specific heat capacities are second derivatives of the basic properties.

By definition, the specific heat capacity at constant volume is

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v. \quad (7.22)$$

But

$$\left(\frac{\partial u}{\partial s}\right)_v = T, \text{ and thus } c_v = T \left(\frac{\partial s}{\partial T}\right)_v. \quad (7.23)$$

Similarly

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = \left(\frac{\partial h}{\partial s}\right)_p \left(\frac{\partial s}{\partial T}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p. \quad (7.24)$$

Consider the variation of the specific heat capacity at constant volume, c_v , with specific volume, v , if the temperature is maintained constant. This can be derived in the following way.

$$\left(\frac{\partial c_v}{\partial v}\right)_T = \frac{\partial}{\partial v} \left[T \left(\frac{\partial s}{\partial T}\right)_v \right] = T \frac{\partial^2 s}{\partial v \partial T} = T \frac{\partial}{\partial T} \left(\frac{\partial s}{\partial v}\right)_T.$$

Now, from Eqn (7.19c),

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v,$$

giving

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \left(\frac{\partial^2 s}{\partial T \partial v}\right) = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v \quad (7.25)$$

7.2.1 SPECIFIC HEAT AT CONSTANT VOLUME, c_v , AS A FUNCTION OF VOLUME

Hence, if data are available for a substance in the form of a p - v - T surface (e.g. Fig. 2.5), or a mathematical relationship, it is possible to evaluate $(\partial^2 p / \partial T^2)_v$ and then $(\partial c_v / \partial v)_T$. By integration, it is then possible to obtain the values of c_v at different volumes. For example, consider whether the specific heat capacity at constant volume is a function of the volume of both an ideal gas and a van der Waals gas.

Ideal gas

The gas relationship for an ideal gas is

$$pv = RT \quad (7.26)$$

and

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}; \text{ and } \left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0. \quad (7.27)$$

Hence

$$c_v \neq f(v)$$

for an ideal gas.

This is in agreement with Joule's experiment for assessing the change of internal energy, u , with volume.

van der Waals gas

The van der Waals gas is discussed in much greater depth in Section 8.2; the equation of state will just be introduced here and some of the concepts developed above will be investigated.

The equation of state of a van der Waals gas is

$$p = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (7.28)$$

where a and b are constants (described in Section 8.2).

Hence

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b}; \text{ and } \left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0. \quad (7.29)$$

Again,

$$c_v \neq f(v)$$

for a van der Waals gas.

So, for 'gases' obeying these state equations $c_v \neq f(v)$, but in certain cases and under certain conditions c_v could be a function of the volume of the system and it would be calculated in this way. Of course, if these equations are to be integrated to evaluate the internal energy it is necessary to know the value of c_v at a datum volume and temperature.

7.2.2 SPECIFIC HEAT AT CONSTANT PRESSURE, C_p , AS A FUNCTION OF PRESSURE

Similarly, the variation of the specific heat capacity at constant pressure with pressure can be investigated by differentiating the specific heat capacity with respect to pressure, giving

$$\left(\frac{\partial c_p}{\partial p}\right)_T = \frac{\partial}{\partial p} \left(T \left(\frac{\partial s}{\partial T} \right)_p \right)_T = T \frac{\partial}{\partial T} \left(\frac{\partial s}{\partial p} \right)_T = -T \left(\frac{\partial^2 v}{\partial T^2} \right)_p \quad (7.30)$$

This equation can be used to see if the specific heat capacity at constant pressure of gases obeying the ideal gas law and those obeying van der Waals equation are functions of pressure. This is done below.

Ideal gas

$$pv = RT \quad (7.26)$$

Hence

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}; \quad \text{and} \quad \left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0. \quad (7.31)$$

This means that the specific heat capacity at constant pressure for a gas obeying the ideal gas law is not a function of pressure, i.e. $c_p \neq f(p)$ for an ideal gas. This conclusion is in agreement with the Joule–Thomson experiment for superheated gases.

van der Waals gas

$$p = \frac{RT}{v - b} - \frac{a}{v^2}. \quad (7.28)$$

Equation (7.28) can be rewritten as

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

which expands to

$$pv + \frac{a}{v} - pb - \frac{ab}{v^2} = RT.$$

Differentiating implicitly gives

$$p \left(\frac{\partial v}{\partial T}\right)_p + (-) \frac{a}{v^2} \left(\frac{\partial v}{\partial T}\right)_p - \frac{(-2)ab}{v^3} \left(\frac{\partial v}{\partial T}\right)_p = R,$$

which can be rearranged to give

$$\left(\frac{\partial v}{\partial T}\right)_p \left\{ p - \frac{a}{v^2} + \frac{2ab}{v^3} \right\} = R,$$

and hence

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p - \frac{a}{v^2} \left(1 - \frac{2b}{v}\right)} \quad (7.33)$$

This can be differentiated again to give

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = \frac{\partial}{\partial T} \left(\frac{\partial v}{\partial T}\right)_p$$

which results in

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p \left\{ p - \frac{a}{v^2} + \frac{2ab}{v^3} \right\} + \left(\frac{\partial v}{\partial T}\right)_p^2 \left\{ \frac{2a}{v^3} - \frac{6ab}{v^4} \right\} = 0$$

giving

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = \frac{-\left(\frac{\partial v}{\partial T}\right)_p^2 \left\{ \frac{2a}{v^3} - \frac{6ab}{v^4} \right\}}{\left\{ p - \frac{a}{v^2} + \frac{2ab}{v^3} \right\}}$$

which, on substituting for $\left(\frac{\partial v}{\partial T}\right)_p$ becomes

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = - \frac{R^2 \left(\frac{2a}{v^3} - \frac{6ab}{v^4} \right)}{\left(p - \frac{a}{v^2} \left(1 - \frac{2b}{v} \right) \right)^3} \quad (7.34)$$

Hence, for a van der Waals gas, $c_p = f(p)$.

This means that allowance would have to be taken of this when evaluating the change of specific heat capacity at constant pressure for a process in which the pressure is changed. This can be evaluated from

$$c_p = \int_{p_1}^{p_2} -T \left(\frac{\partial^2 v}{\partial T^2} \right)_p dp, \quad (7.35)$$

where $\left(\frac{\partial^2 v}{\partial T^2}\right)_p$ is calculated from Eqn (7.34).

7.3 Tds RELATIONSHIPS

Two approaches have been used previously in performing cycle calculations. When evaluating the performance of steam plant and refrigeration equipment, much emphasis was placed on the use of tables and if the work done between two states was required, enthalpy values at these states were evaluated and suitable subtractions were performed. When doing cycle calculations for gas turbines and internal combustion engines, the air was assumed to be an ideal gas and the specific heat capacity

was used. The most accurate way of performing such calculations is, in fact, to use the enthalpy or internal energy values because these implicitly integrate the specific heat capacity over the range involved. The following analyses will demonstrate how these values of internal energy and enthalpy are obtained.

The two-property rule can be used to define entropy as the following functional relationship.

$$s = s(v, T) \quad (7.36)$$

Hence

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv. \quad (7.37)$$

Now, by definition

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v$$

and from the Maxwell relationships, Eqn (7.19c), $\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v$

Hence

$$Tds = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv \quad (7.38)$$

This is called the *first Tds relationship*

The second Tds relationship can be derived in the following way. If it is assumed that entropy, s , is a function of temperature and pressure alone, then

$$s = s(T, p). \quad (7.39)$$

and

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp. \quad (7.40)$$

By definition,

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_p$$

and, from Eqn (7.19d)

$$\left(\frac{\partial s}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p.$$

Thus, the *second Tds relationship* is

$$Tds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp. \quad (7.41)$$

The *third Tds relationship* is derived by assuming that

$$s = s(p, v). \quad (7.42)$$

$$ds = \left(\frac{\partial s}{\partial p} \right)_v dp + \left(\frac{\partial s}{\partial v} \right)_p dv. \quad (7.43)$$

Now, by definition,

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_p = T \left(\frac{\partial s}{\partial v} \right)_p \left(\frac{\partial v}{\partial T} \right)_p,$$

giving

$$\left(\frac{\partial s}{\partial v} \right)_p = \frac{1}{T} c_p \left(\frac{\partial T}{\partial v} \right)_p.$$

A similar expression can be derived for c_v , and this enables the equation

$$Tds = c_v \left(\frac{\partial T}{\partial p} \right)_v dp + c_p \left(\frac{\partial T}{\partial v} \right)_p dv \quad (7.44)$$

to be obtained. This is the *third Tds relationship*.

7.3.1 VARIATION OF INTERNAL ENERGY AND ENTHALPY

It is now possible to investigate the variation of internal energy and enthalpy with independent properties for gases obeying various gas laws.

The internal energy of a substance can be expressed as

$$u = u(T, v). \quad (7.45)$$

Hence, the change in internal energy is

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv \quad (7.46)$$

Now

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v$$

and from the Second Law,

$$du = Tds - pdv. \quad (7.47)$$

Substituting for Tds in Eqn (7.47) from first Tds relation (Eqn (7.38)) gives,

$$du = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv - pdv \quad (7.48)$$

and hence Eqn (7.46) becomes

$$c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv - p dv = c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv. \quad (7.49)$$

or

$$\left(\frac{\partial u}{\partial v} \right)_T = \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] \quad (7.50)$$

Equation (7.50) can be used to evaluate the variation in internal energy with volume for both ideal and van der Waals gases.

Ideal gas

The equation of state of an ideal gas is $pv = RT$ and hence

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v} \quad (7.51)$$

Thus

$$\left(\frac{\partial u}{\partial v} \right)_T = \left[\frac{RT}{v} - p \right] = 0. \quad (7.52)$$

Hence, the specific internal energy of an ideal gas is not a function of its specific volume (or density). This is in agreement with Joule's experiment that $u \neq f(v)$ at constant temperature.

van der Waals gas

The equation of state of a van der Waals gas is

$$p = \frac{RT}{v-b} - \frac{a}{v^2},$$

and hence

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v-b} \quad (7.53)$$

which gives the change of internal energy with volume as

$$\left(\frac{\partial u}{\partial v} \right)_T = \left[\frac{RT}{v-b} - p \right] = \frac{a}{v^2}. \quad (7.54)$$

This means that the internal energy of a van der Waals gas is a function of its specific volume or density. This is not surprising because density is a measure of the closeness of the molecules of the substance (see Section 8.2), and the internal energy variation is related to the force of attraction between the molecules. This means that some of the internal energy in a van der Waals gas is stored in the attraction forces between the molecules, and not all of the thermal energy is due to molecular motion, as was the case for the ideal gas.

Now, if it is required to calculate the total change in internal energy, u , for a change in volume and temperature, it is necessary to use Eqn (7.46)

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv. \quad (7.46)$$

For an *ideal gas*

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT = c_v dT. \quad (7.55)$$

i.e. for an ideal gas

$$u = f(T).$$

It is also possible to use the following approach to show whether $u = f(p)$. This may be done in the following way.

$$\left(\frac{\partial u}{\partial v} \right)_T = \left(\frac{\partial u}{\partial p} \right)_T \left(\frac{\partial p}{\partial v} \right)_T = 0.$$

Now

$$\left(\frac{\partial p}{\partial v} \right)_T = -\frac{p}{v},$$

and since

$$p \neq 0, \left(\frac{\partial u}{\partial p} \right)_T = 0.$$

Hence, for an ideal gas

$$u \neq f(p).$$

For a *van der Waals gas*

$$du = c_v dT + \frac{a}{v^2} dv. \quad (7.56)$$

Hence, for a van der Waals gas $u = f(T, v)$.

7.4 RELATIONSHIPS BETWEEN SPECIFIC HEAT CAPACITIES

These relationships enable the value of one specific heat capacity to be calculated if the other is known. This is useful because it is much easier to measure the specific heat capacity at constant pressure, c_p , than that at constant volume, c_v .

Using the two-property rule it is possible to write

$$s = s(T, v) \quad (7.57)$$

and, if s is a continuous function of temperature and volume

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv. \quad (7.58)$$

If Eqn (7.58) is differentiated with respect to temperature, T , with p maintained constant, then

$$\left(\frac{\partial s}{\partial T} \right)_p = \left(\frac{\partial s}{\partial T} \right)_v + \left(\frac{\partial s}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p. \quad (7.59)$$

The definitions of the specific heat capacities are $c_v = T \left(\frac{\partial s}{\partial T} \right)_v$ and $c_p = T \left(\frac{\partial s}{\partial T} \right)_p$.
Hence

$$\frac{c_p - c_v}{T} = \left(\frac{\partial s}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p. \quad (7.60)$$

From Maxwell relations,

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \quad (7.19c)$$

Thus

$$\frac{c_p - c_v}{T} = \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p. \quad (7.61)$$

The mathematical relationship in Eqn (7.9)

$$\left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T = -1 \quad (7.62)$$

can be rearranged to give

$$\left(\frac{\partial p}{\partial T} \right)_v = - \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p \quad (7.63)$$

Thus

$$c_p - c_v = -T \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p^2 \quad (7.64)$$

Examination of Eqn (7.64) can be used to define which specific heat capacity is the larger. First, it should be noted that T and $\left(\frac{\partial v}{\partial T} \right)_p^2$ are both positive, and hence the sign of $c_p - c_v$ is controlled by the sign of $\left(\frac{\partial p}{\partial v} \right)_T$. Now, for all known substances, $(\partial p / \partial v)_T$ is negative. If it were not negative then the substance would be completely unstable because a positive value means that as the pressure is increased the volume increases, and vice versa. Hence, if the pressure on such a substance were decreased its volume would decrease until it ceased to exist.

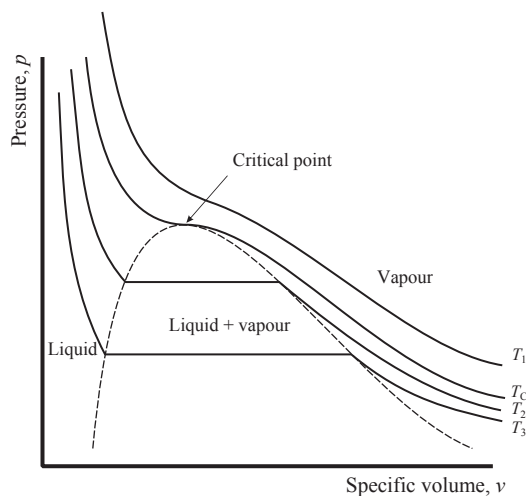


FIGURE 7.2

p - v section of a state diagram showing isotherms.

Thus, $c_p - c_v$ must always be positive or zero, i.e. $c_p \geq c_v$. The circumstances when $c_p = c_v$ are when $T = 0$ or when $(\partial p / \partial T)_v = 0$, e.g. at 4 °C for water (see the p - v - T surfaces in Fig. 2.5). It can also be shown that $c_p \geq c_v$ by considering the terms in Eqn (7.61) in relation to the state diagrams for substances, as shown in Fig. 7.2. The term $(\partial p / \partial T)_v$ that can be evaluated along a line at constant volume, v , can be seen to be positive, because as the temperature increases the pressure increases over the whole of the section. Similarly, $(\partial v / \partial T)_p$, which can be evaluated along a line at constant pressure, p , is also positive. If both these terms are positive then $c_p \geq c_v$.

Now, consider $c_p - c_v$ for an ideal gas that is depicted by the superheated region in Fig. 7.2. The state equation for an ideal gas is

$$pv = RT \quad (7.26)$$

Differentiating gives

$$\left(\frac{\partial p}{\partial v} \right)_T = -\frac{p}{v} \quad (7.65)$$

and

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p} \quad (7.66)$$

Thus

$$c_p - c_v = -T \left(\frac{-p}{v} \right) \frac{R^2}{p^2} = R. \quad (7.67)$$

The definition of an ideal gas is one which obeys the ideal gas equation (Eqn (7.26)), and in which the specific heat capacity at constant volume (or pressure) is a function of temperature alone,

i.e. $c_v = f(T)$. Hence, from Eqn (7.67), $c_p = c_v + R = f(T) + R = f'(T)$ if R is a function of T alone. Hence, the difference of specific heat capacities for an ideal gas is the gas constant, R .

Also

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{1}{kv} \text{ and } \left(\frac{\partial v}{\partial T}\right)_p = \beta v.$$

Thus

$$c_p - c_v = -T \left(\frac{-1}{kv}\right) (\beta v)^2 = \frac{T\beta^2 v}{k}, \quad (7.68)$$

where

β = coefficient of expansion (isobaric expansivity) and
 k = isothermal compressibility.

Expressions for the difference between the specific heat capacities, $c_p - c_v$, have been derived above. It is also interesting to examine the ratio of specific heat capacities, $\kappa = c_p/c_v$.

The definitions of c_p and c_v are $c_v = T \left(\frac{\partial s}{\partial T}\right)_v$ and $c_p = T \left(\frac{\partial s}{\partial T}\right)_p$, and thus the ratio of specific heat capacities is

$$\frac{c_p}{c_v} = \frac{(\partial s/\partial T)_p}{(\partial s/\partial T)_v}. \quad (7.69)$$

Now, from the mathematical relationship (Eqn (7.9)) for the differentials,

$$\left(\frac{\partial s}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial s}\right)_T = -1 = \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T \quad (7.70)$$

giving

$$\frac{c_p}{c_v} = \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial s}{\partial p}\right)_T \quad (7.71)$$

From the Maxwell relationships

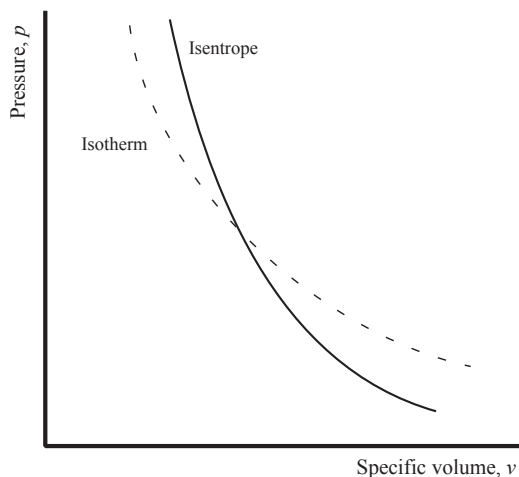
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v, \quad (7.19c)$$

and

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad (7.19d)$$

giving

$$\begin{aligned} \frac{c_p}{c_v} &= -\left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial v}{\partial T}\right)_p \\ &= -\left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \end{aligned} \quad (7.72)$$

**FIGURE 7.3**

Isentropic and isothermal lines for a perfect gas.

Now, from the two-property rule, $T = T(p, v)$ and hence

$$\left(\frac{\partial p}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \quad (7.73)$$

Thus

$$\frac{c_p}{c_v} = \left(\frac{\partial p}{\partial v}\right)_s \bigg/ \left(\frac{\partial p}{\partial v}\right)_T = v \left(\frac{\partial p}{\partial v}\right)_s \bigg/ v \left(\frac{\partial p}{\partial v}\right)_T \quad (7.74)$$

The denominator of Eqn (7.74), $v(\partial p/\partial v)_T$, is the reciprocal of the *isothermal compressibility*, k . By analogy, the numerator can be written as $1/k_s$, where $k_s = \text{adiabatic, or isentropic, compressibility}$.

Thus

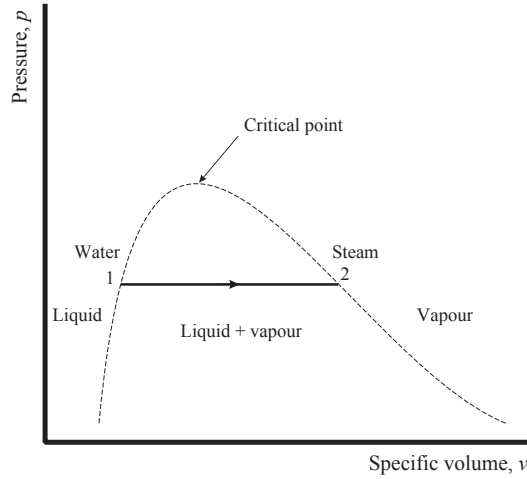
$$\frac{c_p}{c_v} = \frac{k}{k_s} = \kappa. \quad (7.75)$$

If the slopes of isentropes in the p - v plane, are compared with the slopes of isotherms, see Fig. 7.3, it can be seen that $c_p/c_v > 1$ for a gas in the superheat region.

7.5 THE CLAUSIUS–CLAPEYRON EQUATION

From the Maxwell relationships

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v. \quad (7.19c)$$

**FIGURE 7.4**

Change of phase depicted on p - v diagram.

The left hand side of Eqn (7.19c) is the rate of change of entropy with volume at constant temperature.

If the change of phase of water, from, say, liquid to steam is considered, then this takes place at constant pressure and constant temperature, known as *the saturation values*. Hence, if the change of phase between points 1 and 2 on Fig. 7.4 is considered

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{s_2 - s_1}{v_2 - v_1}, \quad (7.76)$$

which, on substituting from Eqn (7.19c) becomes

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{s_2 - s_1}{v_2 - v_1} \quad (7.77)$$

If there is a mixture of two phases, say steam and water, then the pressure is a function of temperature alone, as shown in Section 8.4. Thus

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1}. \quad (7.78)$$

Now $\left(\frac{\partial h}{\partial s}\right)_p = T$, and during a change of phase both T and p are constant, giving $h_2 - h_1 = T(s_2 - s_1)$.

Thus

$$\frac{h_2 - h_1}{v_2 - v_1} = T \frac{dp}{dT} \quad (7.79)$$

This equation is known as the *Clapeyron equation*. Now, $h_2 - h_1$ is the latent heat, h_{fg} . If point 1 is on the saturated liquid line and point 2 is on the saturated vapour line, then Eqn (7.79) can be rewritten as

$$T \frac{dp}{dT} = \frac{h_{fg}}{v_{fg}}. \quad (7.80)$$

This can be depicted graphically, and is shown on [Fig. 7.5](#).

If the processes shown on Figs 7.5(a) and (b) are reversible, then the areas are equivalent to the work done. If the two diagrams depict the same processes on different state diagrams then the areas of the ‘cycles’ must be equal. Hence

$$(v_2 - v_1)dp = (s_2 - s_1)dT \quad (7.81)$$

Now, the change of entropy is

$$s_{fg} = s_2 - s_1 = \frac{h_{fg}}{T}, \quad \text{giving} \quad T \frac{dp}{dT} = \frac{h_{fg}}{v_{fg}} \quad (7.82)$$

The graphical approach has confirmed the *Clausius–Clapeyron equation*.

7.5.1 THE USE OF THE CLAUSIUS–CLAPEYRON EQUATION

If an empirical expression is known for the saturation pressure and temperature, then it is possible to calculate the change of entropy and specific volume due to the change in phase. For example, the change of enthalpy and entropy during the evaporation of water at 120 °C can be evaluated from the slope of the saturation line defined as a function of pressure and temperature. The values of entropy and enthalpy for dry saturated steam can also be evaluated if their values in the liquid state are known. An extract of the properties of water is given in [Table 7.1](#), and values of pressure and temperature on the saturation line have been taken at adjacent temperatures.

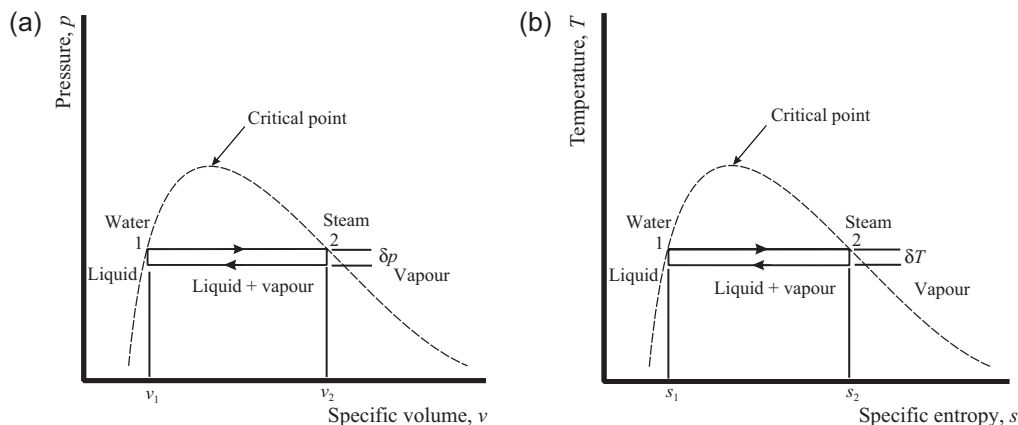


FIGURE 7.5

Evaporation processes shown on state diagrams. (a) p - v diagram; (b) T - s diagram.

Table 7.1 Excerpt from Steam Tables, Showing Values on the Saturated Liquid and Vapour Lines (Rogers and Mayhew (1994)).

Temperature (°C)	Pressure (bar)	Specific Volume (m ³ /kg)	Change of Specific Volume, v_{fg}	Entropy of Liquid, s_f (kJ/kg K)	Enthalpy of Liquid, h_f (kJ/kg K)
115	1.691	0.001060	0.8845	1.530	505
120	1.985				
125	2.321				

At 120 °C, the slope of the saturation line is $\frac{dp}{dT} \approx \frac{2.321 - 1.691}{10} \times 10^5 = 6.30 \times 10^3$.

From the Clausius–Clapeyron equation, Eqn (7.82)

$$\frac{s_2 - s_1}{v_{fg}} = \frac{dp}{dT} = \frac{s_g - s_f}{v_{fg}},$$

giving

$$\begin{aligned} s_g &= s_f + v_{fg} \frac{dp}{dT} = 1.530 + 0.8845 \times 6.30 \times 10^3 / 10^3 \\ &= 1.530 + 5.57235 = 7.102 \text{ kJ/kg K} \end{aligned}$$

The specific enthalpy on the saturated vapour line is

$$\begin{aligned} h_g &= h_f + T s_{fg} \\ &= 505 + (120 + 273) \times 5.57235 \\ &= 2694.9 \text{ kJ/kg K} \end{aligned}$$

These values are in good agreement with the tables of properties; the value of $s_g = 7.127$ kJ/kg K, while $h_g = 2707$ kJ/kg at a temperature of 120.2 °C.

7.6 CONCLUDING REMARKS

Thermodynamic relationships between properties have been developed which are independent of a particular fluid. These can be used to evaluate derived properties from primitive ones and to extend empirical data.

7.7 PROBLEMS

P7.1 For a van der Waals gas that obeys the state equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

shows that the coefficient of thermal expansion, β , is given by

$$\beta = \frac{Rv^2(v-b)}{RTv^3 - 2a(v-b)^2}$$

and the isothermal compressibility, k , is given by

$$k = \frac{v^2(v-b)^2}{RTv^3 - 2a(v-b)^2}$$

Also evaluate $T \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p^2$ for the van der Waals gas. From this find $c_p - c_v$ for an ideal gas,

stating any assumptions made in arriving at the solution.

P7.2 Prove the general thermodynamic relationship

$$\left(\frac{\partial c_p}{\partial p} \right)_T = -T \left(\frac{\partial^2 v}{\partial T^2} \right)_p$$

and evaluate an expression for the variation of c_p with pressure for a van der Waals gas which obeys a law

$$p = \frac{\Re T}{v_m - b} - \frac{a}{v_m^2},$$

where the suffix, m , indicates molar quantities and $\Re$ is the Universal gas constant.

It is possible to represent the properties of water by such an equation, where

$$a = 5.525 \frac{(\text{m}^3)^2 \text{ bar}}{(\text{kmol})^2}; \quad b = 0.03042 \frac{\text{m}^3}{\text{kmol}}; \quad \Re = 8.3143 \text{ kJ/kmol K}.$$

Evaluate the change in c_p as the pressure of superheated water vapour is increased from 175 bar to 200 bar at a constant temperature of 425 °C. Compare this with the value you would expect from the steam tables abstracted below.

	$p = 175 \text{ bar}$		$p = 200 \text{ bar}$	
$t \text{ (}^\circ\text{C)}$	$v \text{ (m}^3\text{/kg)}$	$h \text{ (kJ/kg)}$	$v \text{ (m}^3\text{/kg)}$	$h \text{ (kJ/kg)}$
425	0.013914	3014.9	0.011458	2952.9
450	0.015174	3109.7	0.012695	3060.1

What is the value of $\left(\frac{\partial c_p}{\partial p}\right)_T$ of a gas which obeys the Clausius equation of state, $p = \frac{\Re T}{v_m - b}$?

P7.3 Show that if the ratio of the specific heats is 1.4, then

$$\left(\frac{\partial p}{\partial T}\right)_s = \frac{7}{2} \left(\frac{\partial p}{\partial T}\right)_v.$$

P7.4 Show that

$$(a) \quad h - u = T^2 \left(\left(\frac{\partial(f/T)}{\partial T} \right)_v - \left(\frac{\partial(g/T)}{\partial T} \right)_p \right)$$

$$(b) \quad \frac{c_p}{c_v} = \left(\frac{\partial^2 g}{\partial T^2} \right)_p \bigg/ \left(\frac{\partial^2 f}{\partial T^2} \right)_v.$$

P7.5 Show

$$(a) \quad T ds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp$$

$$(b) \quad T ds = c_v \left(\frac{\partial T}{\partial p} \right)_v dp + c_p \left(\frac{\partial T}{\partial v} \right)_p dv$$

$$(c) \quad \left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p.$$

P7.6 Show that, for a pure substance,

$$\left(\frac{\partial s}{\partial T} \right)_p = \left(\frac{\partial s}{\partial T} \right)_v + \left(\frac{\partial s}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p$$

and from this, prove that

$$c_p - c_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p.$$

The following table gives values of the specific volume of water, in cubic metres per kilogram. A quantity of water is initially at 30 °C, 20 bar and occupies a volume of 0.2 m³. It is heated at constant volume to 50 °C and then cooled at constant pressure to 30 °C. Calculate the net heat transfer to the water.

Pressure (bar)	Specific Volume (m ³ /kg)	
	20	200
Temperature (°C)		
30	0.0010034	0.0009956
50	0.0010112	0.0010034

[438 kJ]

P7.7 Assuming that entropy is a continuous function, $s = s(T, v)$, derive the expression for entropy change

$$ds = c_v \frac{dT}{T} + \left(\frac{\partial p}{\partial T} \right)_v dv$$

and similarly, for $s = s(T, p)$ derive

$$ds = c_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T} \right)_p dp.$$

Apply these relationships to a gas obeying van der Waals equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

and derive an equation for the change of entropy during a process in terms of the basic properties and gas parameters. Also derive an expression for the change of internal energy as such a gas undergoes a process.

$$\left[s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \left(\frac{p_2 + a/v_2^2 - 2a(v-b)/v_2^3}{p_1 + a/v_1^2 - 2a(v-b)/v_1^3} \right); u_2 - u_1 = \int_1^2 c_v dT - a \left(\frac{v_1 - v_2}{v_1 v_2} \right) \right]$$

EQUATIONS OF STATE

8

The properties of fluids can be defined in two ways, either by the use of tabulated data (e.g. steam tables) or by state equations (e.g. perfect gas law). Both of these approaches have been developed by observation of the behaviour of fluids when they undergo simple processes. It has also been possible to model the behaviour of such fluids from ‘molecular’ models, e.g. the kinetic theory of gases. A number of models which describe the relationships between properties for single component fluids, or constant composition mixtures will be developed here.

8.1 IDEAL GAS LAW

The ideal and perfect gas laws can be developed from a number of simple experiments, or a simple molecular model. First the experimental approach will be considered.

If a fixed mass of a single component fluid is contained in a closed system then two processes can be proposed:

1. the volume of the gas can be changed by varying the pressure, while maintaining the temperature constant;
2. the volume of the system can be changed by varying the temperature, while maintaining the pressure constant.

The first process is an *isothermal* one, and is the experiment proposed by Boyle to define Boyle’s law (also known as Amagat’s law in France). The second process is an *isobaric* one and is the one used to define Charles’ law (also known as Gay-Lussac’s law in France).

The process executed in (1) can be described mathematically as

$$v = v(p)_T, \quad (8.1)$$

while the second one, process (2) can be written

$$v = v(T)_p. \quad (8.2)$$

Since these processes can be undergone independently then the relationship between the three properties is

$$v = v(p, T). \quad (8.3)$$

Equation (8.3) is a functional form of the *equation of state* of a single component fluid. It can be seen to obey the two property rule, which states that any property of a single component fluid or

constant composition mixture can be defined as a function of two independent properties. The actual mathematical relationship has to be found from experiment (or a simulation of the molecular properties of the gas molecules), and this can be derived by knowing that, if the property, v , is a continuous function of the other two properties, p and T , as discussed in Chapter 7, then

$$dv = \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT. \quad (8.4)$$

Hence, if the partial derivatives $\left(\frac{\partial v}{\partial p}\right)_T$, and $\left(\frac{\partial v}{\partial T}\right)_p$ can be evaluated then the gas law will be defined. It is possible to evaluate the first derivative by a Boyle's law experiment, and the second one by a Charles' law experiment. It is found from Boyle's law that

$$pv = \text{constant}, \quad (8.5)$$

giving

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{p}{v}. \quad (8.6)$$

Similarly, it is found from Charles' law that

$$\frac{v}{T} = \text{constant}, \quad (8.7)$$

giving

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v}{T}. \quad (8.8)$$

Substituting Eqns (8.6) and (8.8) into Eqn (8.4) gives

$$dv = -\frac{v}{p}dp + \frac{v}{T}dT, \quad (8.9)$$

which may be integrated to give

$$\frac{pv}{T} = \text{constant}. \quad (8.10)$$

Equation (8.10) is known as the *ideal gas law*. This equation contains no information about the internal energy of the fluid, and does not define the specific heat capacities. If the specific heat capacities are not functions of temperature then the gas is said to obey the *perfect gas law*: if the specific heat capacities are functions of temperature (i.e. the internal energy and enthalpy do not vary linearly with temperature) then the gas is called an *ideal gas*.

It is possible to define two coefficients from Eqn (8.4), which are analogous to concepts used for describing the properties of materials. The first is called the *isothermal compressibility*, or *isothermal bulk modulus*, k . This is defined as the 'volumetric strain' produced by a change in pressure, giving

$$k = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T. \quad (8.11)$$

The negative sign is introduced because an increase in pressure produces a decrease in volume and hence $\left(\frac{\partial v}{\partial p}\right)_T < 0$ (see Section 7.4); it is more convenient to have a coefficient with a positive value and the negative sign achieves this. The isothermal compressibility of a fluid is analogous to the Young's modulus of a solid.

The other coefficient that can be defined is the *coefficient of expansion*, β . This is defined as the 'volumetric strain' produced by a change in temperature, giving

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p. \quad (8.12)$$

The coefficient of expansion is analogous to the coefficient of thermal expansion of a solid material.

Hence, Eqn (8.4) may be written

$$\frac{dv}{v} = \frac{dV}{V} = -kdp + \beta dT \quad (8.13)$$

The ideal gas law applies to gases in the superheat phase. This is because when gases are superheated they obey the kinetic theory of gases in which the following assumptions are made:

- molecules are solid spheres;
- molecules occupy a negligible proportion of the total volume of the gas;
- there are no forces of attraction between the molecules, but there are infinite forces of repulsion on contact.

If a gas is not superheated the molecules become closer together and the assumptions are less valid. This has led to the development of other models which take into account the interactions between the molecules.

8.2 VAN DER WAALS EQUATION OF STATE

In an attempt to overcome the limitations of the perfect gas equation a number of modifications have been made to it. The two most obvious modifications are to assume

- the diameters of the molecules are an appreciable fraction of the mean distances between them, and the mean free path between collisions. This basically means that the volume occupied by the molecules is not negligible;
- the molecules exert forces of attraction which vary with the distance between them, while still exerting infinite forces of repulsion on contact.

First, if it is assumed that the molecules occupy a significant part of the volume occupied by the gas then Eqn (8.10) can be modified to

$$p = \frac{\Re T}{v - b}, \quad (8.14)$$

where b is the volume occupied by the molecules. This is called the *Clausius equation of state*.

Second, allowing for the forces of attraction between molecules gives the *van der Waals equation of state*, which is written

$$p = \frac{\Re T}{v - b} - \frac{a}{v^2} \quad (8.15)$$

Figure 8.1 shows five isotherms for water calculated using van der Waals equation (the derivation of the constants in the Eqn (8.15) is described below). It can be seen that Eqn (8.15) is a significant improvement over the perfect gas law as the state of the water approaches the saturated liquid and vapour lines. The line at 374 °C is the isotherm at the critical temperature. This line passes through the critical point, and follows closely the saturated vapour line (in fact, it lies just in the two-phase region, which indicates an inaccuracy in the method). At the critical temperature the isotherm exhibits a point of inflection at the critical point. At temperatures above the critical temperature the isotherms exhibit monotonic behaviour, and by 500 °C the isotherm is close to a rectangular hyperbola, which would be predicted for a perfect gas. At temperatures below the critical isotherm the isotherms are no longer monotonic, but exhibit the characteristics of a cubic equation. While this characteristic is not in agreement with empirical experience it does result in the correct form of function in the saturated liquid region – which could never be achieved by a perfect gas law. It is possible to resolve the problem of the correct pressure to use for an isotherm in the two-phase region by considering the Gibbs energy, which must remain constant during the evaporation process (see Chapter 2). This results in a constant pressure (horizontal) line which obeys an equilibrium relationship described below. It can also be seen from Fig. 8.1 that the behaviour of a substance obeying the van der Waals equation of state approaches that of a perfect gas when

- the temperature is above the critical temperature
- the pressure is low compared to the critical pressure.

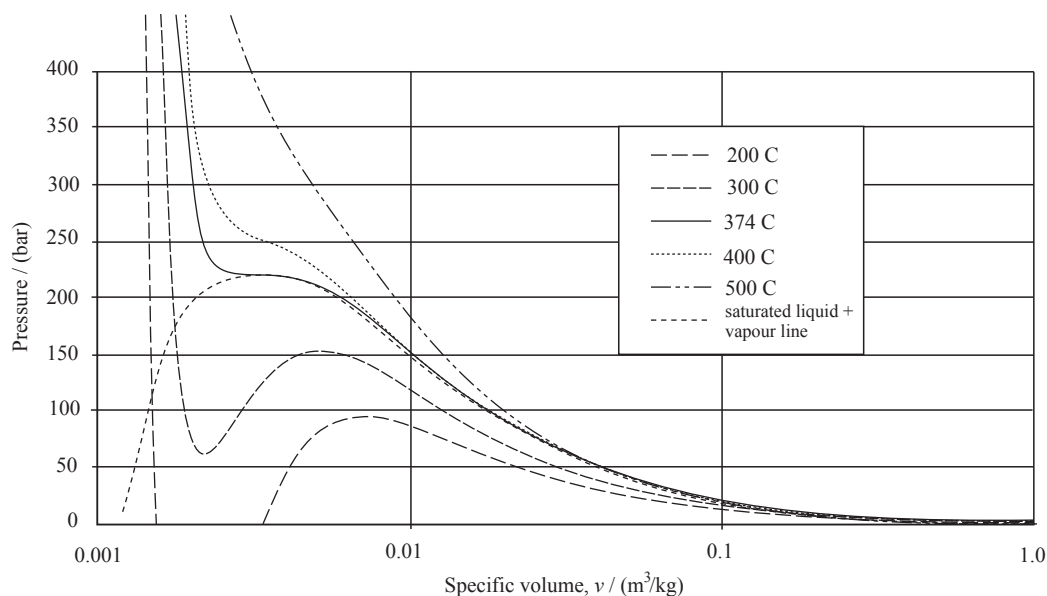


FIGURE 8.1

Isotherms on a p - v diagram calculated using van der Waals equation.

PROBLEM

Evaluate the isothermal compressibility, k , and coefficient of expansion, β , of a van der Waals gas.

8.3 LAW OF CORRESPONDING STATES

If it is assumed that all substances obey an equation of the form defined by the van der Waals equation of state then all state diagrams will be *geometrically similar*. This means that if the diagrams were normalised by dividing the properties defining a particular state point (p, v, T) by the properties at the critical point (p_c, v_c, T_c) then all state diagrams based on these *reduced properties* will be identical. Thus there would be a general relationship

$$v_R = f(p_R, T_R), \quad (8.16)$$

where $v_R = v/v_c =$ reduced volume;

$p_R = p/p_c =$ reduced pressure;

$T_R = T/T_c =$ reduced temperature.

To be able to define the general equation that might represent all substances, it is necessary to evaluate the values at the critical point in relation to the other parameters. It has been seen from Fig. 8.1 that the critical point is the boundary between two different forms of behaviour of the van der Waals equation. At temperatures above the critical point the curves are monotonic, whereas below the critical point they exhibit maxima and minima. Hence, the critical isotherm has the following characteristics:

$$(\partial p / \partial v)_{T_c} \text{ and } (\partial^2 p / \partial v^2)_{T_c} = 0.$$

Consider van der Waals equation

$$p = \frac{RT}{v-b} - \frac{a}{v^2}. \quad (8.15)$$

This can be differentiated to give the two differentials, giving

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}, \quad (8.17)$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}. \quad (8.18)$$

and at the critical point

$$-\frac{RT_c}{(v_c-b)^2} + \frac{2a}{v_c^3} = 0, \quad (8.19)$$

$$\frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0. \quad (8.20)$$

giving

$$v_c = 3b; \quad T_c = \frac{8a}{27bR}; \quad p_c = \frac{a}{27b^2}. \quad (8.21)$$

Hence,

$$a = 3p_c v_c; \quad b = \frac{v_c}{3}; \quad R = \frac{8}{3} \frac{p_c v_c}{T_c}. \quad (8.22)$$

The equation of state for a gas obeying the law of corresponding states can be written

$$p_R = \frac{8T_R}{(3v_R - 1)} - \frac{3}{v_R^2}, \quad (8.23)$$

or

$$\left(p_R + \frac{3}{v_R^2}\right)(3v_R - 1) = 8T_R. \quad (8.24)$$

Equation (8.24) is the equation of state for a substance obeying van der Waals equation: it should be noted that it does not explicitly contain values of a and b . It is possible to obtain a similar solution which omits a and b for any two-parameter state equation, but such a solution has not been found for state equations with more than two parameters. The law of corresponding states based on van der Waals equation does not give a very accurate prediction of the properties of substances over their whole range, but it does demonstrate some of the important differences between real substances and perfect gases. Figure 8.1 shows the state diagram for water evaluated using parameters in van der Waals equation based on the law of corresponding states. The parameters used for the calculation of Fig. 8.1 will now be evaluated.

The values of the relevant parameters defining the critical point of water are

$$v_c = 0.00317 \text{ m}^3/\text{kg}; \quad p_c = 221.2 \text{ bar}; \quad T_c = 374.15^\circ\text{C}$$

which gives

$$b = \frac{v_c}{3} = \frac{0.00317}{3} = 0.0010567 \text{ m}^3/\text{kg}; \quad a = 3p_c v_c^2 = 3 \times 221.2 \times 0.00317^2 = 0.0066684 \text{ bar m}^6/\text{kg}^2$$

$$R = \frac{8 \times 221.2 \times 0.00317}{3 \times (374.15 + 273)} = 0.002889 \text{ bar m}^3/\text{kg K}$$

Thus, the van der Waals equation for water is

$$p = \frac{0.002889T}{(v - 0.0010567)} - \frac{0.0066684}{v^2}. \quad (8.25)$$

Note that the value for ' R ' in this equation is not the same as the specific gas constant for the substance behaving as a perfect gas. This is because it has been evaluated using values of parameters at the critical point, which is not in the region where the substance performs as a perfect gas.

It is possible to manipulate the coefficients of van der Waals equation to use the correct value of R for the substance involved. This does not give a very good approximation for the critical isotherm, but is reasonable elsewhere. Considering Eqn (8.22), the term for v_c can be eliminated to give

$$a = \frac{27R^2 T_c^2}{64p_c}, \quad \text{and} \quad b = \frac{RT_c}{8p_c}. \quad (8.26)$$

Substituting the values of p_c and T_c into these terms gives

$$a = \frac{27 \times (8.3143 \times 10^3 / 18)^2 \times (374.1 + 273)^2}{64 \times 221.2 \times 10^5} = 1703.4 \text{ Pa m}^6/\text{kg}^2 = 0.017034 \text{ bar m}^6/\text{kg}^2$$

$$b = \frac{8.3143 \times 10^3 \times (374.1 + 273)}{18 \times 8 \times 221.2 \times 10^5} = 0.0016891 \text{ m}^3/\text{kg}$$

which results in the following van der Waals equation for water

$$p = \frac{0.004619T}{(v - 0.0016891)} - \frac{0.017034}{v^2} \quad (8.27)$$

It can be readily seen that Eqn (8.27) does not accurately predict the critical isotherm at low specific volumes, because the value of b is too big. However, it gives a reasonable prediction of the saturated vapour region, as will be demonstrated for the isotherms at 200 °C, 300 °C and the critical isotherm at 374 °C. These are shown in Fig. 8.2, where the predictions are compared with those from Eqn (8.25).

It is interesting to compare the values calculated using van der Waals equation with those in tables. This has been done for the isotherm at 200 °C, and a pressure of 15 bar (see Fig. 8.3) and the results are shown in Table 8.1.

The above diagrams and tables show that van der Waals equation does not give a good overall representation of the behaviour of a gas in the liquid and mixed state regions. However, it is a great improvement on the perfect, or ideal, gas equation in regions away from superheat. It will be shown later that van der Waals equation is capable of demonstrating certain characteristics of gases in the

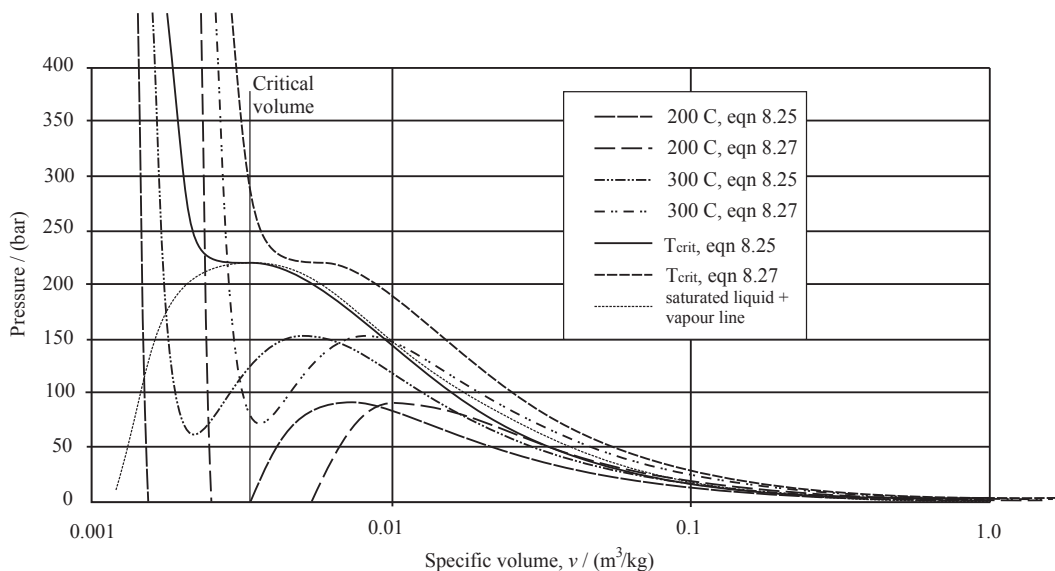


FIGURE 8.2

Comparison of isotherms calculated by van der Waals equation based on Eqns 8.25 and 8.27.

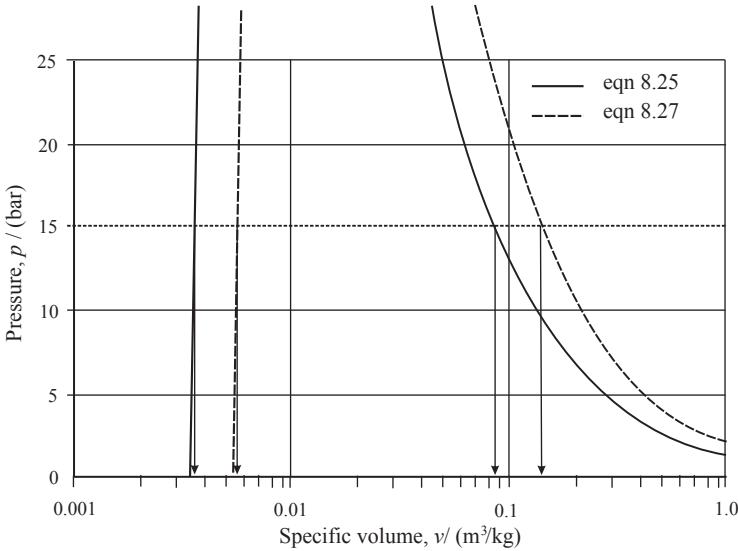


FIGURE 8.3

Expanded diagram of 200 °C isotherms, showing specific volumes at 15 bar.

two-phase region, e.g. liquefaction. There are other more accurate equations for evaluating the properties of substances, and these include

- the virial equation;

$$pv = RT \left(1 + \frac{b}{v} + \frac{c}{v^2} + \frac{d}{v^3} + \dots \right) \quad (8.28)$$

- the Beattie-Bridgeman equation;

$$p = \frac{RT}{v^2} (1 - e)(v + B) - \frac{A}{v^2}, \quad (8.29)$$

where $A = A_0 \left(1 - \frac{a}{v} \right)$, $B = B_0 \left(1 - \frac{b}{v} \right)$, $e = \frac{c}{vT^3}$

- the Bertholet equation;

$$p = \frac{RT}{v - b} - \frac{a}{Tv^2} \quad (8.30)$$

Table 8.1 Specific Volume at 200 °C and 15 bar			
Region	Specific Volume from Eqn (8.25) m³/kg	Specific Volume from Eqn (8.27) m³/kg	Specific Volume from Tables m³/kg
Saturated liquid	0.0016	0.0017	0.001157
Saturated vapour	0.09	0.14	0.1324

- the Dieterici equation.

$$p = \frac{RT}{v-b} e^{-a/RTv} \quad (8.31)$$

Returning to the van der Waals gas, examination of Eqn (8.22) shows that

$$z_c = \frac{p_c v_c}{RT_c} = \frac{3}{8} = 0.375 \quad (8.32)$$

This value, z_c (sometimes denoted μ_c) is the compression coefficient, or compressibility factor, of a substance at the critical point. In general, the compression coefficient, z , is defined as

$$z = \frac{pv}{RT} \quad (8.33)$$

It is obvious that, for a real gas, z is not constant, because $z = 1$ for a perfect gas (i.e. in the superheat region), but it is 0.375 (ideally) at the critical point. There are tables and graphs which show the variation of z with state point, and these can be used to calculate the properties of real gases. These were originally derived by Obert (1960), and are reproduced in, for example, Bejan (1988) and Moran and Shapiro (1988).

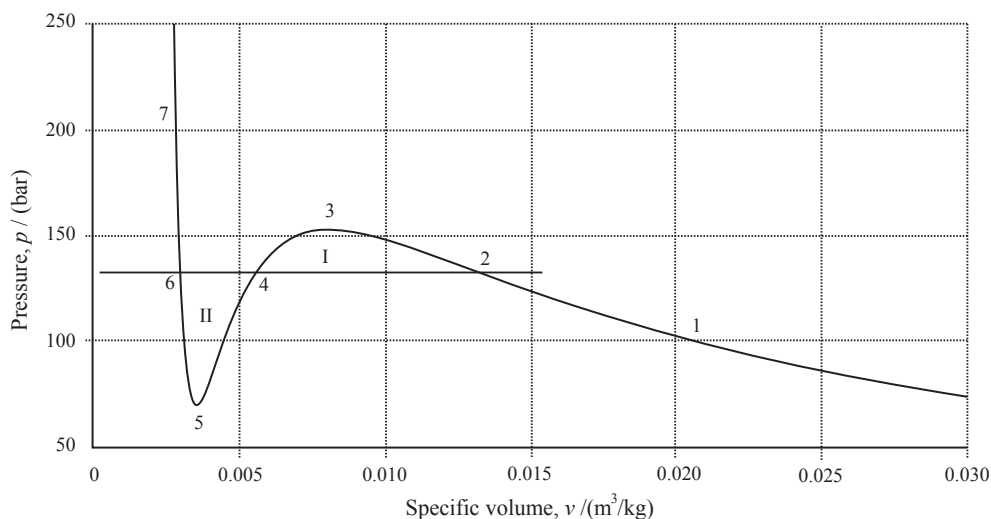
8.4 ISOTHERMS OR ISOBARS IN THE TWO-PHASE REGION

Equation (8.15) predicts that along an isotherm the pressure is related to the specific volume by a cubic equation, and this means that in some regions there are three values of volume which satisfy a particular pressure. Since the critical point has been defined as an inversion point then the multi-valued region lies below the critical point, and experience indicates this is the two-phase (liquid + vapour) region. It is known that pressure and temperature are not independent variables in this region, and that fluids evaporate at constant temperature in a constant pressure chamber; hence these isotherms should be at constant pressure. This anomaly can be resolved by considering the Gibbs energy of the fluid in the two-phase region. Since the evaporation must be an equilibrium process then it must obey the conditions of equilibrium. Considering the isotherm shown in Fig. 8.4, which has been calculated using Eqn (8.27) for water at 300 °C, it can be seen that in the regions from 3 to 1, and from 7 to 5 a decrease in pressure results in an increase in the specific volume. However, in the region between 5 and 3 an increase in pressure results in an increase in specific volume: this situation is obviously unstable. It was shown in Chapter 2 that equilibrium was defined by $\partial G|_{p,T} \geq 0$. Now

$$dg = vdp - sdT \quad (8.34)$$

and hence, along an isotherm the variation of Gibbs energy from an initial point, say, 1 to another point is

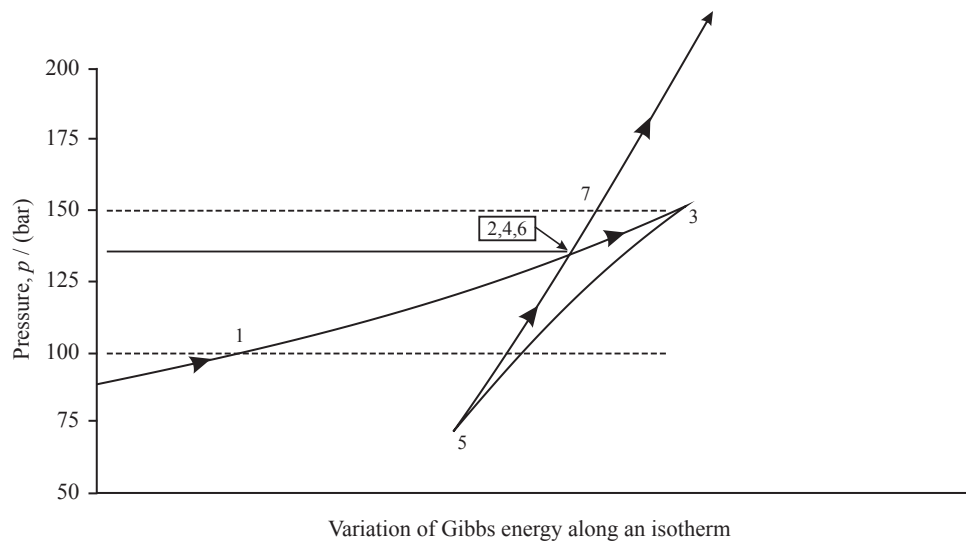
$$\Delta g = g - g_1 = \int_{p_1}^p vdp \quad (8.35)$$

**FIGURE 8.4**

Variation of pressure and specific volume for water along the 300 °C isotherm.

This variation has been calculated for the region between points 1 and 7 in Fig. 8.4, and is shown in Fig. 8.5.

It can be seen from Fig. 8.5 that the Gibbs energy increases along the isotherm from point 1 to point 3. Between point 3 and point 5 the Gibbs energy decreases, but then begins to increase again

**FIGURE 8.5**

Variation of Gibbs energy for water along the 300 °C isotherm.

as the fluid passes from 5 to 7. The regions between 1 and 3, and 5 and 7 can be seen to be stable in terms of variation of Gibbs energy, whereas that between 3 and 5 is unstable: this supports the argument introduced earlier based on the variation of pressure and volume. Figure 8.5 also shows that the values of Gibbs energy and pressure are all equal at the points 2, 4 and 6, which is a line of constant pressure on Figure 8.4. This indicates that the Gibbs energy of the liquid and vapour phases can be equal if the two ends of the evaporation process are at equal pressures for an isotherm. Now considering the region between the saturated liquid and saturated vapour lines; the Gibbs energy along the ‘isotherm’ shown in Fig. 8.4 will increase between points 2 and 3, and the substance would attempt to change spontaneously back from 3 to 2, or from 3 to 4, and hence point 3 is obviously unstable. In a similar manner the stability of point 5 can be considered. An isobar at 100 bar is shown on fig. 8.5, and it can be seen that it crosses the Gibbs energy line at three points – the lowest Gibbs energy is at state 1. Hence, state 1 is more stable than the other points. If that isobar were moved down further until it passed through point 5, then there would be other points of higher stability than point 5 and the system would tend to move to these points. This argument has still not defined the equilibrium line between the liquid and vapour lines, but this can be defined by ensuring that the Gibbs energy remains constant in the two-phase region, and this means the equilibrium state must be defined by constant temperature and constant Gibbs energy. Three points on that line are defined by states 2, 4 and 6. The pressure which enables constant Gibbs energy to be achieved is such that

$$\int_{p_2}^{p_6} v dp = 0 \quad \text{between points 2 and 6} \quad (8.36)$$

and this means that

$$\underbrace{\int_{p_2}^{p_4} v dp}_{\text{Region I}} + \underbrace{\int_{p_4}^{p_6} v dp}_{\text{Region II}} = 0 \quad (8.37)$$

which means that the area of the region between the equilibrium isobar and line 2-3-4 (Region I) must be equal to that between the isobar and line 4-5-6 (Region II). This is referred to as Maxwell’s equal area rule, and the areas are labelled I and II in Fig. 8.4.

8.5 CONCLUDING REMARKS

A number of different equations of state have been introduced which can describe the behaviour of substances over a broader range than the common perfect gas equation. van der Waals equation has been analysed quite extensively, and it has been shown to be capable of defining the behaviour of gases close to the saturated vapour line. The law of corresponding states has been developed, and this enables a general equation of state to be considered for all substances. The region between the saturated liquid and vapour lines has been analysed and Gibbs energy has been used to define the equilibrium state.

8.6 PROBLEMS

P8.1 The Dieterici equation for a pure substance is given by

$$p = \frac{\Re T}{v - b} e^{-\frac{a}{\Re T v}}$$

Determine

- (a) the constants a and b in terms of the critical pressure and temperature;
- (b) the compressibility factor at the critical condition;
- (c) the law of corresponding states.

$$\left[a = \frac{4\Re^2 T_c^2}{p_c e^2}; \quad b = \frac{\Re T_c}{p_c e^2}; \quad z_c = 0.2707; \quad p_R = \frac{T_R}{(2v_R - 1)} \exp\left(2\left(1 - \frac{1}{v_R T_R}\right)\right) \right]$$

P8.2 Derive expressions for $\left(\frac{\partial c_v}{\partial v}\right)_T$ for substances obeying the following laws:

- (a) $p = \frac{\Re T}{v - b} e^{-\frac{a}{\Re T v}}$
- (b) $p = \frac{\Re T}{v - b} - \frac{a}{T v^2}$
- (c) $p = \frac{\Re T}{v - b} - \frac{a}{v(v - b)} + \frac{c}{v^3}$.

Discuss the physical implication of the results.

$$\left[\frac{p a^2}{\Re^2 v^2 T^3}; \quad -\frac{2a}{v^2 T^2}; \quad 0 \right]$$

P8.3 The difference of specific heats for an ideal gas, $c_{p,m} - c_{v,m} = \Re$. Evaluate the difference in specific heats for gases obeying (1) the van der Waals and (2) the Dieterici equations of state. Comment on the results for the difference in specific heat for these gases compared with the ideal gas.

$$\left[\Re / \left(1 - \frac{2a(v - b)^2}{\Re T v^3} \right) \right]$$

P8.4 Derive an expression for the law of corresponding states for a gas represented by the following expression:

$$p = \frac{\Re T}{v - b} - \frac{a}{T v^2}.$$

$$\left[p_R = \frac{8T_R}{3v_R - 1} - \frac{3}{T_R v_R^2} \right]$$

P8.5 Show, for a gas obeying the state equation

$$pv = (1 + \alpha)\Re T$$

where α is a function of temperature alone, that the specific heat at constant pressure is given by

$$c_p = -\Re T \frac{d^2(\alpha T)}{dT^2} \ln p + c_{p_0}$$

where c_{p_0} is the specific heat at unit pressure.

$$\left[c_p = -\Re T \frac{d^2(\alpha T)}{dT^2} \ln p + c_{p_0} \right]$$

P8.6 The virial equation of state is

$$pv = \Re T \left(b_1 + \frac{b_2}{v} + \frac{b_3}{v^2} + \dots \right)$$

Compare this equation with van der Waals equation of state and determine the first two virial coefficients, b_1 and b_2 , as a function of temperature and the van der Waals constants.

Determine the critical temperature and volume (T_c, v_c) for the van der Waals gas, and show that

$$b_2 = \frac{v_c}{3} \left(1 - \frac{27T_c}{8v_c} \right).$$

$$[b_1 = 1; b_2 = (b - a/\Re T)]$$

P8.7 The equation of state for a certain gas is

$$\frac{pv}{\Re T} = 1 + pe^{-AT}$$

where A is constant.

Show that if the specific heat at constant pressure at some datum pressure p_0 is c_{p_0} , then the value of the specific heat at constant pressure at the state (T, p) is given by

$$c_p - c_{p_0} = \Re T A e^{-AT} (2 - AT) (p - p_0).$$

- P8.8** How can the equation of state in the form of a relationship between pressure, volume and temperature be used to extend limited data on the entropy of a substance. A certain gas, A, has the equation of state

$$pv = \Re T (1 + \alpha p),$$

where α is a function of temperature alone. Show that

$$\left(\frac{\delta s}{\delta p} \right)_T = -\Re \left(\frac{1}{p} + \alpha + T \frac{d\alpha}{dT} \right).$$

Another gas B behaves as an ideal gas. If the molar entropy of gas A is equal to that of gas B when both are at pressure p_0 and the same temperature T , show that if the pressure is increased to p with the temperature maintained constant at T the molar entropy of gas B exceeds that of gas A by an amount

$$\Re (p - p_0) \left(\alpha + T \frac{d\alpha}{dT} \right).$$

- P8.9** A gas has the equation of state

$$\frac{pv}{\Re T} = a - bT,$$

where a and b are constants. If the gas is compressed reversibly and isothermally at the temperature T' show that the compression will also be adiabatic if

$$T' = \frac{a}{2b}.$$

THERMODYNAMIC PROPERTIES OF IDEAL GASES AND IDEAL GAS MIXTURES OF CONSTANT COMPOSITION

It was shown in Chapter 8 that it is necessary to use quite sophisticated equations of state to define the properties of vapours which are close to the saturated vapour line. However, for gases in the superheat region the ideal gas equation gives sufficient accuracy for most purposes. The equation of state for an ideal gas, in terms of mass, is

$$pV = mRT \quad (9.1)$$

where

p = pressure (N/m^2)

V = volume (m^3)

m = mass (kg)

R = specific gas constant (kJ/kg K)

T = absolute (or thermodynamic) temperature (K)

This can be written in more general terms using the amount of substance, when

$$pV = n\mathcal{R}T \quad (9.2)$$

where

n = amount of substance, or chemical amount (kmol)

$\mathcal{R}$ = universal gas constant (kJ/kmol K)

Equation (9.2) is more useful than Eqn (9.1) for combustion calculations because the combustion process takes place on a molar basis. To be able to work on a molar basis it is necessary to know the molecular weights (or relative molecular masses) of the elements and compounds involved in a reaction.

9.1 MOLECULAR WEIGHTS

The molecular weight (or relative molecular mass) of a substance is the mass of its molecules relative to that of other molecules. The datum for molecular weights is carbon-12, and this is given a molecular weight of 12. All other elements and compounds have molecular weights relative to this, and their

Table 9.1 Molecular Weights of Elements and Compounds Commonly Encountered in Combustion

	Air	O ₂	N ₂	Atmospheric N ₂	H ₂	CO	CO ₂	H ₂ O	C
m_w	28.97	32	28	28.17	2	28	44	18	12

molecular weights are not integers. To be able to perform combustion calculations it is necessary to know the atomic or molecular weights of commonly encountered elements: these can be combined to give other compounds. Table 9.1 gives the data for individual elements or compounds in integral numbers (except air which is a mixture of gases): in reality only carbon-12 (used as the basis for atomic/molecular weights) has an integral value, but most values are very close to integral ones and will be quoted as such.

9.1.1 AIR

As stated previously, most combustion takes place between a hydrocarbon fuel and air. Air is a mixture of gases, the most abundant being oxygen and nitrogen with small proportions of other gases. In fact, in practice air is a mixture of all elements and compounds because everything will evaporate in air until the partial pressure of its atoms, or molecules, achieves its saturated vapour pressure. In reality, this evaporation can usually be neglected, except in the case of water. Table 9.1 shows that the molecular weight of atmospheric nitrogen is higher than that of pure nitrogen; this is because ‘atmospheric nitrogen’ is taken to be a mixture of nitrogen and about 1.8% by mass of argon, carbon dioxide and other gases: the molecular weight of atmospheric nitrogen includes the effect of the other substances.

The composition of air is defined as 21% O₂ and 79% N₂ by volume (this can be written 21 mol% O₂ and 79 mol% N₂). This is equivalent to 23.2% O₂ and 76.8% N₂ by mass.

9.2 STATE EQUATION FOR IDEAL GASES

The equation of state for an ideal gas, a , is

$$pV = m_a R_a T \quad (9.3)$$

If the mass of gas, m_a , is made equal to the molecular weight of the gas in the appropriate units, then the amount of substance a is known as a **mole** (if the mass is in kg then the amount of substance is called a **kmol**). If the volume occupied by this amount of substance is denoted v_m then

$$v_m = \frac{m_{wa} R_a T}{p}, \quad (9.4)$$

where v_m is the molar specific volume, and has the units of m³/mol, or m³/kmol.

Now Avogadro’s Principle states that

‘equal volumes of all ideal gases at a particular temperature and pressure contain the same number of molecules (and hence the same amount of substance)’.

Table 9.2 Values of the Universal Gas Constant, $\mathfrak{R}$, in Various Units

8314 J/kmol K
1.985 kcal/kmol K
1.985 Btu/lb-mol K
1.985 CHU/lb-mol R
2782 ft lb _f /lb-mol K
1545 ft lb _f /lb-mol R

Hence, any other gas, b , at the same pressure and temperature will occupy the same volume as gas a , i.e.

$$\frac{pV_m}{T} = m_{w_a}R_a = m_{w_b}R_b = \dots m_{w_i}R_i = \dots = \mathfrak{R}. \quad (9.5)$$

If a system contains an amount of substance n_a of gas, a , then Eqn (9.5) may be written

$$pV_m = n_a m_{w_a} R_a T = n_a \mathfrak{R} T. \quad (9.6)$$

It can be seen that for ideal gases the product $m_{w_i}R_i$ is the same for all gases: it is called the **universal gas constant**, $\mathfrak{R}$. The values of the universal gas constant, $\mathfrak{R}$, together with its various units are shown in Table 9.2.

9.2.1 IDEAL GAS EQUATION

The evaluation of the properties of an ideal gas will now be considered. It has been shown that the internal energy and enthalpy of an ideal gas are not functions of the volume or pressure, and hence these properties are simply functions of temperature alone. This means that the specific heats at constant volume and constant pressure are not partial derivatives of temperature, but can be written

$$\begin{aligned} c_v &= \left(\frac{\partial u}{\partial T} \right)_v = \frac{du}{dT} \\ c_p &= \left(\frac{\partial h}{\partial T} \right)_p = \frac{dh}{dT}. \end{aligned} \quad (9.7)$$

Also, if c_v and c_p in molar quantities are denoted by $c_{v,m}$ and $c_{p,m}$ then, for ideal and perfect gases

$$c_{p,m} - c_{v,m} = \mathfrak{R}. \quad (9.8)$$

It is possible to evaluate the properties of substances in terms of unit mass (specific properties) or unit amount of substance (molar properties). The former will be denoted by lower case letters (e.g. v , u , h , g , etc.), and the latter will be denoted by lower case letters and a suffix m

(e.g. v_m , u_m , h_m , g_m , etc.). The molar properties are more useful for combustion calculations, and these will be considered here.

The molar internal energy and molar enthalpy can be evaluated by integrating Eqn (9.7), giving

$$\begin{aligned} u_m &= \int_{T_0}^T c_{v,m} dT + u_{0,m} \\ h_m &= \int_{T_0}^T c_{p,m} dT + h_{0,m} \end{aligned} \quad (9.9)$$

where $u_{0,m}$ and $h_{0,m}$ are the values of u_m and h_m at the datum temperature T_0 .

Now, by definition,

$$h_m = u_m + pv_m, \text{ and for an ideal gas } pv_m = \Re T, \text{ thus } h_m = u_m + \Re T. \quad (9.10)$$

Hence, at $T = 0$, $u_m = h_m$, i.e. $u_{0,m} = h_{0,m}$. (A similar relationship exists for the specific properties, u and h .)

To be able to evaluate the internal energy or enthalpy of an ideal gas using Eqn (9.10), it is necessary to know the variation of specific heat with temperature. It is possible to derive such a function from empirical data by curve-fitting techniques, if such data is available. In some regions of the state diagram it is necessary to use quantum mechanics to evaluate the data, but this is beyond the scope of this text. It will be assumed here that the values of c_v are known in the form

$$c_{v,m} = a + bT + cT^2 + dT^3 \quad (9.11)$$

where a , b , c and d have been evaluated from experimental data. Since $c_{p,m} - c_{v,m} = \Re$ then an expression for $c_{p,m}$ can be easily obtained. Hence it is possible to find the values of internal energy and enthalpy at any temperature if the values at T_0 can be evaluated. This problem is not a major one if the composition of the gas remains the same because the datum levels will cancel out. However, if the composition varies during the process it is necessary to know the individual datum values. They can be measured by calorimetric or spectrographic techniques. The ‘thermal’ part of the internal energy and enthalpy, i.e. that which is a function of temperature, will be denoted

$$\begin{aligned} u_m(T) &= \int_{T_0}^T c_{v,m} dT \\ h_m(T) &= \int_{T_0}^T c_{p,m} dT \end{aligned} \quad (9.12)$$

and then Eqns (9.9) become

$$\begin{aligned} u_m &= u_m(T) + u_{0,m} \\ h_m &= h_m(T) + h_{0,m} \end{aligned} \quad (9.13)$$

assuming that the base temperature is absolute zero.

Enthalpy or internal energy data are generally presented in tabular or graphical form. The two commonest approaches are described in [Section 9.3](#) below. First, it is useful to consider further the terms involved.

9.2.2 THE SIGNIFICANCE OF $u_{0,m}$ AND $h_{0,m}$

As previously discussed, $u_{0,m}$ and $h_{0,m}$ are the values of molar internal energy, u_m , and molar enthalpy, h_m , at the reference temperature, T_0 . If $T_0 = 0$ then, for an ideal gas,

$$u_{0,m} = h_{0,m} \quad (9.14)$$

If $T_0 \neq 0$, then $u_{0,m}$ and $h_{0,m}$ are different. Most calculations involve changes in enthalpy or internal energy, and if the composition during a process is invariant the values of $h_{0,m}$ or $u_{0,m}$ will cancel.

However, if the composition changes during a process it is necessary to know the difference between the values of $u_{0,m}$ or $h_{0,m}$ for the different species at the reference temperature. This is discussed below.

Obviously $u_{0,m}$ and $h_{0,m}$ are consequences of the ideal gas assumption and the [Eqn \(9.3\)](#)

$$h = h(T) + h_0$$

contains the assumption that the ideal gas law applies down to T_0 . If $T_0 = 0$, or a value outside the superheat region for the gas being considered, then the gas ceases to be ideal, often becoming either liquid or solid. To allow for this it is necessary to include latent heats. This will not be dealt with here, but the published data do include these corrections.

9.2.3 ENTROPY OF AN IDEAL GAS – THIRD LAW OF THERMODYNAMICS

The change in entropy during a process is defined as

$$ds_m = \frac{dh_m}{T} - \frac{\Re dp}{p} \quad (9.15)$$

If the functional relationship $h_m = h_m(T)$ is known then [Eqn \(9.15\)](#) may be evaluated, giving

$$s_m - s_{0,m} = \int_{T_0}^T \frac{dh_m}{T} - \Re \ln \frac{p}{p_0} \quad (9.16)$$

where $s_{0,m}$ = value of s_m at T_0 and p_0 .

It is convenient to take the reference temperature, T_0 , as absolute zero. It was previously shown that

$$dh_m = c_{p,m}(T)dT \text{ and hence } \frac{dh_m}{T} = \frac{c_{p,m}(T)dT}{T}. \quad (9.17)$$

Consider $\lim_{T \rightarrow 0} \left(\frac{dh_m}{T} \right)$.

If $c_{p,m}(T_0) \geq 0$ then the expression is either infinite or indeterminate. However, before reaching absolute zero the substance will cease to be an ideal gas and will become a solid. It can be shown by the Debye T^3 law (Atkins (1996)) and experiment that the specific heat of a solid is given by the law $c_p = aT^3$.

Hence

$$\lim_{T \rightarrow 0} \left(\frac{dh_m}{T} \right) = \lim_{T \rightarrow 0} \left(\frac{aT^3 dT}{T} \right) = \lim_{T \rightarrow 0} (aT^2 dT) \rightarrow 0. \quad (9.18)$$

To integrate from absolute zero to T it is necessary to include the latent heats, but still it is possible to evaluate $\int \frac{dh_m}{T}$.

If $s_m(T)$ is defined as

$$s_m(T) = \int_{T_0}^T \frac{dh_m}{T} dT \quad (9.19)$$

then entropy

$$s_m = s_m(T) - \Re \ln \frac{p}{p_0} + s_{0,m}. \quad (9.20)$$

The term $s_{0,m}$ is the constant of integration and this can be compared with $u_{0,m}$ and $h_{0,m}$. If the composition is invariant then the value of $s_{0,m}$ will cancel out when evaluating changes in s and it is not necessary to know its value. If the composition varies then it is necessary to know, at least, the difference between s_0 values for the substances involved. It is not possible to obtain any information about s_0 from classical (macroscopic) thermodynamics but statistical thermodynamics shows that ‘for an isothermal process involving *only phases in internal equilibrium* the *change in entropy approaches zero at absolute zero*’. This means that for substances that exist in crystalline or liquid form at low temperatures it is possible to evaluate entropy changes by assuming that differences in $s_{0,m}$ are zero.

It should also be noted that the pressure term, p , in Eqn (9.20) is the **partial pressure** of the gas if it is contained in a mixture, and p_0 is a datum pressure (often chosen as 1 bar or, in the past, 1 atm).

9.2.4 THE GIBBS ENERGY OF AN IDEAL GAS

The Gibbs energy will now be derived for use later when considering the equilibrium composition of mixtures (dissociation).

By definition

$$g_m = h_m - Ts_m \quad (9.21)$$

and

$$h_m = h_m(T) + h_{0,m} \quad (9.22)$$

If the pressure ratio, p/p_0 , is denoted by the symbol p_r , i.e. $p_r = p/p_0$, then

$$s_m = s_m(T) - \Re \ln p_r + s_{0,m} \quad (9.23)$$

and

$$\begin{aligned} g_m &= h_m(T) + h_{0,m} - T(s_m(T) - \Re \ln p_r + s_{0,m}) \\ &= (h_{0,m} - Ts_{0,m}) + (h_m(T) - Ts_m(T)) + \Re T \ln p_r. \end{aligned} \quad (9.24)$$

If the terms at T_0 are combined to give

$$g_{0,m} = h_{0,m} - Ts_{0,m} \quad (9.25)$$

and the temperature dependent terms are combined to give

$$g_m(T) = h_m(T) - Ts_m(T) \quad (9.26)$$

then

$$g_m = g_m(T) + \Re T \ln p_r + g_{0,m}. \quad (9.27)$$

Often $g_m(T)$ and $g_{0,m}$ are combined to give g_m^0 , which is the pressure independent portion of the Gibbs energy, i.e. $g_m^0 = g_m(T) + g_{0,m}$, and then

$$g_m = g_m^0 + \Re T \ln p_r. \quad (9.28)$$

g_m^0 is the value of the molar Gibbs energy at a temperature, T , and a pressure of p_0 , and it is a function of temperature alone. The datum pressure, p_0 , is usually chosen as 1 bar nowadays (although much data is published based on a datum pressure of 1 atm: the difference is not usually significant in engineering problems, but it is possible to convert some of the data, e.g. equilibrium constants).

Gibbs energy presents the same difficulty when dealing with mixtures of varying composition as u_0 , h_0 and s_0 . If the composition is invariant, changes in Gibbs energy are easily calculated because the g_0 terms cancel. For mixtures of varying composition g_0 must be known. It can be seen from Eqn (9.26) that if the reference temperature, T_0 , equals zero then

$$g_{0,m} = h_{0,m} = u_{0,m} \quad (9.29)$$

9.3 TABLES OF $u(T)$ AND $h(T)$ AGAINST T

These tables are based on polynomial equations defining the enthalpy of the gas. The number of terms can vary depending on the required accuracy and the temperature range to be covered. This section will limit the number of coefficients to six, based on Benson (1977). The equation used is of the form

$$\frac{h_m(T)}{\Re T} = \frac{h_m - h_{0,m}}{\Re T} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad (9.30)$$

The values of the coefficients for various gases are listed in Table 9.3, for the range 500–3000 K. If used outside these ranges the accuracy of the calculation will diminish.

Table 9.3 Enthalpy Coefficients for Selected Gases Found in Combustion Processes (Based on kJ/kmol, with the Temperature in K)

Substance	a_5	a_4	a_3	a_2	a_1	a_6	$h_0 = a_0$ kJ/kmol
H ₂	0.0000	-1.44392e-11	9.66990e-08	-8.18100e-6	3.43328	-3.84470	0.0000
CO	0.0000	-2.19450e-12	-3.22080e-8	3.76970e-4	3.317000	4.63284	-1.13882e5
N ₂	0.0000	-6.57470e-12	1.95300e-9	2.94260e-4	3.34435	3.75863	0.0000
NO	0.0000	-4.90360e-12	-9.58800e-9	2.99380e-4	3.50174	5.11346	8.99147e4
CO ₂	0.0000	8.66002e-11	-7.88542e-7	2.73114e-3	3.09590	6.58393	-3.93405e5
O ₂	0.0000	1.53897e-11	-1.49524e-7	6.52350e-4	3.25304	5.71243	0.0000
H ₂ O	0.0000	-1.81802e-11	4.95240e-8	5.65590e-4	3.74292	9.65140e-1	-2.39082e5
CH ₄	-8.58611e-15	1.62497e-10	-1.24402e-6	4.96462e-3	1.93529	8.15300	-6.6930e4
O	0.0000	-1.38670e-11	1.00187e-7	-2.51427e-4	2.76403	3.73309	2.46923e5

Hence the enthalpy, internal energy, entropy and Gibbs energy can be evaluated as follows.

Enthalpy

$$\begin{aligned}
 h_m(T) &= \Re T (a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \\
 &= \Re (a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5) \\
 &= \Re \sum_{i=1}^5 a_i T^i.
 \end{aligned} \tag{9.31}$$

Internal energy

$$\begin{aligned}
 u_m(T) &= \Re T ((a_1 - 1) + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \\
 &= \Re ((a_1 - 1)T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5) \\
 &= \Re \sum_{i=1}^5 a_i T^i - \Re T = h(T) - \Re T.
 \end{aligned} \tag{9.32}$$

Entropy

This is defined by Eqn (9.15) as

$$ds_m = \frac{dh_m}{T} - \Re \frac{dp}{p} \tag{9.15}$$

Integrating Eqn (9.15) gives

$$s_m(T) = s_m - s_{0,m} = \int_{T_0}^T \frac{dh_m}{T} - \Re \ln \left(\frac{p}{p_0} \right), \tag{9.20}$$

Equation (9.20) introduces some problems in solution. The first is that $\int_{T_0}^T \frac{dh_m}{T} = \int_{T_0}^T \frac{c_{p,m} dT}{T}$, and this results in $\ln(0)$ when $T = T_0$. Fortunately these problems can be overcome by use of the

Van't Hoff equation, which will be derived in section (12.8) where dissociation is introduced. This states that

$$h_m = -T^2 \left(\frac{d}{dT} (\mu_m^0/T) \right) \quad (9.33)$$

where, for $T_0 = 0$ K,

$$\mu_m^0 = \text{chemical potential term} = g_m(T) + g_{0,m} = g_m(T) + h_{0,m} \quad (9.34)$$

and

$$h_m = h_m(T) + h_{0,m}. \quad (9.13)$$

(Note: the term μ_m^0 , is similar to g_m^0 , which was introduced in Eqn (9.28). At this stage it is sufficient to note that chemical potential has the same numerical value as the specific Gibbs energy. The chemical potential will be defined in the Section 12.2.)

By definition, in Eqn (9.31),

$$\frac{h_m(T)}{\Re T} = \frac{h_m - h_{0,m}}{\Re T} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4, \quad (9.35)$$

giving

$$\frac{h_m(T)}{\Re T^2} = \frac{a_1}{T} + a_2 + a_3 T + a_4 T^2 + a_5 T^3. \quad (9.36)$$

Substituting Eqns (9.34), (9.13) and (9.36) into Eqn (9.33) and rearranging gives

$$-\left\{ \frac{a_1}{T} + a_2 + a_3 T + a_4 T^2 + a_5 T^3 + \frac{h_{0,m}}{\Re T^2} \right\} dT = \frac{1}{\Re} d \left(\frac{g_m(T) + h_{0,m}}{T} \right), \quad (9.37)$$

which can be integrated to

$$-\left\{ a_1 \ln T + a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} - \frac{h_{0,m}}{\Re T} \right\} + A = \frac{g_m(T) + h_{0,m}}{\Re T}. \quad (9.38)$$

It is conventional to let

$$A = a_1 - a_6 \quad (9.39)$$

and then

$$\frac{g_m(T)}{\Re T} = a_1 (1 - \ln T) - \left\{ a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} \right\} - a_6. \quad (9.40)$$

The value of entropy can then be obtained from

$$s_m(T) = \frac{h_m(T) - g_m(T)}{T}, \quad (9.41)$$

giving

$$s_m(T) = \Re \left(a_1 \ln T + 2a_2 T + \frac{3}{2} a_3 T^2 + \frac{4}{3} a_4 T^3 + \frac{5}{4} a_5 T^4 + a_6 \right). \quad (9.42)$$

Gibbs energy

The Gibbs energy can be evaluated from Eqn (9.40) or Eqn (9.26)

$$g_m(T) = h_m(T) - Ts_m(T) \quad (9.26)$$

The values obtained from this approach, using Eqns (9.31)–(9.42) are given in Table 9.4 for oxygen, nitrogen, hydrogen, water, carbon monoxide, carbon dioxide, nitric oxide and methane. The tables have been evaluated up to 3500 K, slightly beyond the range stated in relation to Table 9.3, but the error is not significant. This enables more combustion problems to be solved using this data. Other commonly used tables are those of JANAF (1971).

9.3.1 TABLES OF MEAN SPECIFIC HEAT

Sometimes data are given in terms of mean specific heat rather than the actual specific heat at a particular temperature. This approach will now be described.

Consider the change of enthalpy, h , between temperatures T_1 and T_2 . This is

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p(T) dT = h(T_2) - h(T_1) \quad (9.43)$$

Now, this can be written

$$\bar{c}_p(T_2 - T_1) = h(T_2) - h(T_1), \quad (9.44)$$

where $\bar{c}_p$ is the mean specific heat between T_1 and T_2 . Normally $\bar{c}_p$ is given at a particular temperature, T , and it is then defined as the mean specific heat between the temperature T and a reference temperature T_{ref} .

i.e.
$$(\bar{c}_p)_T = \frac{h(T) - h(T_{ref})}{T - T_{ref}} \quad (9.45)$$

It is also possible to write the mean specific heat as a polynomial function of temperature, in which case

$$(\bar{c}_p)_T = a + bT + cT^2 + \dots \quad (9.46)$$

where a , b and c are tabulated coefficients.

If it is required to calculate the enthalpy difference between two temperatures T_1 and T_2 then

$$h_2 - h_1 = (\bar{c}_p)_{T_2}(T_2 - T_{ref}) - (\bar{c}_p)_{T_1}(T_1 - T_{ref}) \quad (9.47)$$

Having calculated the change in enthalpy, $h_2 - h_1$, then the change in internal energy, $u_2 - u_1$, may be evaluated as

$$u_2 - u_1 = h_2 - RT_2 - (h_1 - RT_1) = h_2 - h_1 - R(T_2 - T_1) \quad (9.48a)$$

or, in molar terms by

$$u_{m,2} - u_{m,1} = h_{m,2} - \mathcal{R}T_2 - (h_{m,1} - \mathcal{R}T_1) = h_{m,2} - h_{m,1} - \mathcal{R}(T_2 - T_1) \quad (9.48b)$$

Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Molecular oxygen, O_2 : $h_0 = 0.0000$ kJ/kmol					Molecular nitrogen, N_2 : $h_0 = 0.0000$ kJ/kmol				
50	1365.74	950.03	153.84	-6326.3	50	1396.41	980.70	140.27	-5617.2
100	2757.68	1926.25	173.12	-14553.9	100	2805.07	1973.64	159.79	-13174.0
150	4174.92	2927.77	184.60	-23515.4	150	4225.96	2978.82	171.31	-21470.5
200	5616.56	3953.70	192.89	-32962.1	200	5659.09	3996.23	179.55	-30251.7
250	7081.75	5003.18	199.43	-42775.9	250	7104.43	5025.86	186.00	-39396.4
298	8509.70	6032.04	204.65	-52477.3	298	8503.43	6025.77	191.12	-48450.8
300	8569.64	6075.35	204.85	-52886.8	300	8561.97	6067.68	191.32	-48833.3
350	10079.40	7169.40	209.51	-63248.6	350	10031.66	7121.65	195.85	-58515.2
400	11610.23	8284.51	213.60	-73828.2	400	11513.46	8187.74	199.81	-68408.6
450	13161.33	9419.89	217.25	-84601.0	450	13007.34	9265.90	203.32	-78488.4
500	14731.93	10574.78	220.56	-95547.5	500	14513.22	10356.07	206.50	-88735.2
550	16321.30	11748.43	223.59	-106652.2	550	16031.05	11458.18	209.39	-99133.4
600	17928.68	12940.10	226.39	-117902.4	600	17560.74	12572.16	212.05	-109670.4
650	19553.39	14149.09	228.99	-129287.4	650	19102.23	13697.93	214.52	-120335.4
700	21194.71	15374.70	231.42	-140798.2	700	20655.41	14835.40	216.82	-131119.6
750	22851.99	16616.26	233.71	-152426.8	750	22220.19	15984.47	218.98	-142015.2
800	24524.55	17873.11	235.86	-164166.6	800	23796.47	17145.03	221.01	-153015.5
850	26211.78	19144.62	237.91	-176011.4	850	25384.12	18316.97	222.94	-164114.8
900	27913.05	20430.18	239.85	-187955.8	900	26983.03	19500.16	224.77	-175307.9
950	29627.76	21729.18	241.71	-199995.3	950	28593.06	20694.47	226.51	-186590.2
1000	31355.35	23041.05	243.48	-212125.3	1000	30214.07	21899.77	228.17	-197957.5
1050	33095.25	24365.23	245.18	-224342.1	1050	31845.92	23115.90	229.76	-209406.1
1100	34846.92	25701.19	246.81	-236642.0	1100	33488.45	24342.72	231.29	-220932.8
1150	36609.84	27048.40	248.38	-249021.9	1150	35141.49	25580.04	232.76	-232534.4
1200	38383.52	28406.36	249.89	-261478.6	1200	36804.88	26827.72	234.18	-244208.0
1250	40167.47	29774.59	251.34	-274009.5	1250	38478.43	28085.55	235.54	-255951.3
1300	41961.22	31152.63	252.75	-286612.0	1300	40161.95	29353.36	236.86	-267761.7
1350	43764.34	32540.04	254.11	-299283.6	1350	41855.26	30630.95	238.14	-279637.0
1400	45576.41	33936.39	255.43	-312022.2	1400	43558.13	31918.11	239.38	-291575.2
1450	47397.01	35341.28	256.71	-324825.7	1450	45270.36	33214.63	240.58	-303574.5
1500	49225.76	36754.31	257.95	-337692.1	1500	46991.73	34520.28	241.75	-315632.9
1550	51062.30	38175.14	259.15	-350619.6	1550	48722.01	35834.85	242.88	-327748.9
1600	52906.28	39603.40	260.32	-363606.5	1600	50460.96	37158.08	243.99	-339920.9
1650	54757.37	41038.78	261.46	-376651.1	1650	52208.33	38489.74	245.06	-352147.3
1700	56615.26	42480.95	262.57	-389752.0	1700	53963.87	39829.56	246.11	-364426.8

Continued

Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases—cont'd

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Molecular oxygen, O ₂ : $h_0 = 0.0000$ kJ/kmol					Molecular nitrogen, N ₂ : $h_0 = 0.0000$ kJ/kmol				
1750	58479.67	43929.65	263.65	−402907.6	1750	55727.32	41177.30	247.13	−376758.1
1800	60350.32	45384.58	264.70	−416116.5	1800	57498.40	42532.66	248.13	−389139.9
1850	62226.96	46845.50	265.73	−429377.5	1850	59276.85	43895.39	249.11	−401570.9
1900	64109.36	48312.19	266.74	−442689.3	1900	61062.36	45265.19	250.06	−414050.2
1950	65997.31	49784.42	267.72	−456050.7	1950	62854.64	46641.76	250.99	−426576.5
2000	67890.61	51262.01	268.68	−469460.6	2000	64653.40	48024.80	251.90	−439148.9
2050	69789.09	52744.78	269.61	−482918.0	2050	66458.32	49414.00	252.79	−451766.3
2100	71692.60	54232.57	270.53	−496421.6	2100	68269.07	50809.04	253.67	−464427.8
2150	73600.99	55725.25	271.43	−509970.7	2150	70085.34	52209.60	254.52	−477132.5
2200	75514.16	57222.70	272.31	−523564.2	2200	71906.79	53615.33	255.36	−489879.5
2250	77432.00	58724.83	273.17	−537201.2	2250	73733.06	55025.89	256.18	−502668.0
2300	79354.44	60231.55	274.02	−550880.9	2300	75563.81	56440.92	256.98	−515497.1
2350	81281.41	61742.81	274.84	−564602.5	2350	77398.68	57860.08	257.77	−528366.0
2400	83212.89	63258.57	275.66	−578365.1	2400	79237.30	59282.98	258.55	−541274.1
2450	85148.84	64778.80	276.46	−592168.0	2450	81079.29	60709.25	259.31	−554220.4
2500	87089.26	66303.51	277.24	−606010.4	2500	82924.26	62138.51	260.05	−567204.4
2550	89034.18	67832.71	278.01	−619891.8	2550	84771.83	63570.36	260.78	−580225.3
2600	90983.62	69366.44	278.77	−633811.2	2600	86621.58	65004.40	261.50	−593282.5
2650	92937.65	70904.76	279.51	−647768.3	2650	88473.12	66440.22	262.21	−606375.3
2700	94896.35	72447.74	280.24	−661762.2	2700	90326.01	67877.40	262.90	−619503.0
2750	96859.80	73995.47	280.96	−675792.5	2750	92179.84	69315.52	263.58	−632665.0
2800	98828.11	75548.07	281.67	−689858.5	2800	94034.17	70754.13	264.25	−645860.8
2850	100801.43	77105.68	282.37	−703959.7	2850	95888.56	72192.81	264.90	−659089.7
2900	102779.90	78668.43	283.06	−718095.5	2900	97742.56	73631.09	265.55	−672351.1
2950	104763.70	80236.52	283.74	−732265.5	2950	99595.70	75068.51	266.18	−685644.4
3000	106753.02	81810.12	284.41	−746469.2	3000	101447.52	76504.62	266.81	−698969.2
3050	108748.05	83389.44	285.07	−760706.1	3050	103297.54	77938.92	267.42	−712324.8
3100	110749.05	84974.72	285.72	−774975.8	3100	105145.28	79370.95	268.02	−725710.7
3150	112756.24	86566.20	286.36	−789277.8	3150	106990.25	80800.21	268.61	−739126.4
3200	114769.90	88164.14	286.99	−803611.7	3200	108831.95	82226.19	269.19	−752571.4
3250	116790.32	89768.85	287.62	−817977.1	3250	110669.87	83648.39	269.76	−766045.1
3300	118817.80	91380.61	288.24	−832373.6	3300	112503.49	85066.30	270.32	−779547.1
3350	120852.67	92999.76	288.85	−846800.9	3350	114332.28	86479.38	270.87	−793076.8
3400	122895.26	94626.64	289.46	−861258.7	3400	116155.72	87887.10	271.41	−806633.8
3450	124945.95	96261.62	290.06	−875746.5	3450	117973.26	89288.93	271.94	−820217.5
3500	127005.11	97905.06	290.65	−890264.2	3500	119784.36	90684.31	272.46	−833827.5

Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases—cont'd

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Carbon monoxide, $\text{CO}; h_0 = -113,882.3 \text{ kJ/kmol}$					Carbon dioxide, $\text{CO}_2; h_0 = -393,404.9 \text{ kJ/kmol}$				
50	1386.73	971.01	146.72	-5949.2	50	1342.97	927.25	157.68	-6541.2
100	2788.93	1957.50	166.15	-13825.6	100	2794.62	1963.19	177.72	-14977.7
150	4206.39	2959.24	177.64	-22439.0	150	4350.19	3103.05	190.31	-24196.3
200	5638.90	3976.04	185.88	-31536.3	200	6005.05	4342.19	199.82	-33958.6
250	7086.27	5007.69	192.33	-40997.3	250	7754.65	5676.08	207.62	-44150.0
298	8489.51	6011.84	197.47	-50356.0	298	9519.29	7041.63	214.07	-54273.9
300	8548.26	6053.97	197.66	-50751.1	300	9594.56	7100.27	214.32	-54702.3
350	10024.68	7114.67	202.22	-60750.8	350	11520.46	8610.46	220.26	-65569.5
400	11515.29	8189.57	206.20	-70963.2	400	13528.14	10202.42	225.62	-76718.5
450	13019.87	9278.44	209.74	-81363.2	450	15613.47	11872.04	230.53	-88123.7
500	14538.21	10381.06	212.94	-91931.5	500	17772.48	13615.33	235.08	-99765.1
550	16070.08	11497.21	215.86	-102652.5	550	20001.26	15428.39	239.32	-111626.2
600	17615.24	12626.66	218.55	-113513.6	600	22296.03	17307.45	243.32	-123693.2
650	19173.47	13769.17	221.04	-124504.1	650	24653.12	19248.83	247.09	-135954.1
700	20744.52	14924.51	223.37	-135615.0	700	27068.96	21248.95	250.67	-148398.8
750	22328.17	16092.44	225.56	-146838.7	750	29540.09	23304.37	254.08	-161018.1
800	23924.16	17272.72	227.62	-158168.5	800	32063.16	25411.72	257.33	-173804.0
850	25532.26	18465.11	229.57	-169598.5	850	34634.93	27567.78	260.45	-186749.2
900	27152.23	19669.36	231.42	-181123.5	900	37252.26	29769.39	263.44	-199847.1
950	28783.80	20885.22	233.18	-192738.8	950	39912.12	32013.54	266.32	-213091.6
1000	30426.74	22112.44	234.87	-204440.3	1000	42611.60	34297.30	269.09	-226477.3
1050	32080.79	23350.77	236.48	-216224.3	1050	45347.89	36617.87	271.76	-239998.8
1100	33745.68	24599.95	238.03	-228087.3	1100	48118.27	38972.54	274.34	-253651.6
1150	35421.17	25859.72	239.52	-240026.3	1150	50920.17	41358.72	276.83	-267431.0
1200	37106.98	27129.82	240.95	-252038.4	1200	53751.08	43773.92	279.24	-281332.9
1250	38802.85	28409.98	242.34	-264120.9	1250	56608.63	46215.76	281.57	-295353.4
1300	40508.52	29699.93	243.68	-276271.5	1300	59490.55	48681.96	283.83	-309488.7
1350	42223.72	30999.41	244.97	-288487.9	1350	62394.68	51170.37	286.02	-323735.3
1400	43948.16	32308.14	246.23	-300768.0	1400	65318.96	53678.94	288.15	-338089.8
1450	45681.58	33625.84	247.44	-313109.8	1450	68261.44	56205.70	290.21	-352549.2
1500	47423.69	34952.24	248.62	-325511.6	1500	71220.29	58748.84	292.22	-367110.3
1550	49174.22	36287.06	249.77	-337971.6	1550	74193.77	61306.60	294.17	-381770.3
1600	50932.88	37630.00	250.89	-350488.3	1600	77180.26	63877.38	296.07	-396526.4
1650	52699.38	38980.79	251.98	-363060.0	1650	80178.25	66459.66	297.91	-411376.1
1700	54473.44	40339.13	253.03	-375685.3	1700	83186.33	69052.02	299.71	-426316.8
1750	56254.75	41704.73	254.07	-388363.0	1750	86203.20	71653.17	301.46	-441346.1
1800	58043.03	43077.29	255.07	-401091.6	1800	89227.66	74261.92	303.16	-456461.7
1850	59837.98	44456.53	256.06	-413870.1	1850	92258.64	76877.19	304.82	-471661.4
1900	61639.29	45842.12	257.02	-426697.1	1900	95295.17	79498.00	306.44	-486943.2
1950	63446.67	47233.79	257.96	-439571.6	1950	98336.36	82123.48	308.02	-502304.9

Continued

Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases—cont'd

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Carbon monoxide, CO: $h_0 = -113,882.3$ kJ/kmol					Carbon dioxide, CO ₂ : $h_0 = -393,404.9$ kJ/kmol				
2000	65259.81	48631.21	258.88	-452492.6	2000	101381.47	84752.87	309.56	-517744.7
2050	67078.39	50034.07	259.77	-465458.9	2050	104429.85	87385.53	311.07	-533260.6
2100	68902.11	51442.08	260.65	-478469.7	2100	107480.95	90020.92	312.54	-548850.9
2150	70730.65	52854.90	261.51	-491523.9	2150	110534.33	92658.58	313.98	-564513.9
2200	72563.69	54272.23	262.36	-504620.8	2200	113589.67	95298.21	315.38	-580248.0
2250	74400.92	55693.74	263.18	-517759.3	2250	116646.75	97939.57	316.75	-596051.5
2300	76242.01	57119.12	263.99	-530938.7	2300	119705.46	100582.57	318.10	-611923.0
2350	78086.64	58548.03	264.79	-544158.2	2350	122765.79	103227.19	319.42	-627861.0
2400	79934.47	59980.15	265.56	-557417.0	2400	125827.86	105873.54	320.70	-643864.1
2450	81785.19	61415.15	266.33	-570714.3	2450	128891.87	108521.83	321.97	-659931.0
2500	83638.45	62852.70	267.08	-584049.4	2500	131958.14	111172.39	323.21	-676060.5
2550	85493.91	64292.45	267.81	-597421.5	2550	135027.11	113825.64	324.42	-692251.4
2600	87351.25	65734.07	268.53	-610830.1	2600	138099.31	116482.13	325.62	-708502.5
2650	89210.11	67177.22	269.24	-624274.4	2650	141175.38	119142.48	326.79	-724812.6
2700	91070.16	68621.55	269.93	-637753.9	2700	144256.08	121807.47	327.94	-741180.9
2750	92931.04	70066.71	270.62	-651267.7	2750	147342.28	124477.95	329.07	-757606.3
2800	94792.40	71512.36	271.29	-664815.4	2800	150434.93	127154.89	330.19	-774087.8
2850	96653.90	72958.15	271.95	-678396.4	2850	153535.12	129839.36	331.28	-790624.7
2900	98515.18	74403.71	272.59	-692010.0	2900	156644.02	132532.55	332.37	-807216.0
2950	100375.87	75848.68	273.23	-705655.7	2950	159762.95	135235.76	333.43	-823861.0
3000	102235.62	77292.72	273.86	-719332.9	3000	162893.29	137950.39	334.48	-840558.9
3050	104094.07	78735.45	274.47	-733041.1	3050	166036.55	140677.93	335.52	-857309.2
3100	105950.84	80176.51	275.07	-746779.8	3100	169194.35	143420.02	336.55	-874111.0
3150	107805.57	81615.53	275.67	-760548.4	3150	172368.42	146178.38	337.57	-890964.0
3200	109657.89	83052.13	276.25	-774346.4	3200	175560.59	148954.83	338.57	-907867.5
3250	111507.42	84485.95	276.82	-788173.3	3250	178772.80	151751.32	339.57	-924821.0
3300	113353.79	85916.60	277.39	-802028.7	3300	182007.10	154569.91	340.55	-941824.0
3350	115196.61	87343.71	277.94	-815912.1	3350	185265.64	157412.74	341.53	-958876.3
3400	117035.50	88766.88	278.49	-829822.9	3400	188550.70	160282.08	342.51	-975977.4
3450	118870.08	90185.75	279.02	-843760.7	3450	191864.64	163180.30	343.48	-993127.0
3500	120699.96	91599.91	279.55	-857725.0	3500	195209.95	166109.90	344.44	-1010324.9

Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases—cont'd

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Molecular hydrogen, H_2 : $h_0 = 0.0000$ kJ/kmol					Water, H_2O : $h_0 = -239,081.7$ kJ/kmol				
50	1427.20	1011.48	79.70	-2557.8	50	1567.79	1152.08	130.24	-4944.1
100	2854.64	2023.21	99.49	-7094.2	100	3159.40	2327.97	152.28	-12068.9
150	4282.92	3035.78	111.07	-12377.6	150	4775.08	3527.94	165.38	-20031.6
200	5712.58	4049.72	119.30	-18146.6	200	6415.10	4752.24	174.81	-28547.1
250	7144.17	5065.60	125.68	-24277.0	250	8079.69	6001.11	182.24	-37479.7
298	8520.79	6043.13	130.72	-30434.3	298	9700.99	7223.33	188.17	-46373.3
300	8578.21	6083.92	130.91	-30695.9	300	9769.04	7274.75	188.40	-46749.9
350	10015.20	7105.19	135.34	-37355.1	350	11483.36	8573.35	193.68	-56304.9
400	11455.63	8129.91	139.19	-44220.6	400	13222.78	9897.06	198.33	-66107.3
450	12899.96	9158.53	142.59	-51266.8	450	14987.47	11246.03	202.48	-76129.3
500	14348.65	10191.50	145.65	-58474.1	500	16777.52	12620.37	206.25	-86349.1
550	15802.13	11229.26	148.42	-65826.7	550	18593.04	14020.18	209.71	-96749.5
600	17260.81	12272.23	150.95	-73311.8	600	20434.10	15445.52	212.92	-107316.2
650	18725.08	13320.79	153.30	-80918.9	650	22300.74	16896.45	215.91	-118037.6
700	20195.34	14375.33	155.48	-88638.9	700	24192.99	18372.98	218.71	-128903.7
750	21671.92	15436.20	157.51	-96464.3	750	26110.85	19875.13	221.36	-139905.9
800	23155.19	16503.75	159.43	-104388.4	800	28054.30	21402.86	223.86	-151036.9
850	24645.46	17578.30	161.24	-112405.4	850	30023.31	22956.15	226.25	-162290.3
900	26143.03	18660.16	162.95	-120510.4	900	32017.79	24534.92	228.53	-173660.3
950	27648.20	19749.61	164.58	-128698.8	950	34037.68	26139.09	230.72	-185141.8
1000	29161.23	20846.93	166.13	-136966.7	1000	36082.85	27768.55	232.81	-196730.4
1050	30682.38	21952.37	167.61	-145310.5	1050	38153.17	29423.15	234.83	-208421.8
1100	32211.88	23066.15	169.04	-153726.9	1100	40248.48	31102.75	236.78	-220212.5
1150	33749.95	24188.51	170.40	-162213.1	1150	42368.62	32807.17	238.67	-232099.0
1200	35296.78	25319.62	171.72	-170766.4	1200	44513.37	34536.21	240.49	-244078.3
1250	36852.56	26459.68	172.99	-179384.3	1250	46682.51	36289.64	242.26	-256147.4
1300	38417.44	27608.85	174.22	-188064.6	1300	48875.80	38067.21	243.98	-268303.8
1350	39991.57	28767.26	175.41	-196805.3	1350	51092.97	39868.66	245.66	-280545.1
1400	41575.07	29935.05	176.56	-205604.5	1400	53333.72	41693.70	247.29	-292868.9
1450	43168.06	31112.33	177.67	-214460.4	1450	55597.74	43542.00	248.88	-305273.2
1500	44770.62	32299.17	178.76	-223371.5	1500	57884.69	45413.24	250.43	-317755.9
1550	46382.83	33495.66	179.82	-232336.1	1550	60194.21	47307.04	251.94	-330315.3
1600	48004.73	34701.85	180.85	-241352.9	1600	62525.92	49223.04	253.42	-342949.5
1650	49636.37	35917.77	181.85	-250420.5	1650	64879.42	51160.82	254.87	-355656.9
1700	51277.76	37143.45	182.83	-259537.7	1700	67254.27	53119.96	256.29	-368436.0
1750	52928.90	38378.88	183.79	-268703.4	1750	69650.03	55100.00	257.68	-381285.3

Continued

Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases—cont'd

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Molecular hydrogen, H_2 : $h_0 = 0.0000$ kJ/kmol					Water, H_2O : $h_0 = -239,081.7$ kJ/kmol				
1800	54589.77	39624.03	184.73	-277916.4	1800	72066.22	57100.48	259.04	-394203.3
1850	56260.35	40878.89	185.64	-287175.6	1850	74502.34	59120.89	260.37	-407188.7
1900	57940.56	42143.39	186.54	-296480.1	1900	76957.88	61160.71	261.68	-420240.2
1950	59630.34	43417.46	187.42	-305829.0	1950	79432.30	63219.41	262.97	-433356.6
2000	61329.61	44701.01	188.28	-315221.4	2000	81925.03	65296.43	264.23	-446536.7
2050	63038.25	45993.93	189.12	-324656.3	2050	84435.48	67391.17	265.47	-459779.4
2100	64756.13	47296.10	189.95	-334133.0	2100	86963.05	69503.02	266.69	-473083.4
2150	66483.11	48607.36	190.76	-343650.8	2150	89507.10	71631.36	267.89	-486447.9
2200	68219.03	49927.57	191.56	-353208.8	2200	92066.98	73775.52	269.06	-499871.7
2250	69963.71	51256.54	192.34	-362806.3	2250	94642.01	75934.83	270.22	-513353.9
2300	71716.95	52594.06	193.11	-372442.8	2300	97231.49	78108.60	271.36	-526893.4
2350	73478.53	53939.93	193.87	-382117.4	2350	99834.70	80296.09	272.48	-540489.4
2400	75248.23	55293.91	194.62	-391829.6	2400	102450.89	82496.57	273.58	-554141.0
2450	77025.78	56655.74	195.35	-401578.8	2450	105079.29	84709.26	274.66	-567847.1
2500	78810.91	58025.16	196.07	-411364.3	2500	107719.12	86933.37	275.73	-581607.1
2550	80603.35	59401.88	196.78	-421185.6	2550	110369.56	89168.10	276.78	-595419.9
2600	82402.77	60785.59	197.48	-431042.1	2600	113029.77	91412.59	277.81	-609284.8
2650	84208.86	62175.97	198.17	-440933.3	2650	115698.90	93666.00	278.83	-623200.9
2700	86021.28	63572.67	198.84	-450858.6	2700	118376.06	95927.45	279.83	-637167.5
2750	87839.67	64975.34	199.51	-460817.6	2750	121060.35	98196.02	280.82	-651183.8
2800	89663.63	66383.59	200.17	-470809.6	2800	123750.84	100470.80	281.79	-665248.9
2850	91492.79	67797.04	200.82	-480834.3	2850	126446.58	102750.82	282.74	-679362.1
2900	93326.72	69215.25	201.45	-490891.1	2900	129146.60	105035.13	283.68	-693522.6
2950	95165.00	70637.82	202.08	-500979.6	2950	131849.91	107322.73	284.60	-707729.7
3000	97007.17	72064.27	202.70	-511099.3	3000	134555.49	109612.59	285.51	-721982.7
3050	98852.76	73494.15	203.31	-521249.7	3050	137262.29	111903.68	286.41	-736280.8
3100	100701.29	74926.96	203.91	-531430.3	3100	139969.26	114194.93	287.29	-750623.2
3150	102552.25	76362.21	204.51	-541640.9	3150	142675.31	116485.26	288.15	-765009.3
3200	104405.12	77799.36	205.09	-551880.8	3200	145379.33	118773.57	289.01	-779438.4
3250	106259.36	79237.89	205.66	-562149.6	3250	148080.18	121058.71	289.84	-793909.6
3300	108114.42	80677.23	206.23	-572447.1	3300	150776.73	123339.54	290.67	-808422.4
3350	109969.70	82116.80	206.79	-582772.6	3350	153467.78	125614.88	291.48	-822976.0
3400	111824.63	83556.01	207.34	-593125.8	3400	156152.15	127883.53	292.27	-837569.8
3450	113678.59	84994.25	207.88	-603506.3	3450	158828.60	130144.27	293.05	-852202.9
3500	115530.94	86430.89	208.41	-613913.6	3500	161495.91	132395.86	293.82	-866874.8

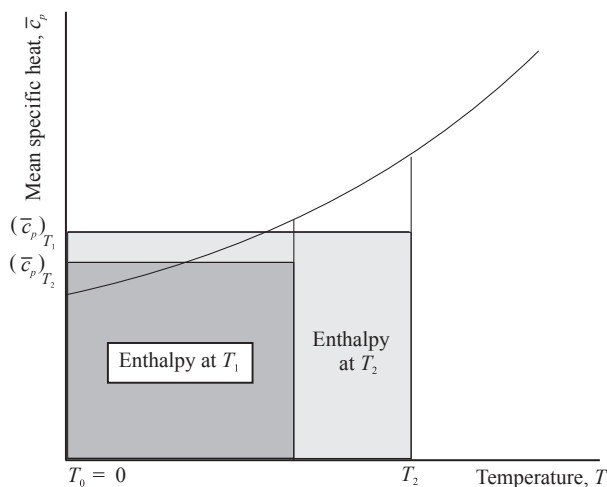
Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases—cont'd

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Nitric oxide, NO: $h_0 = 89,914.7$ kJ/kmol					Methane, CH₄: $h_0 = -66,930.5$ kJ/kmol				
50	1461.94	1046.22	156.66	-6371.1	50	906.44	490.72	134.82	-5834.7
100	2936.26	2104.83	177.09	-14772.6	100	2011.62	1180.19	149.99	-12987.2
150	4422.89	3175.75	189.14	-23948.2	150	3308.10	2060.95	160.45	-20759.5
200	5921.77	4258.91	197.76	-33630.9	200	4788.60	3125.74	168.94	-29000.2
250	7432.80	5354.22	204.51	-43693.6	250	6446.08	4367.50	176.33	-37635.7
298	8894.74	6417.08	209.85	-53641.9	298	8197.36	5719.70	182.73	-46255.4
300	8955.89	6461.60	210.06	-54061.8	300	8273.64	5779.35	182.98	-46621.1
350	10490.97	7580.97	214.79	-64685.9	350	10264.62	7354.62	189.11	-55925.6
400	12037.92	8712.20	218.92	-75530.9	400	12412.51	9086.79	194.85	-65526.5
450	13596.65	9855.21	222.59	-86570.5	450	14711.00	10969.57	200.26	-75406.0
500	15167.03	11009.88	225.90	-97784.3	500	17153.96	12996.81	205.41	-85549.6
550	16748.95	12176.09	228.92	-109155.9	550	19735.44	15162.57	210.33	-95945.2
600	18342.30	13353.72	231.69	-120672.0	600	22449.65	17461.07	215.05	-106582.5
650	19946.93	14542.63	234.26	-132321.5	650	25291.00	19886.70	219.61	-117452.3
700	21562.71	15742.70	236.65	-144095.0	700	28254.05	22434.04	224.00	-128546.8
750	23189.50	16953.77	238.90	-155984.4	750	31333.53	25097.81	228.26	-139858.8
800	24827.15	18175.71	241.01	-167982.7	800	34524.35	27872.91	232.38	-151381.7
850	26475.50	19408.35	243.01	-180083.8	850	37821.57	30754.41	236.39	-163109.8
900	28134.40	20651.53	244.91	-192282.1	900	41220.40	33737.53	240.29	-175037.6
950	29803.68	21905.10	246.71	-204573.0	950	44716.23	36817.65	244.08	-187160.3
1000	31483.16	23168.86	248.44	-216952.0	1000	48304.59	39990.29	247.78	-199473.3
1050	33172.68	24442.66	250.08	-229415.2	1050	51981.17	43251.16	251.38	-211972.4
1100	34872.03	25726.30	251.66	-241959.2	1100	55741.80	46596.07	254.91	-224653.9
1150	36581.03	27019.58	253.18	-254580.7	1150	59582.46	50021.02	258.34	-237514.1
1200	38299.48	28322.32	254.65	-267276.7	1200	63499.28	53522.12	261.71	-250549.7
1250	40027.19	29634.31	256.06	-280044.5	1250	67488.52	57095.65	265.00	-263757.9
1300	41763.93	30955.34	257.42	-292881.6	1300	71546.59	60738.00	268.22	-277135.7
1350	43509.49	32285.19	258.74	-305785.7	1350	75670.02	64445.71	271.37	-290680.7
1400	45263.66	33623.64	260.01	-318754.6	1400	79855.49	68215.47	274.46	-304390.6
1450	47026.20	34970.47	261.25	-331786.4	1450	84099.80	72044.07	277.49	-318263.4
1500	48796.88	36325.43	262.45	-344879.0	1500	88399.88	75928.43	280.46	-332297.0
1550	50575.47	37688.30	263.62	-358030.9	1550	92752.80	79865.63	283.38	-346490.0
1600	52361.70	39058.82	264.75	-371240.2	1600	97155.72	83852.84	286.25	-360840.9
1650	54155.33	40436.74	265.86	-384505.5	1650	101605.94	87887.35	289.06	-375348.3
1700	55956.11	41821.80	266.93	-397825.2	1700	106100.89	91966.58	291.83	-390011.4
1750	57763.77	43213.74	267.98	-411198.0	1750	110638.09	96088.06	294.55	-404829.3

Continued

Table 9.4 Values of Enthalpy, Internal Energy, Entropy, and Gibbs Energy for Gases—cont'd

T	$h(T)$	$u(T)$	$s(T)$	$g(T)$	T	$h(T)$	$u(T)$	$s(T)$	$g(T)$
Nitric oxide, NO: $h_0 = 89,914.7$ kJ/kmol					Methane, CH ₄ : $h_0 = -66,930.5$ kJ/kmol				
1800	59578.03	44612.29	269.00	-424622.6	1800	115215.17	100249.43	297.23	-419801.3
1850	61398.62	46017.17	270.00	-438097.7	1850	119829.90	104448.44	299.87	-434927.0
1900	63225.26	47428.09	270.97	-451622.0	1900	124480.12	108682.95	302.47	-450206.2
1950	65057.66	48844.77	271.92	-465194.5	1950	129163.80	112950.91	305.03	-465638.8
2000	66895.51	50266.91	272.85	-478814.1	2000	133878.99	117250.39	307.55	-481225.1
2050	68738.53	51694.22	273.76	-492479.7	2050	138623.86	121579.55	310.04	-496965.3
2100	70586.41	53126.38	274.66	-506190.3	2100	143396.66	125936.63	312.50	-512860.1
2150	72438.82	54563.08	275.53	-519944.9	2150	148195.74	130320.00	314.93	-528910.1
2200	74295.46	56004.00	276.38	-533742.7	2200	153019.54	134728.08	317.33	-545116.4
2250	76155.99	57448.81	277.22	-547582.7	2250	157866.57	139159.40	319.71	-561480.1
2300	78020.08	58897.19	278.04	-561464.1	2300	162735.46	143612.57	322.06	-578002.6
2350	79887.40	60348.79	278.84	-575386.1	2350	167624.89	148086.28	324.39	-594685.5
2400	81757.59	61803.27	279.63	-589347.8	2400	172533.63	152579.31	326.69	-611530.6
2450	83630.32	63260.29	280.40	-603348.6	2450	177460.54	157090.50	328.98	-628539.8
2500	85505.22	64719.47	281.16	-617387.6	2500	182404.53	161618.78	331.25	-645715.4
2550	87381.94	66180.47	281.90	-631464.0	2550	187364.61	166163.14	333.50	-663059.7
2600	89260.09	67642.91	282.63	-645577.4	2600	192339.82	170722.64	335.74	-680575.5
2650	91139.32	69106.42	283.35	-659726.8	2650	197329.31	175296.42	337.96	-698265.5
2700	93019.23	70570.62	284.05	-673911.7	2700	202332.27	179883.66	340.17	-716132.8
2750	94899.44	72035.11	284.74	-688131.4	2750	207347.95	184483.62	342.37	-734180.8
2800	96779.56	73499.52	285.42	-702385.4	2800	212375.65	189095.61	344.57	-752412.8
2850	98659.18	74963.43	286.08	-716672.8	2850	217414.75	193719.00	346.75	-770832.7
2900	100537.91	76426.44	286.73	-730993.3	2900	222464.67	198353.20	348.93	-789444.4
2950	102415.33	77888.15	287.38	-745346.1	2950	227524.88	202997.69	351.11	-808252.1
3000	104291.02	79348.12	288.01	-759730.8	3000	232594.89	207651.99	353.29	-827260.2
3050	106164.57	80805.95	288.63	-774146.7	3050	237674.27	212315.65	355.46	-846473.4
3100	108035.53	82261.20	289.24	-788593.3	3100	242762.61	216988.28	357.63	-865896.5
3150	109903.48	83713.43	289.83	-803070.0	3150	247859.57	221669.52	359.81	-885534.8
3200	111767.97	85162.21	290.42	-817576.4	3200	252964.82	226359.06	361.99	-905393.4
3250	113628.55	86607.08	291.00	-832111.8	3250	258078.08	231056.60	364.17	-925478.1
3300	115484.78	88047.59	291.56	-846675.9	3300	263199.09	235761.90	366.36	-945794.7
3350	117336.18	89483.28	292.12	-861268.1	3350	268327.62	240474.72	368.56	-966349.4
3400	119182.30	90913.68	292.67	-875887.8	3400	273456.95	245188.33	370.77	-987145.1
3450	121022.66	92338.32	293.21	-890534.7	3450	278606.50	249922.16	372.99	-1008198.3
3500	122856.78	93756.73	293.73	-905208.2	3500	283756.50	254656.45	375.22	-1029506.1

**FIGURE 9.1**

Mean specific heat at constant pressure.

If the change of internal energy, $u_2 - u_1$, is known then the change of enthalpy, $h_2 - h_1$, may be calculated in a similar way. The use of mean specific heat values enables more accurate evaluation of temperature changes because the mean specific heats enable the energy equation to be solved with an allowance for the variation of specific heats. The mean specific heats approach is depicted in Fig. 9.1.

9.4 MIXTURES OF IDEAL GASES

Many problems encountered in engineering involve mixtures of gases – air itself is a mixture of many gases although it can be considered to be oxygen and atmospheric nitrogen (which can be assumed to contain the nitrogen in the air and the other ‘inert’ gases such as argon and carbon dioxide). If the gases in a mixture are at a temperature well above their critical temperature and a pressure below the critical pressure they act as ideal gases. Expressions relating the properties of mixtures of *ideal gases* will now be formulated. These expressions are a direct consequence of the Gibbs–Dalton laws.

9.4.1 DALTON PRINCIPLE

Dalton stated that

any gas is as a vacuum to any gas mixed with it.

This statement was expanded and clarified by Gibbs to give the Gibbs–Dalton laws.

9.4.2 GIBBS–DALTON LAW

1. A gas mixture as a whole obeys the equation of state (Eqn (9.2))

$$pV = n\mathcal{R}T$$

where n is the *total* amount of substance in mixture.

2. The total pressure exerted by a mixture is the sum of the pressures exerted by the individual components as each occupies the *whole volume* of the mixture at the same temperature.
3. The internal energy, enthalpy and entropy of the mixture are respectively equal to the sums of the internal energy, enthalpy and entropy of the various components as each occupies the *whole volume* at the temperature of the mixture.

9.4.3 MIXTURE RELATIONSHIPS

The total mass, m , of a mixture can be related to the mass of constituents by

$$m = m_a + m_b + m_c + \dots = \sum_{i=1}^n m_i \quad (9.49)$$

From the ideal gas law (Eqn (9.2))

$$pV = mRT = \frac{m}{m_w} m_w RT = n\mathfrak{R}T$$

and hence for the individual constituents

$$\begin{aligned} pV_a &= m_a R_a T = n_a \mathfrak{R}T, \\ pV_b &= m_b R_b T = n_b \mathfrak{R}T, \\ pV_c &= m_c R_c T = n_c \mathfrak{R}T, \text{ etc.} \end{aligned} \quad (9.50)$$

In Eqn (9.50) V_a = volume of constituent a at the pressure and temperature of mixture, and V_b and V_c are similar volumes for constituents b and c . But the total volume, V , is given by

$$V = V_a + V_b + V_c + \dots = \sum_{i=1}^n V_i, \quad (9.51)$$

and therefore

$$n = n_a + n_b + n_c + \dots = \sum_{i=1}^n n_i \quad (9.52)$$

Let $\frac{n_a}{n} = x_a$ = molar fraction of a in the mixture. (9.53)

Similarly, $n_b/n = x_b$ and $n_c/n = x_c$, etc, with $n_i/n = x_i$.

Therefore

$$x_a + x_b + x_c + \dots = \sum_{i=1}^n x_i = 1 \quad (9.54)$$

It is possible to develop the term for the **partial pressure** of each constituent from statement (2) of the Gibbs–Dalton laws. Then, for constituent a occupying the total volume of the mixture at the pressure and temperature of the mixture

$$p_a V = n_a \mathfrak{R}T \quad (9.50)$$

But, for the mixture as a whole

$$pV = n\mathfrak{R}T$$

Hence, by dividing Eqn (9.50) by Eqn (9.2)

$$\frac{p_a}{p} = \frac{n_a}{n} = x_a, \quad (9.55)$$

giving

$$p_a = x_a p, \text{ and in general } p_i = x_i p \quad (9.56)$$

and, also

$$\sum_{i=1}^n p_i = \sum_{i=1}^n x_i p = p \sum_{i=1}^n x_i = p \quad (9.57)$$

Often mixtures are analysed on a volumetric basis, and from the volumetric results it is possible to obtain the partial pressures and molar fractions of the components. Normally volumetric analyses are performed at constant pressure and temperature. Then, considering the i th component

$$V_i = \frac{n_i \mathfrak{R}T}{p}, \quad (9.58)$$

and the total volume of the mixture, V , is

$$V = \frac{n \mathfrak{R}T}{p}. \quad (9.59)$$

Hence, from Eqns (9.58) and (9.59)

$$\frac{V_i}{V} = \frac{n_i}{n} = x_i, \quad (9.60)$$

If the gas composition is given in volume percentage of the mixture, the molar fraction is

$$x_i = \frac{V_i(\%)}{100}, \quad (9.61)$$

and the partial pressure is

$$p_i = \frac{V_i(\%)}{100} p. \quad (9.62)$$

The terms relating to the energy of a mixture can be evaluated from statement (3) of the Gibbs–Dalton laws. If e_m = molar internal energy, and h_m = molar enthalpy, then for the mixture

$$E = ne_m = \sum_{i=1}^n n_i e_{m,i}, \quad (9.63)$$

and

$$H = nh_m = \sum_{i=1}^n n_i h_{m,i} \quad (9.64)$$

If the molar internal energy, and molar enthalpy *of the mixture* are required then

$$e_m = \frac{1}{n} \sum_{i=1}^n n_i e_{m,i} = \sum_{i=1}^n x_i e_{m,i}, \quad (9.65)$$

and

$$h_m = \frac{1}{n} \sum_{i=1}^n n_i h_{m,i} = \sum_{i=1}^n x_i h_{m,i} \quad (9.66)$$

Neglecting motion, gravity, electricity, magnetism and capillary effects, then $e_m = u_m$, and hence

$$u_m = \sum x_i u_{m,i} \quad (9.67)$$

The definition of enthalpy for an ideal gas is

$$h_m = u_m + \Re T. \quad (9.68)$$

Thus, for the mixture

$$\begin{aligned} h_m &= \sum (x_i (u_m + \Re T))_i \\ &= \sum x_i u_{m,i} + \sum x_i \Re T = \sum x_i u_{m,i} + \Re T \sum x_i \\ &= \sum x_i u_{m,i} + \Re T. \end{aligned} \quad (9.69)$$

9.4.4 SPECIFIC HEATS OF MIXTURES

Statement (3) of the Gibbs–Dalton law and the above expressions show that (Eqn (9.67))

$$u_m = \sum x_i u_{m,i}$$

And (Eqn (9.69)) $h_m = \sum x_i h_{m,i}$

By definition, the specific heats are $c_v = \frac{du}{dT}$ and $c_p = \frac{dh}{dT}$.
Thus

$$c_{v,m} = \left(\frac{du_m}{dT} \right) = \sum x_i \left(\frac{du_{m,i}}{dT} \right)_i = \sum x_i (c_{v,m})_i \quad (9.70)$$

and, similarly,

$$c_{p,m} = \sum x_i (c_{p,m})_i \quad (9.71)$$

9.5 ENTROPY OF MIXTURES

Consider a mixture of two ideal gases, a and b . The entropy of the mixture is equal to the sum of the entropies which each component of the mixture would have *if it alone occupied the whole volume of the mixture at the same temperature*. This concept can present some difficulty because it means that when gases are separate but all at the same temperature and pressure they have a lower entropy than when they are mixed together in a volume equal to the sums of their previous volumes: the situation can be envisaged from Fig. 9.2. This can be analysed by considering the mixing process in the following way:

1. Gases a and b , at the same pressure, are contained in a control volume but prevented from mixing by an impermeable membrane.
2. The membrane is then removed, and the components mix due to diffusion i.e. due to the concentration gradient there will be a net migration of molecules from their original volumes. This means that the probability of finding a particular molecule at *any particular* point in the volume is decreased, and the system is in a less ordered state. This change in probability can be related to an increase in entropy by statistical thermodynamics. Hence, qualitatively it can be expected that mixing will give rise to an increase in entropy.

$$p_a = p_b = p.$$

Considering the mixing process from a macroscopic viewpoint, when the membrane is broken the pressure is unaffected *but the partial pressures of the individual components are decreased*.

The expression for entropy of a gas is (Eqn (9.20))

$$s_m = s_m(T) - \Re \ln \frac{p}{p_0} + s_{0,m}$$

where $s_m(T)$ = function of T alone. Hence, considering the pressure term, which is actually the *partial pressure* of a component, a decrease in the partial pressure will cause an increase in the entropy of the gas. Equation (9.20) can be simplified by writing the pressure ratio as $p_r = p/p_0$, giving

$$s_m = s_m(T) - \Re \ln p_r + s_{0,m} \quad (9.20a)$$

Now consider the change from an analytical viewpoint. Consider the two gases a and b .

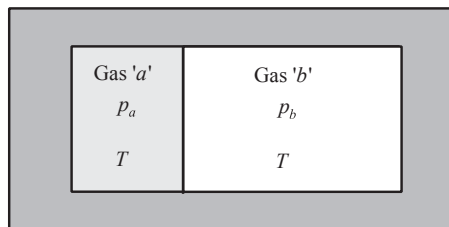


FIGURE 9.2

Two gases at the same pressure, p , contained in an insulated container, and separated by a membrane.

The total amount of substance in the gases is

$$n_T = n_a + n_b. \quad (9.72)$$

The entropies of the gases before mixing are

$$S_{m_a} = n_a s_{m_a} = n_a [s_{m_a}(T) - \Re \ln p_{r_a} + s_{0,m_a}]; \quad (9.73)$$

and

$$S_{m_b} = n_b s_{m_b} = n_b [s_{m_b}(T) - \Re \ln p_{r_b} + s_{0,m_b}]; \quad (9.74)$$

giving the sum of the entropies before mixing (i.e. separated) as

$$(S_{m_T})_{\text{sep}} = (n_T s_{m_T})_{\text{sep}} = n_T [x_a s_{m_a}(T) + x_b s_{m_b}(T) + x_a s_{0,m_a} + x_b s_{0,m_b} - \Re (x_a \ln p_{r_a} + x_b \ln p_{r_b})] \quad (9.75)$$

Since the gases are separated and both at the pressure, p_r , then

$$(S_{m_T})_{\text{sep}} = n_T [x_a s_{m_a}(T) + x_b s_{m_b}(T) + x_a s_{0,m_a} + x_b s_{0,m_b} - \Re \ln p] \quad (9.76)$$

Hence, the molar entropy, when the gases are separate, is

$$\begin{aligned} (s_{m_T})_{\text{sep}} &= x_a s_{m_a}(T) + x_b s_{m_b}(T) + x_a s_{0,m_a} + x_b s_{0,m_b} - \Re \ln p \\ &= \sum x_i s_{m_i} + \sum x_i s_{0,m_i} - \Re \ln p \end{aligned} \quad (9.77)$$

The entropy of the gases after mixing is

$$(S_{m_T})_{\text{mix}} = n_T s_{m_T} = \sum n s_m = n_a s_{m_a} + n_b s_{m_b} \quad (9.78)$$

where S_{m_a} and S_{m_b} are the molar entropies if each component occupied the whole volume.

Thus, substituting for s_m from Eqn (9.20a) gives

$$(n_T s_{m_T})_{\text{mix}} = n_a s_{m_a}(T) + n_b s_{m_b}(T) - \Re (n_a \ln p_{r_a} + n_b \ln p_{r_b}) + n_a s_{0,m_a} + n_b s_{0,m_b} \quad (9.79)$$

$$(s_{m_T})_{\text{mix}} = x_a s_{m_a}(T) + x_b s_{m_b}(T) - \Re (x_a \ln p_{r_a} + x_b \ln p_{r_b}) + x_a s_{0,m_a} + x_b s_{0,m_b} \quad (9.80)$$

where $p_{r_i} = p_i/p_0$, and p_i is partial pressure of constituent i .

Equation (9.80) may be written

$$(s_{m_T})_{\text{mix}} = \sum x_i s_{m_i}(T) + \sum x_i s_{0,m_i} - \Re \sum x_i \ln p_{r_i} \quad (9.81)$$

Now, consider the final term in Eqn (9.81), based on two constituents to simplify the mathematics,

$$\begin{aligned} x_a \ln p_{r_a} + x_b \ln p_{r_b} &= x_a \ln (x_a p_r) + x_b \ln (x_b p_r) \\ &= x_a \ln x_a + x_a \ln p_r + x_b \ln x_b + x_b \ln p_r \\ &= \sum x_i \ln x_i + \ln p_r \sum x_i \\ &= \sum x_i \ln x_i + \ln p_r = \ln p_r - \sum x_i \ln \frac{1}{x_i} \end{aligned} \quad (9.82)$$

Hence,

$$(s_{m_T})_{\text{mix}} = \sum x_i s_{m_i}(T) + \sum x_i s_{0,m_i} + \Re \left(\sum x_i \ln \frac{1}{x_i} - \ln p_r \right). \quad (9.83)$$

Considering the terms on the right hand side of Eqn (9.83).

1st and 2nd terms: summation of entropies before mixing, $(s_{m_T})_{\text{sep}}$.

3rd term: change of entropy due to mixing. This is due to *change of partial pressures* when mixed.

4th term: pressure term.

The change of entropy due to mixing is given by

$$\Delta S = (s_{m_T})_{\text{mix}} - (s_{m_T})_{\text{sep}} \quad (9.84)$$

which is the difference between Eqns (9.83) and (9.77). This gives

$$\Delta S = \Re \sum x_i \ln \frac{1}{x_i} \quad (9.85)$$

The numerical value of ΔS must be positive because x_i is always less than unity.

Equation (9.85) shows that there is an entropy increase due to mixing, and this is caused by the reduction in the order of the molecules. Before mixing it is possible to go into one side of the container and guarantee taking a particular molecule because only molecules of *a* are in the left-hand container, and only molecules of *b* are in the right-hand container. After mixing it is not possible to know whether the molecule obtained will be of *a* or *b*; the order of the system has been reduced.

*What happens if both *a* and *b* in Fig. 9.2 are the same gas?*

Superficially it might be imagined that there will still be an increase of entropy on mixing. However, since *a* and *b* are now the same there is **no change in partial pressure due to mixing**. This means that the molar fraction is unaltered and

$$\Delta S = 0. \quad (9.86)$$

9.6 CONCLUDING REMARKS

A detailed study of ideal gases and ideal gas mixtures has been undertaken in preparation for later chapters. Equations have been developed for all properties, and simplified enthalpy coefficients have been introduced for nine commonly encountered gases. Tables of gas properties have been presented for most gases occurring in combustion calculations.

Equations for gas mixtures have been developed and the effects of mixing on entropy and Gibbs energy have been shown.

9.7 PROBLEMS

Assume that air consists of 79% N₂ and 21% O₂ by volume

P9.1 A closed vessel of 0.15 m³ capacity contains a mixture of methane (CH₄) and air, the air being 20% in excess of that required for chemically correct combustion. The pressure and temperature in the vessel before combustion are respectively 3 bar and 100 °C.

Determine:

- the individual partial pressures and the weights of methane, nitrogen and oxygen present before combustion;
- the individual partial pressures of the burnt products, on the assumption that these are cooled to 100 °C without change of volume and that all the vapour produced by combustion is condensed.

[(a) 0.2415, 2.179, 0.579 bar; 0.01868, 0.2951, 0.08969 kg. (b) 2.179, 0.2415, 0.0966 bar]

P9.2 An engine runs on a rich mixture of methyl and ethyl alcohol and air. At a pressure of 1 bar and 10 °C the fuel is completely vapourised. Calculate the air–fuel ratio by volume under these conditions, and the percentage of ethyl alcohol in the fuel by weight. If the total pressure of the exhaust gas is 1 bar, calculate the dew point of the water vapour in the exhaust and the percentage by volume of carbon monoxide in the dry exhaust gas assuming all the hydrogen in the fuel forms water vapour.

Vapour pressures at 10 °C: methyl alcohol (CH₃OH), 0.0745 bar; and ethyl alcohol (C₂H₅OH), 0.310 bar.

[63 °C; 4.15%]

P9.3 An engine working on the constant volume (Otto) cycle has a compression ratio of 6.5 to 1, and the compression follows the law $pV^{1.3} = C$, the initial pressure and temperature being 1 bar and 40 °C. The specific heats at constant pressure and constant volume throughout compression and combustion are $0.96 + 0.00002T$ kJ/kg K and $0.67 + 0.00002T$ kJ/kg K respectively, where T is in K.

Find:

- the change in entropy during compression;
- the heat rejected per unit mass during compression;
- the heat rejected per unit mass during combustion if the maximum pressure is 43 bar and the energy liberated by the combustion is 2150 kJ/kg of air.

[(a) -0.1621 kJ/kg K; (b) -67.8 kJ/kg; (c) -1090.6 kJ/kg]

P9.4 A compression-ignition engine runs on a fuel of the following analysis by weight: carbon 84%, hydrogen 16%. If the pressure at the end of combustion is 55 bar, the volume ratio of expansion is 15:1, the pressure and temperature at the end of expansion are 1.75 bar and 600 °C respectively, calculate:

- the variable specific heat at constant volume for the products of combustion; and
- the change in entropy during the expansion stroke per kg molecule.

The expansion follows the law $pV^n = C$ and there is 60% excess air. The specific heats at constant volume in kJ/kmol K between 600 °C and 2400 °C are:

O ₂	$32 + 0.0025T$	N ₂	$29 + 0.0025T$
H ₂ O	$34 + 0.08T$	CO ₂	$50 + 0.0067T$

The water vapour (H₂O) may be considered to act as a perfect gas.

[(a) $22.1 + 0.0184T$; (b) -11.42 kJ/kmol K]

- P9.5** The exhaust gases of a compression-ignition engine are to be used to drive an exhaust gas turbo-supercharger. Estimate the mean pressure ratio of expansion and the isentropic enthalpy drop per kmol of gas in the turbine if the mean exhaust temperature is 600 °C and the isentropic temperature drop is 100 °C. The composition of the exhaust gas by volume is CO₂, 8%; H₂O, 9.1%; O₂, 7.5%; N₂, 75.4%.

The specific heats at constant volume in kJ/kmol K are

O ₂	$32 + 0.0025T$	N ₂	$29 + 0.0025T$
H ₂ O	$34 + 0.08T$	CO ₂	$50 + 0.0067T$

The water vapour (H₂O) may be considered to act as a perfect gas.

[1.946; -4547.1 kJ/kmol]

- P9.6** (a) An amount of substance equal to 2 kmols of an ideal gas at temperature T and pressure p is contained in a compartment. In an adjacent compartment is an amount of substance equal to 1 kmol of an ideal gas at temperature $2T$ and pressure p . The gases mix adiabatically but do not react chemically when a partition separating the compartments is withdrawn. Show that, as a result of the mixing process, the entropy increases by

$$\Re \left(\ln \frac{27}{4} + \frac{\kappa}{\kappa - 1} \ln \frac{32}{27} \right)$$

provided that the gases are different and that κ , the ratio of specific heats, is the same for both gases and remains a constant in the temperature range T to $2T$.

(b) What would be the entropy change if the gases being mixed were of the same species?

$$\left[\frac{\kappa \Re}{\kappa - 1} \ln \frac{32}{27} \right]$$

- P9.7** The exhaust gas from a two-stroke cycle compression-ignition engine is exhausted at an elevated pressure into a large chamber. The gas from the chamber is subsequently expanded in a turbine. If the mean temperature in the chamber is 811 K and the pressure ratio of expansion in the turbine is 4:1, calculate the isentropic enthalpy drop in the turbine per unit mass of gas.

[256.68 kJ/kg]

- P9.8** The following data refer to an analysis of a dual combustion cycle with a gas having specific heats varying linearly with temperature:

The pressure and temperature of the gas at the end of compression are 31 bar and 227 °C respectively; the maximum pressure achieved during the cycle is 62 bar, while the maximum temperature achieved is 1700 °C. The temperature at the end of the expansion stroke is 1240 °C. The increases in entropy during constant volume and constant pressure combustion are 0.882 and 1.450 kJ/kg K respectively. Assuming that the fluid behaves as an ideal gas of molecular weight, $m_w = 30.5$ calculate the equations for the specific heats, and also the expansion ratio if that process is isentropic.

[0.6747 + 0.000829T; 0.94735 + 0.000829T; 7.814]

- P9.9** Distinguish between an ideal and a perfect gas and show that in both cases the specific entropy, s , is given by

$$s = s_0 + \int_{T_0}^T \frac{dh}{T} - \Re \ln \left(\frac{p}{p_0} \right)$$

Two streams of perfect gases, A and B, mix adiabatically at constant pressure and without chemical change to form a third stream. The molar specific heat at constant pressure $c_{p,m}$ of the gas in stream A is equal to that in stream B. Stream A flows at M kmol/s and is at a temperature T_1 , while stream B flows at 1 kmol/s and is at a temperature nT_1 . Assuming that the gases A and B are different, show that the rate of entropy increase is

$$c_p \ln \left[\frac{1}{n} \left(\frac{M+n}{M+1} \right)^{M+1} \right] - \Re \ln \left[\frac{1}{M} \left(\frac{M}{M+1} \right)^{M+1} \right]$$

How is the above expression modified if the gases A and B are the same?

For the case $n = 1$, evaluate the rate of entropy increase

- when different gases mix, and
- when the gas in each stream is the same.

$$\left[c_{p,m} \ln \left\{ \frac{1}{n} \left[\frac{M+n}{M+1} \right]^{M+1} \right\}; \quad - \Re \ln \left\{ \frac{1}{M} \left[\frac{M}{M+1} \right]^{M+1} \right\} \right]$$

- P9.10** A jet engine burns a weak mixture of octane (C_8H_{18}) and air, with an equivalence ratio, $\phi = 2$. The products of combustion, in which dissociation may be neglected, enter the nozzle with negligible velocity at a temperature of 1000 K. The gases, which may be considered to be ideal, leave the nozzle at atmospheric pressure of 1.013 bar with an exit velocity of 500 m/s.

The nozzle may be considered to be adiabatic and frictionless.

Determine:

- the specific heat at constant pressure c_p , of the products as a function of temperature;
- the molecular weight, m_w , of the products;
- the temperature of the products at the nozzle exit;
- the pressure of the products at the nozzle inlet.

Specific heat at constant pressure $c_{p,m}$ in J/kmol K, with T in K

$$\text{CO}_2 \quad c_{p,m} = 21 \times 10^3 + 34.0T$$

$$\text{H}_2\text{O} \quad c_{p,m} = 33 \times 10^3 + 8.3T$$

$$\text{O}_2 \quad c_{p,m} = 28 \times 10^3 + 6.4T$$

$$\text{N}_2 \quad c_{p,m} = 29 \times 10^3 + 3.4T$$

[$0.9986 \times 10^3 + 0.2105T$; 28.71; 895.7 K; 1.591 bar]

- P9.11** The products of combustion of a jet engine have a molecular weight, m_w , of 30 and a molar specific heat at constant pressure given by $c_{p,m} = 3.3 \times 10^4 + 15T$ J/kmol K where T is the gas temperature in Kelvin. When the jet pipe stagnation temperature is 1200 K the gases leave the nozzle at a relative speed of 600 m/s. Evaluate the static temperature of the gas at the nozzle exit and estimate the total to static pressure ratio across the nozzle. Assume that the products of combustion behave as an ideal gas and that the flow is isentropic.

In a frictional nozzle producing the same mean outlet speed from the same inlet *gas* temperature, what would be the effect on

- (a) the mean outlet static temperature, and
- (b) the total to static pressure ratio?

[1092 K; 1.732; (a) unaffected; (b) increased]

THERMODYNAMICS
OF COMBUSTION

10

Combustion is an oxidation process and is usually exothermic (i.e. releases the chemical (or bond) energy contained in a fuel as thermal energy). The most common combustion processes encountered in engineering are those which convert a hydrocarbon fuel (which might range from pure hydrogen to almost pure carbon e.g. coal) into carbon dioxide and water. This combustion is usually performed using air because it is freely available although other oxidants can be used in special circumstances e.g. rocket motors. The theory which will be developed here will be applicable to any mixture of fuel and oxidant and any ratio of components in the products; however, it will be described in terms of commonly available hydrocarbon fuels of the type used in combustion engines or boilers.

The simplest description of combustion is of a process that converts the *reactants* available at the beginning of combustion into *products* at the end of the process. This model presupposes that combustion is a process that can take place in only one direction and it ignores the true statistical nature of chemical change. Combustion is the combination of various atoms and molecules, which takes place when they are close enough to interact: but there is also the possibility of atoms which have previously joined together to make a product molecule, separating to form reactants again. The whole mixture is really taking part in a molecular ‘barn dance’ and the tempo of the dance is controlled by the temperature of the mixture. The process of molecular breakdown is referred to as *dissociation*; this will be introduced in Chapter 12. In reality, a true combustion process is even more complex than this because the actual rate at which the reactions can occur is finite (even if extremely fast). This rate is the basic cause of some of the pollutants produced by engines, particularly NO_x . In fact, in most combustion processes the situation is even more complex because there is an additional factor affecting combustion which is related to the rate at which the fuel and air can mix. These ideas will be introduced in Chapter 15. Hence, this approach to combustion is a simplified one but, in reality, it gives a reasonable assessment of what would be expected under good combustion conditions. It cannot really be used to assess emissions levels but it can be extended to this simply by the introduction of additional equations: the basic approach is still valid.

The manner in which combustion takes place is governed by the detailed design of the combustion system. The various different types of combustion process are listed in Table 10.1, and some examples are given of where the processes might be found. There is an interdependence between thermodynamics and fluid mechanics in combustion, and this interaction is the subject of current research. This book will concentrate on the thermodynamics of combustion, both in equilibrium and nonequilibrium states. The first part of the treatment of combustion will be based on equilibrium

Table 10.1 Factors Affecting Combustion Processes

Conditions of Combustion	Classification	Examples
Time dependence	Steady Unsteady	Gas turbine combustion chamber, boilers Petrol engine, diesel engine
Spatial dependence	Zero-dimensional One-dimensional Two-dimensional Three-dimensional	Only used for modelling purposes, well-stirred reactors Approximated in pipe flows, flat flame burners Axisymmetric flames e.g. Bunsen burner General combustion
Mixing of initial reactants	Premixed Non-premixed	Petrol, or spark ignition, engine Diesel engine, gas turbine combustion chamber
Flow	Laminar Turbulent	Special cases for measuring flame speed Most real engine cases, boilers
Phase of reactants	Single Multiphase	Spark-ignited gas engines, petrol engines with fuel completely evaporated; gas-fired boilers Diesel engines, gas turbines, coal- and oil-fired boilers
Reaction sites	Homogeneous Heterogeneous	Spark-ignition engines Diesel engines, gas turbines, coal-fired boilers
Reaction rate	Equilibrium chemistry (infinite rate) Finite rate	Approached by some processes in which the combustion period is long compared with the reaction rate All real processes: cause many pollutant emissions
Convection conditions	Natural Forced	Bunsen flame, gas cooker, central heating boiler Gas turbine combustion chamber, large boilers
Compressibility	Incompressible Compressible	Free flames Engine flames
Speed of combustion	Deflagration Detonation	Most normal combustion processes 'knock' in spark-ignition engines, explosions

thermodynamics, and will cover combustion processes both with and without *dissociation*. It will be found that equilibrium thermodynamics enables a large number of calculations to be performed but, even with dissociation included, it does not allow the calculation of formation of pollutants the production of which are controlled both by mixing rates (fluid mechanics) and reaction rates (thermodynamics).

10.1 SIMPLE CHEMISTRY

Combustion is a chemical reaction and hence a knowledge of basic chemistry is required before it can be analysed. An extremely simple reaction can be written as



This basically means that two molecules of carbon monoxide (CO) will combine with one molecule of oxygen (O₂) to create two molecules of carbon dioxide (CO₂). Both CO and O₂ are

diatomic gases, whereas CO_2 is a *triatomic* gas. Equation (10.1) also indicates that two molecules of CO_2 will always break down into two molecules of CO and one molecule of O_2 : this is signified by the symbol $\rightleftharpoons$ which indicates that the processes can go in both directions. It is conventional to refer to the components to the left of the arrow as the *reactants* and that to the right as the *products*: this is because exothermic combustion (i.e. in which energy is released by the process) would require CO and O_2 to combine to give CO_2 . Not all reactions are exothermic and the formation of NO during dissociation occurring in an internal combustion (i.c.) engine is actually endothermic.

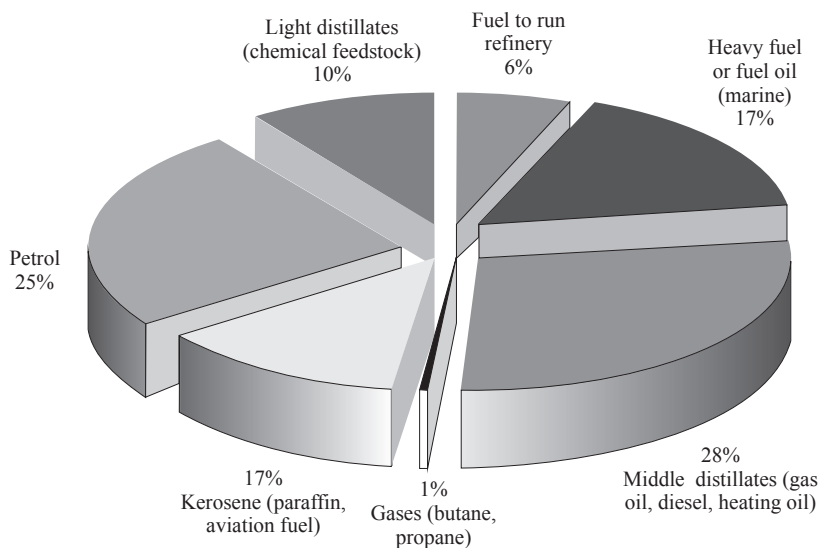
It should be noted from the combustion Eqn (10.1) that three molecules of reactants combine to produce two molecules of products, hence there is not necessarily a balance in the number of molecules on either side of a chemical reaction. However, there is a balance in the number of atoms of each constituent in the equation and so mass is conserved.

10.1.1 FUELS

In 1973, the price of crude oil rapidly increased to three to four times its pre-1973 cost. This major price change had a marked impact on the economy of the industrial nations. It also provided a sharp reminder of their vulnerability to the pricing and conservation policies of the oil-producing countries, and of the finite nature of the world's petroleum supplies. This problem was ameliorated during the 1980s with the discovery and capture of alternative supplies in other parts of the world. At present, in 2014, the situation is changing again with the development of fracking to access gases trapped in the rock strata. However, no matter how effective man becomes at obtaining fossil fuels, in the end they will prove to be a finite resource, and their price will rise. The downside of accessing more sources of fossil fuels is that their combustion will form more carbon dioxide, carbon monoxide and nitrogen oxides to be produced, with the possibility of further global warming. It is possible that this problem can be reduced by carbon sequestration, but at what energy cost – and where will it come from? The most dominant fuel issues of today are those of cost and availability.

Crude oil is known to exist at various depths beneath land and sea in most parts of the world, but commercial quantities are produced mainly in four areas – North America, the Caribbean, the Middle East, and the Soviet Union. Crude oils are extremely complex mixtures of gases, liquids and dissolved solids that always consist mainly of hydrocarbons, with small amounts of nitrogenous substances and organic sulphur compounds. A typical barrel of crude oil contains a range of hydrocarbons, and these are separated at a refinery; the oil produces the constituents shown broadly in Fig. 10.1. Hydrocarbon fuels are rarely single component in nature due to the methods of formation of the raw material and its extraction from the ground. Invariably they also contain traces of various metallic constituents. It is usual to classify the hydrocarbons present in petroleum fuel into four main groups: paraffinic, olefinic, naphthenic and aromatic. The proportions in which these groups are present largely define the character of the fuel. The chemical structure of fuels will be discussed in some detail in Chapter 11.

Fuels for spark-ignition engines require an ability to resist spontaneous ignition at the high pressures and temperatures achieved after compression, and in the end gas during combustion: this characteristic is defined by the octane number of the fuel. A fuel with a high octane number will be more resistant to spontaneous ignition than one with a low octane number, and can run in an engine with a higher compression ratio. Spontaneous combustion results in detonation, which can be an audible 'tink-tink' at low speed; at high speed the combustion 'knocks' causing major damage to combustion chamber components. Knock is much less prevalent in engines nowadays because 'knock'

**FIGURE 10.1**

Typical constituents of a barrel of crude oil.

sensors are fitted to engines, and these retard the ignition when knock is detected. Octane number is evaluated by running a calibration engine on the fuel and comparing its performance with the engine using a mixture of isooctane (100) and heptane (0). The octane number is equal to the proportion of octane in the calibration mixture. A high octane number does not indicate that the fuel has more energy than one with a low octane number. Two octane numbers are quoted: the Research Octane Number (RON) determined simply by varying the compression ratio, and the Motor Octane Number (MON) which is assessed under more realistic operating conditions. MON is usually between 8 and 10 points lower than RON.

Fuels for compression ignition, or diesel, engines require a high cetane number (CN): this is a measure of the ability of the fuel to ignite after compression – it is almost the inverse of the octane number. Higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. Therefore, higher cetane fuel usually causes an engine to run more smoothly and quietly, and reduces diesel ‘knock’, which occurs when the fuel that has been initially injected into the cylinder suddenly ignites (see Fig. 16.7). Generally, diesel engines operate well with a CN from 40 to 55, and modern high-speed diesel engines operate more effectively with higher CN fuels. Diesel fuel is about 11% denser than petrol, while the lower enthalpy of combustion is about the same – hence the energy per unit volume is about 11% higher, so (for equivalent energy of combustion) a diesel engine should have a fuel consumption (miles/gallon) at least 11% higher.

In general, for any given aircraft turbine application, the optimal fuel is the one that represents the best compromise to the various problems confronting the fuel companies, the engine and aircraft manufacturers and the operators. For civil aircraft the main requirements are safety, reliability, low cost and ease of handling. For military aircraft fuel cost is of secondary importance compared with

availability, supply logistics and the need for trouble-free operation over a wide range of conditions. Industrial and marine gas turbines can compete effectively with the diesel engine only through the use of very cheap fuels, such as residual oil or surplus gas. As a rule, gaseous fuels present no special problems, but residual oils produce a highly destructive ash and sometimes copious amounts of exhaust smoke. Attempts to burn pulverized solid fuels in open-cycle gas turbines have generally proved unsuccessful. However, developments in fluidised-bed combustion could dramatically change that situation.

One fuel which approaches single component composition is 'natural gas' which consists largely of methane (CH_4). Methane is the simplest member of a family of hydrocarbons referred to as *paraffins* or, more recently, *alkanes* which have a general formula $\text{C}_n\text{H}_{2n+2}$. The lower alkanes are methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) etc. Two other alkanes that occur in discussion of liquid fuels are heptane (C_7H_{16}) and octane (C_8H_{18}). The alkanes are referred to as *saturated hydrocarbons* because it is not physically possible to add more hydrogen atoms to them. However, it is possible to find hydrocarbons with less than $2n + 2$ hydrogen atoms and these are referred to as *unsaturated hydrocarbons*: a simple unsaturated hydrocarbon is acetylene (C_2H_2), which belongs to a chemical family called *alkenes*. Some fuels contain other constituents in addition to carbon and hydrogen. For example, the alcohols contain oxygen in the form of an OH radical. The chemical symbol for methanol is CH_3OH , and that for ethanol is $\text{C}_2\text{H}_5\text{OH}$: these are the alcohol equivalents of methane and ethane.

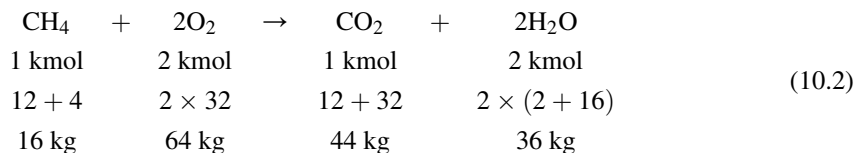
Often fuels are described by a mass analysis which defines the proportion by mass of the carbon and hydrogen e.g. a typical hydrocarbon fuel might be defined as 87% C and 13% H without specifying the actual components of the liquid. Solid fuels, such as various coals, have a much higher carbon/hydrogen ratio but contain other constituents including oxygen and ash.

The molecular weights (or relative molecular masses) of fuels can be evaluated by adding together the molecular (or atomic) weights of their constituents. Three examples are given below.

$$\begin{array}{ll} \text{Methane (CH}_4\text{)} & (m_w)_{\text{CH}_4} = 12 + 4 \times 1 = 16 \\ \text{Octane (C}_8\text{H}_{18}\text{)} & (m_w)_{\text{C}_8\text{H}_{18}} = 8 \times 12 + 18 \times 1 = 114 \\ \text{Methanol (CH}_3\text{OH)} & (m_w)_{\text{CH}_3\text{OH}} = 12 + 3 \times 1 + 16 + 1 = 32 \end{array}$$

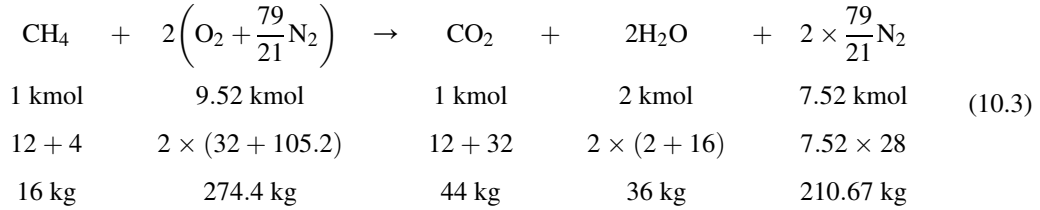
10.2 COMBUSTION OF SIMPLE HYDROCARBON FUELS

The combustion of a hydrocarbon fuel takes place according to the constraints of chemistry. The combustion of methane with oxygen is defined by:



In this particular case, there is both a molar balance and a mass balance: the latter is essential but the former is not. Usually combustion takes place between a fuel and air (a mixture of oxygen and

nitrogen). It is normal to assume, at this level, that the nitrogen is an inert gas and takes no part in the process. Combustion of methane with air is given by



10.2.1 STOICHIOMETRY

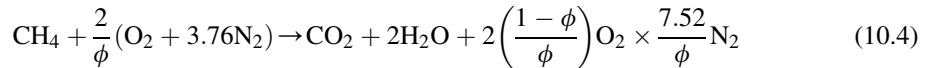
There is a clearly defined, and fixed, ratio of the masses of air and fuel that will result in complete combustion of the fuel. This mixture is known as a *stoichiometric* one and the ratio is referred to as the *stoichiometric air-fuel ratio*. The stoichiometric air-fuel ratio, ϵ_{stoic} , for methane can be evaluated from the chemical equation (Eqn (10.3)). This gives

$$\epsilon_{\text{stoic}} = \frac{\text{mass of air}}{\text{mass of fuel}} = \frac{2 \times (32 + 105.33)}{16} = 17.17$$

This means that to obtain complete combustion of 1 kg CH_4 it is necessary to provide 17.17 kg of air. If the quantity of air is less than 17.17 kg then complete combustion will not occur and the mixture is known as *rich*. If the quantity of air is greater than that required by the stoichiometric ratio then the mixture is *weak*.

10.2.2 COMBUSTION WITH WEAK MIXTURES

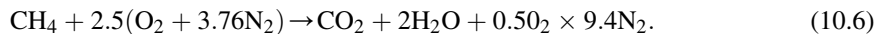
A weak mixture occurs when the quantity of air available for combustion is greater than the chemically correct quantity for complete oxidation of the fuel; this means that there is excess air available. In this simple analysis, neglecting reaction rates and dissociation etc., this excess air passes through the process without taking part in it. However, even though it does not react chemically, it has an effect on the combustion process simply because it lowers the temperatures achieved due to its capacity to absorb energy. The equation for combustion of a weak mixture is



where ϕ is called the *equivalence ratio*, and

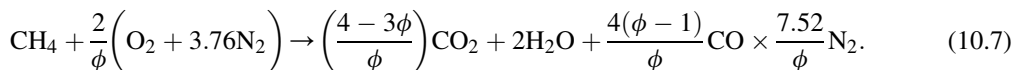
$$\phi = \frac{\text{actual fuel - air ratio}}{\text{stoichiometric fuel - air ratio}} \quad (10.5)$$

For a weak mixture ϕ is less than unity. Consider a weak mixture with $\phi = 0.8$, then

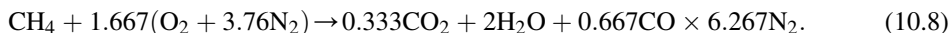


10.2.3 COMBUSTION WITH RICH MIXTURES

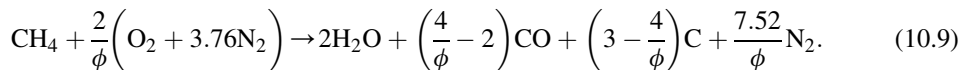
A rich mixture occurs when the quantity of air available is less than the stoichiometric quantity; this means that there is not sufficient air to burn the fuel. In this simplified approach it is assumed that the hydrogen combines preferentially with the oxygen and the carbon does not have sufficient oxygen to be completely burned to carbon dioxide: this results in partial oxidation of part of the carbon to carbon monoxide. It will be shown in Chapter 12 that the equilibrium equations, which control the way in which the hydrocarbon fuel oxidizes, govern the proportions of oxygen taken by the carbon and hydrogen of the fuel and that the approximation of preferential combination of oxygen and hydrogen is a reasonable one. In this case, to define a rich mixture, ϕ is greater than unity. Then



If the equivalence ratio is 1.2, then Eqn (10.7) is



It is quite obvious that operating the combustion on rich mixtures results in the production of carbon monoxide (CO), an extremely toxic gas. For this reason it is now not acceptable to operate combustion systems with rich mixtures. Note that Eqn (10.7) cannot be used with values of $\phi > 4/3$, otherwise the amount of CO_2 becomes negative. At this stage it must be assumed that the carbon is converted to carbon monoxide and carbon. The resulting equation is



Equation (10.9) is a very hypothetical one because during combustion extensive dissociation occurs and this liberates oxygen by breaking down the water molecules: this oxygen is then available to create carbon monoxide and carbon dioxide rather than carbon molecules.

In reality it is also possible to produce pollutants even when the mixture is weaker than stoichiometric simply due to poor mixing of fuel and air, quenching of flames on cold cylinder or boiler walls, trapping of mixture in crevices (fluid mechanics effects) and also due to thermodynamic limitations in the process.

10.3 HEATS OF FORMATION AND HEATS OF REACTION

Combustion of fuels takes place either in a closed system or an open system. The relevant property of the fuel to be considered is the *internal energy or enthalpy, respectively, of formation or reaction*. In a naive manner it is often considered that combustion is a process of energy addition to the system. This is not true because the energy released during a combustion process is already contained in the reactants, in the form of the chemical energy of the fuel (see Chapter 11). Hence it is possible to talk of *adiabatic combustion* as a process in which no energy (heat) is transferred to, or from, the system – the temperature of the system increases because of a rearrangement of the chemical bonds in the fuel and oxidant.

Mechanical engineers are usually concerned with the combustion of hydrocarbon fuels, such as petrol, diesel oil, or methane. These fuels are commonly used because of their ready availability (at present) and high-energy density in terms of both mass and volume. The combustion normally takes place in the presence of air. In some other applications, e.g. space craft, rockets, etc., fuels which are not hydrocarbons are burned in the presence of other oxidants; these will not be considered here.

Hydrocarbon fuels are stable compounds of carbon and hydrogen which have been formed through the decomposition of animal and vegetable matter over many millennia. It is also possible to synthesise hydrocarbons by a number of processes in which hydrogen is added to a carbon-rich fuel. The South African Sasol plant uses the Lurgi and Fischer–Tropsch processes to convert coal from a solid fuel to a liquid one. The chemistry of fuels is considered in Chapter 11.

10.4 APPLICATION OF THE ENERGY EQUATION TO THE COMBUSTION PROCESS – A MACROSCOPIC APPROACH

Equations (10.3)–(10.6) show that combustion can take place at various air-fuel ratios and it is necessary to be able to account for the effect of mixture strength on the combustion process, especially the temperature rise that will be achieved. It is also necessary to be able to account for the different fuel composition: not all fuels will release the same quantity of energy per unit mass and hence it is required to characterise fuels by some capacity to release chemical energy in a thermal form. Both of these effects obey the First Law of Thermodynamics i.e. the energy equation.

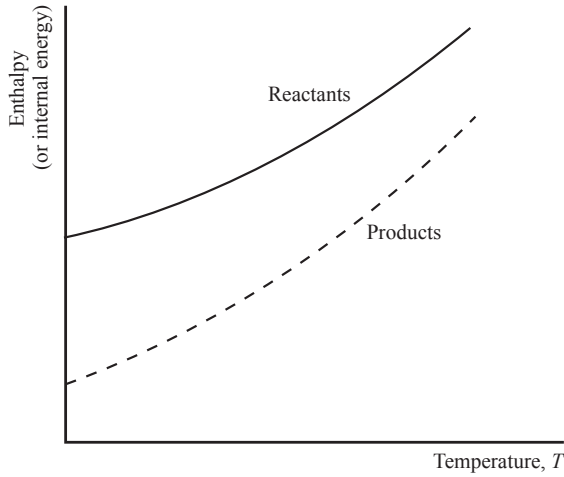
10.4.1 INTERNAL ENERGIES AND ENTHALPIES OF IDEAL GASES

It was shown previously (Chapter 7, Section 7.2) that the internal energies and enthalpies of ideal gases are functions of temperature alone (c_p and c_v might still be functions of temperature). This means that the internal energy and enthalpy can be represented on U – T and H – T diagrams. It is then possible to draw a U – T , or H – T line for both reactants and products (Fig. 10.2). The reactants will be basically diatomic gases (neglecting the effect of the fuel) whereas the products will be a mixture of diatomic and triatomic gases – see Eqn (10.3).

The next question which arises is what is the spacing between the reactants and products lines: this spacing represents the energy that can be released by the fuel.

10.4.2 HEATS OF REACTION AND FORMATION

The energy contained in the fuel can also be assessed by burning it under a specified condition: this energy is referred to as the *heat of reaction of the fuel*. The heat of reaction for a fuel is dependent on the process by which it is measured. If it is measured by a constant volume process in a combustion bomb then the *internal energy of reaction* is obtained. If it is measured in a constant pressure device then the *enthalpy of reaction* is obtained. It is more normal to measure the enthalpy of reaction because it is much easier to achieve a constant pressure process. The enthalpy of reaction of a fuel can be evaluated by burning the fuel in a stream of air, and measuring the quantity of energy that must be removed to achieve equal reactant and product temperatures, see Fig. 10.3.


FIGURE 10.2

Enthalpy (or internal energy) of reactants and products.

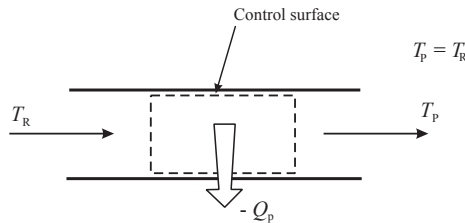
Applying the steady flow energy equation

$$\dot{Q} - \dot{W}_s = \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) - \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) \quad (10.10)$$

and neglecting the kinetic and potential energy terms then

$$(Q_p)_T = (H_P)_T - (H_R)_T = n_P(h_P)_T - n_R(h_R)_T \quad (10.11)$$

where n denotes the amount of substance either in the products or reactants; this is identical to the term n which was used for the amount of substance in Chapter 9. The suffix T defines the temperature at which the enthalpy of reaction was measured. $(Q_p)_T$ is a function of this temperature and normally it is evaluated at a standard temperature of 25 °C (298 K). When $(Q_p)_T$ is evaluated at a standardised temperature it will be denoted by the symbol $(Q_p)_s$. Most values of Q_p that are used in combustion calculations are the $(Q_p)_s$ ones. (In a similar way, $(Q_v)_s$ will be used for internal energy of reaction at the standard temperature). The sign of Q_p is negative for fuels because heat must be transferred from


FIGURE 10.3

Constant pressure measurement of enthalpy reaction.

the ‘calorimeter’ to achieve equal temperatures for the reactants and products (it is positive for some reactions, meaning that heat has to be transferred *to* the calorimeter to maintain constant temperatures). The value of the constant volume heat of reaction, the internal energy of reaction, $(Q_v)_s$, can be calculated from $(Q_p)_s$ as shown in Eqn (10.13) below, or measured using a constant volume combustion ‘bomb’; again $(Q_v)_s$ has a negative value. $(Q_p)_s$ and $(Q_v)_s$ are shown in Fig. 10.4(a) and (b) respectively. The term calorific value of the fuel was used in the past to define the ‘heating’ value of the fuel: this is actually the *negative* value of the heat of reaction, and is usually a positive number. It is usually associated with analyses in which ‘heat’ is added to a system during the combustion process, e.g. the air standard cycles introduced in Chapter 3.

Applying the First Law for a closed system to constant volume combustion gives

$$(Q_v)_T = (U_P)_T - (U_R)_T = n_P(u_P)_T - n_R(u_R)_T. \quad (10.12)$$

If both the products and reactants are ideal gases then

$$h = \int c_{p,m} dT, \text{ and } u = \int c_{v,m} dT,$$

which can be evaluated from the polynomial expressions derived in Chapter 9 (Table 9.4).

Thus

$$\begin{aligned} (Q_p)_s - (Q_v)_s &= n_P(h_P)_T - n_R(h_R)_T - \{n_P(u_P)_T - n_R(u_R)_T\} \\ &= n_P\{(h_P)_T - (u_P)_T\} - n_R\{(h_R)_T - (u_R)_T\} \\ &= \Re T(n_P - n_R). \end{aligned} \quad (10.13)$$

This result is quite logical because the definitions of $(Q_p)_s$ and $(Q_v)_s$ require that T_P and T_R are equal. Hence the constant pressure and constant volume processes are identical if the amounts of substance in the products and the reactants are equal. If the amounts of substance change during the reaction then the

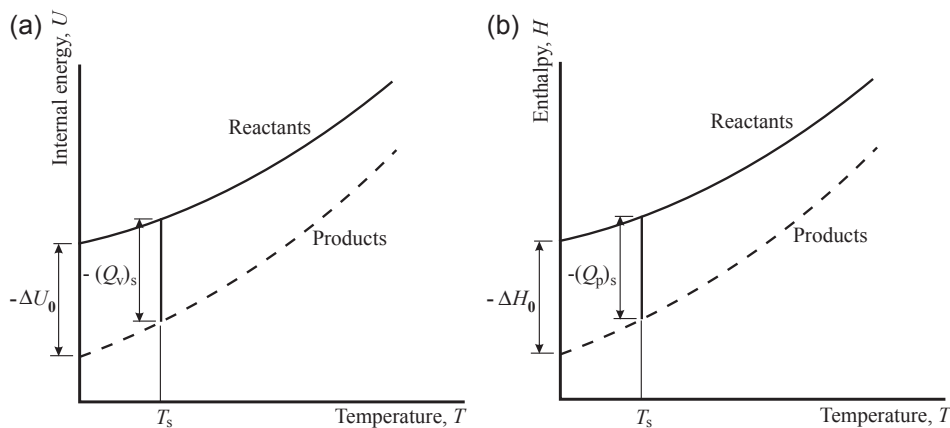


FIGURE 10.4

Internal energy and enthalpy of reaction depicted on (a) internal energy–temperature and (b) enthalpy–temperature diagrams.

processes cease to be identical and, in the case of a combustion *bomb*, a piston would have to move to maintain the conditions. The movement of the piston produces work equal to $\Re T (n_P - n_R)$.

It is also possible to relate the quantity of energy that is chemically bound up in the fuel to a value at absolute zero of temperature. These values are denoted as $-\Delta H_0$ and $-\Delta U_0$ and will be returned to later.

10.4.3 HEAT OF FORMATION – HESS'S LAW

The heat of formation of a compound is the quantity of energy absorbed (or released) during its formation from its elements (the end pressures and temperatures being maintained equal).

For example, if CO_2 is formed from carbon and oxygen by the reaction



then in a constant pressure steady flow process with equal temperature end states, the reaction results in heat transfer of Q_p given by

$$(Q_p) = H_P - H_R \quad (10.15)$$

$$= -394 \text{ MJ/kmol.} \quad (10.16)$$

If a slightly different reaction is performed giving the same end product, e.g.



then it is not possible to use the same simple approach because the reactants are a mixture of elements and compounds. However Hess's law can be used to resolve this problem. This states that:

1. if a reaction at constant pressure or constant volume is carried out in stages the algebraic sum of the amounts of heat evolved in the separate stages is equal to the total evolution of heat when the reaction occurs directly;

or

2. the heat liberated by a reaction is independent of the path of the reaction between the initial and final states.

Both of these are simply statements of the law of energy conservation and the definition of properties. However, this allows complex reactions to be built up from elemental ones. For example, the reaction



can be subdivided into two different reactions.



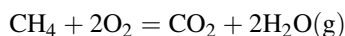
The heat of formation of CO may be evaluated by reaction (Eqn (10.19a)) and then used in reaction (Eqn (10.19b)) to give the heat of reaction of that process. From experiment the heat of formation of carbon monoxide (CO) is -110.5 MJ/kmol and hence, for reaction (Eqn (10.19b)), the energy released is

$$Q_p = H_P - H_R = -393.5 - (-110.5) = -283 \text{ MJ/kmol} \quad (10.20)$$

Hence the heat of reaction for $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ is -283 MJ/kmol.

The heats of formation of any compounds can be evaluated by building up simple reactions, having first designated the *heats of formation of elements as zero*. This enables the enthalpy of formation of various compounds to be built up from component reactions. Enthalpies of formation are shown in Table 10.2.

These enthalpies of formation can be used to evaluate heats of reaction of more complex molecules e.g. for methane (CH_4) the equation is



giving

$$\begin{aligned} (Q_p)_{25} &= (\Delta H_f)_{\text{CO}_2(\text{g})} + 2(\Delta H_f)_{\text{H}_2\text{O}(\text{g})} - (\Delta H_f)_{\text{CH}_4(\text{g})} \\ &= -802279 \text{ kJ/kmol.} \end{aligned}$$

This gives an enthalpy of reaction per kilogram of CH_4 of $-50,142$ kJ/kg.

Table 10.2 Enthalpies of Formation of Some Common Elements and Compounds

Species	Reaction	State	ΔH_f (kJ/kmol)
Oxygen, O_2	—	Gas 25 °C, 1 atm	0, element
Hydrogen, H_2	—	Gas 25 °C, 1 atm	0, element
Carbon, C	—	Gas 25 °C, 1 atm	0, element
Carbon dioxide, CO_2	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	Gas 25 °C, 1 atm ^a	-393,522
Carbon monoxide, CO	$\text{C} + \text{O} \rightarrow \text{CO}$	Gas 25 °C, 1 atm ^a	-110,529
Water vapour, H_2O	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}(\text{g})$	Gas 25 °C, 1 atm ^a	-241,827
Water (liquid), H_2O	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}(\text{l})$	Liquid 25 °C, 1 atm	-285,800
Nitric oxide (NO)	$\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}$	Gas 25 °C, 1 atm ^a	+89,915
Methane, CH_4	$\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4(\text{g})$	Gas 25 °C, 1 atm ^a	-74,897
Ethane, C_2H_6	$2\text{C} + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_6(\text{g})$	Gas 25 °C, 1 atm	-84,725
Propane, C_3H_8	$3\text{C} + 4\text{H}_2 \rightarrow \text{C}_3\text{H}_8(\text{g})$	Gas 25 °C, 1 atm	-103,916
Butane, C_4H_{10}	$4\text{C} + 5\text{H}_2 \rightarrow \text{C}_4\text{H}_{10}(\text{g})$	Gas 25 °C, 1 atm	-124,817
Isooctane, C_8H_{18}	$8\text{C} + 9\text{H}_2 \rightarrow \text{C}_8\text{H}_{18}(\text{g})$	Gas 25 °C, 1 atm	-224,100
Isooctane, C_8H_{18}	$8\text{C} + 9\text{H}_2 \rightarrow \text{C}_8\text{H}_{18}(\text{l})$	Liquid 25 °C, 1 atm	-259,280
Methyl alcohol, CH_3OH	$\text{C} + 2\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{OH}(\text{g})$	Gas 25 °C, 1 atm	-201,200
Methyl alcohol, CH_3OH	$\text{C} + 2\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{OH}(\text{l})$	Liquid 25 °C, 1 atm	-238,600
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	$2\text{C} + 3\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$	Gas 25 °C, 1 atm	-234,600
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	$2\text{C} + 3\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$	Liquid 25 °C, 1 atm	-277,000

^anote: the values of ΔH_f given in the tables of gas properties are based on 0 K.

10.4.3.1 Higher and lower calorific values

The enthalpy of reaction of CH_4 derived above ($-50,178 \text{ kJ/kg}$) is the negative of the lower calorific value (LCV) because it is based on gaseous water ($\text{H}_2\text{O}(\text{g})$) in the products. If the water in the products (exhaust) was condensed to a liquid then extra energy could be released by the process. In this case the enthalpy of reaction would be

$$\begin{aligned} (Q_p)_{25} &= (\Delta H_f)_{\text{CO}_2} + 2(\Delta H_f)_{\text{H}_2\text{O}(\text{l})} - (\Delta H_f)_{\text{CH}_4} \\ &= -890225 \text{ kJ/kmol} \end{aligned}$$

This gives an enthalpy of reaction per kilogram of CH_4 of $-55,639 \text{ kJ/kg}$. This is the negative of the higher calorific value.

Normally the LCV, or lower internal energy or enthalpy of reaction, is used in engine calculations because the water in the exhaust system is usually in the vapour phase.

10.5 COMBUSTION PROCESSES

10.5.1 ADIABATIC COMBUSTION

The heats of reaction of fuels have been described in terms of isothermal processes i.e. the temperature of the products is made equal to the temperature of the reactants. However, it is common experience that combustion is definitely not isothermal; in fact, its major characteristic is to raise the temperature of a system. How can this be depicted on the enthalpy–temperature diagram?

Consider a constant pressure combustion process, as might occur in a gas turbine, in which there is no heat or work transfer (Fig. 10.5(a)).

Applying the steady flow energy equation, Eqn (10.11), to the combustion chamber shown in Fig. 10.5(a) gives

$$H_P = H_R. \quad (10.21)$$

Hence *adiabatic combustion is a process which occurs at constant enthalpy* (or internal energy, in the case of combustion at constant volume), and the criterion for equilibrium is that the enthalpies at the beginning and end of the process are equal. This process can be shown on an H – T diagram (Fig. 10.5(b)) and it is possible to develop from this an equation suitable for evaluating the product temperature. The sequences of reactions defining combustion are denoted by the ‘cycle ABCD’. Going clockwise around the cycle, from A, gives

$$-(Q_p)_s + [H_R(T_R) - H_R(T_s)] - [H_P(T_P) - H_P(T_s)] = 0 \quad (10.22)$$

The term $[H_R(T_R) - H_R(T_s)]$ is the difference between the enthalpy of the reactants at the temperature at the start of combustion (T_R) and the standardised temperature (T_s). The term $[H_P(T_P) - H_P(T_s)]$ is a similar one for the products. These terms can be written as

$$[H_R(T_R) - H_R(T_s)] = \sum_{i=1}^n n_{R_i} h_{R_i}(T_R) - \sum_{i=1}^n n_{R_i} h_{R_i}(T_s) = \sum_{i=1}^n n_{R_i} \{h_{R_i}(T_R) - h_{R_i}(T_s)\} \quad (10.23)$$

where i is the particular component in the reactants and n is the number of components over which the summation is made.

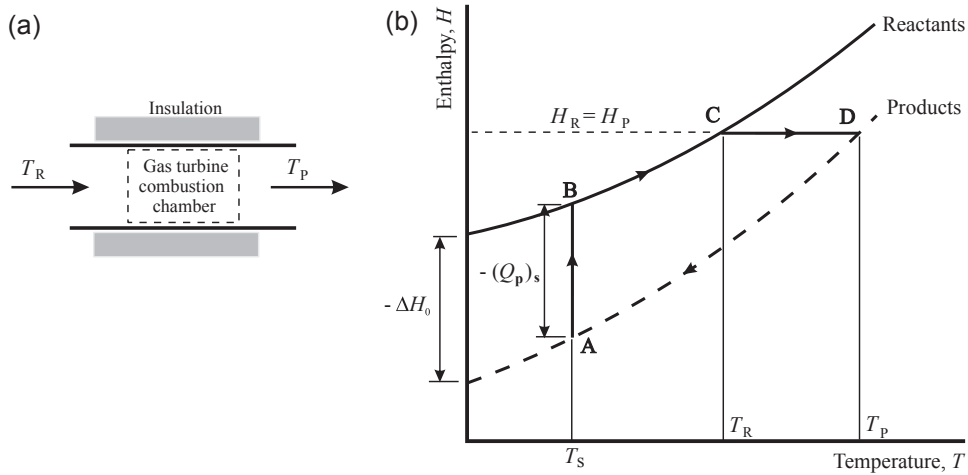


FIGURE 10.5

Adiabatic combustion depicted on enthalpy–temperature diagram (a) schematic of gas turbine combustion chamber (b) enthalpy – temperature diagram of *adiabatic* combustion process.

From Eqn (10.22)

$$H_P(T_P) = -(Q_P)_s + [H_R(T_R) - H_R(T_s)] + H_P(T_s) \quad (10.24)$$

If the process had been a constant volume one, as in an idealised (i.e. adiabatic) i.c. engine, then

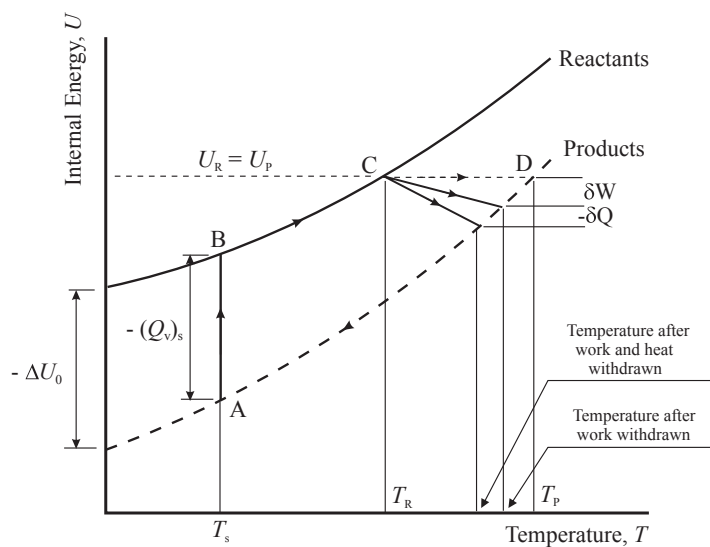
$$U_P(T_P) = -(Q_v)_s + [U_R(T_R) - U_R(T_s)] + U_P(T_s) \quad (10.25)$$

This possibly seems to be a complex method for evaluating a combustion process compared to the simpler heat release approach. However, the advantage of this method is that it results in a true *energy balance*: the enthalpy of the products is always equal to the enthalpy of the reactants. Also, because it is written in terms of enthalpy, the variation of gas properties due to temperature and composition changes can be taken into account correctly. An approach such as this can be applied to more complex reactions which involve dissociation and rate kinetics: other simpler methods cannot give such accurate results.

10.5.2 COMBUSTION WITH HEAT AND WORK TRANSFER

The combustion process shown in Fig. 10.5(b) is an adiabatic one, and the enthalpy of the products is equal before and after combustion. However, if there is heat transfer or work transfer taking place in the combustion process, as might occur during the combustion process in an i.c. engine, then Fig. 10.5(b) is modified to that shown in Fig. 10.6.

The effect of heat transfer from the cylinder, $-\Delta Q$, reduces the temperature of the products from T_{P1} to T_{P2} , while if the engine also provides a work output of $p\Delta V$ the temperature of the products is

**FIGURE 10.6**

Combustion with heat transfer and work output.

reduced further to T_{P3} . These effects can be incorporated into the energy equation in the following way. The First Law for the process is

$$\Delta Q - \Delta W = dU = U_P(T_P) - U_R(T_R) \quad (10.26)$$

Hence

$$U_P(T_P) = U_R(T_R) + \Delta Q - \Delta W. \quad (10.27)$$

This means that heat transfer away from the cylinder, as will normally happen in the case of an engine during the combustion phase, tends to reduce the internal energy of the products compared to the reactants. Also, if work is taken out of the cylinder due to the piston moving away from top dead-centre, the internal energy is further reduced.

10.5.3 INCOMPLETE COMBUSTION

The value of enthalpy (or internal energy) of reaction for a fuel applies to complete combustion of that fuel to carbon dioxide and water. However, if the mixture is a rich one then there will be insufficient oxidant to convert all the fuel to CO_2 and H_2O , and it will be assumed here that some of the carbon is converted only to CO . The chemical equations of this case are shown in [Section 10.2.3](#). Here the effect of incomplete combustion on the energy released will be considered. Incomplete combustion can be depicted as an additional line on the enthalpy–temperature diagram – the position of this line indicates how far the combustion process has progressed (see [Fig. 10.7](#)). In this case the amount of energy released can be evaluated from the energies of formation, in a similar manner to that in [Eqn \(10.8\)](#).

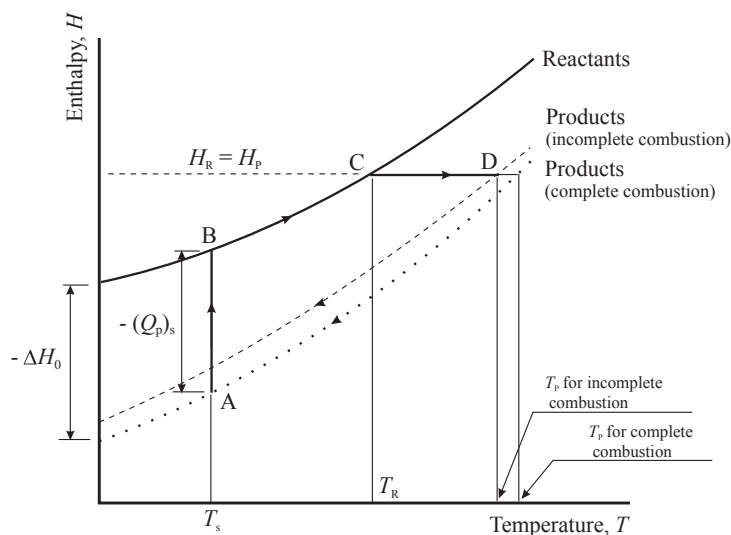


FIGURE 10.7

Enthalpy-temperature diagram for incomplete combustion, including rich mixtures and dissociation.

10.6 EXAMPLES

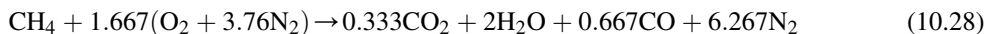
The examples quote solutions to the resolution of a calculator. This is to aid readers in identifying errors in their calculations, and does not mean the data are accurate to this level.

Example 1: incomplete combustion

Evaluate the energy released from constant pressure combustion of a rich mixture of methane and air: use $\phi = 1.2$.

Solution

The chemical equation is



The nitrogen (N_2) takes no part in this reaction and does not need to be considered. The energy liberated in the reaction (Q_p) is the difference between the enthalpies of formation of the products and reactants.

Enthalpy of formation of reactants,

$$(\Delta H_f)_R = (\Delta H_f)_{\text{CH}_4} = -74897 \text{ kJ/kmol}$$

Enthalpy of formation of products,

$$\begin{aligned} (\Delta H_f)_P &= 0.333(\Delta H_f)_{\text{CO}_2} + 2(\Delta H_f)_{\text{H}_2\text{O}} + 0.667(\Delta H_f)_{\text{CO}} \\ &= 0.333(-393522) + 2(-241827) + 0.667(-110529) \\ &= -688420 \text{ kJ/kmol.} \end{aligned}$$

Hence the energy released by this combustion process is

$$\begin{aligned} Q_p &= (\Delta H_f)_P - (\Delta H_f)_R \\ &= -688420 - (-74897) \\ &= -613523 \text{ kJ/kmol.} \end{aligned}$$

It can be seen that this process has released only 76.4% of the energy that was available from complete combustion ($-802,279 \text{ kJ/kmol}$). This is because the carbon has not been fully oxidised to carbon dioxide, and energy equal to $0.667 \times -282 \text{ MJ/kmol CH}_4$ (equivalent to the product of the quantity of carbon monoxide and the heat of reaction for Eqn (10.18)) is unavailable in the form of thermal energy. This is equivalent to $188,094 \text{ kJ/kmol CH}_4$, and is the remaining 23.6% of the energy which would be available from complete combustion. While the incomplete combustion in Eqn (10.34) has occurred because of the lack of oxygen in the rich mixture, a similar effect occurs with dissociation, when the products are partially broken down into reactants.

Example 2: adiabatic combustion in an engine

A stoichiometric mixture of methane (CH_4) and air is burned in an engine which has an effective compression ratio of 8:1. Calculate the conditions at the end of combustion at constant volume if the initial temperature and pressure are 27°C and 1 bar respectively. The LCV of methane is $50,144 \text{ kJ/kg}$ at 25°C . Assume the ratio of specific heats (κ) for the compression stroke is 1.4 (Fig. 10.8).

Solution

Chemical equation is

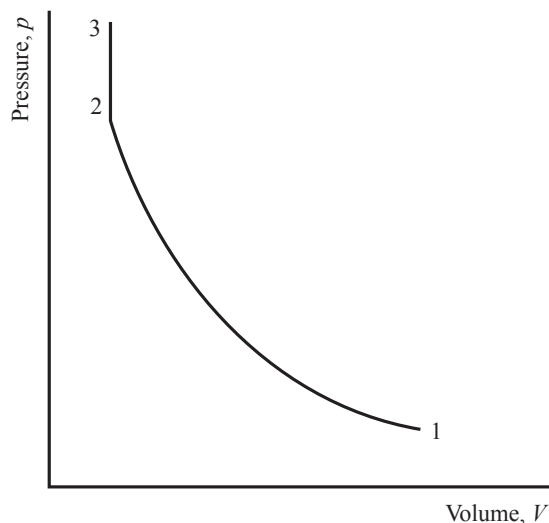
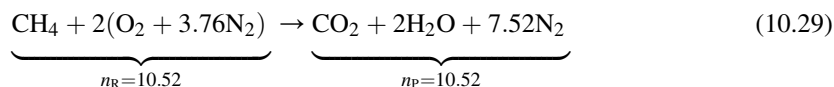


FIGURE 10.8

p – V diagram for constant volume combustion.

$$p_1 = 1 \text{ bar}$$

$$T_1 = 300\text{K}$$

$$p_2 = p_1 \left(\frac{V_1}{V_2} \right)^{1.4} = 1 \times 8^{1.4} = 18.379 \text{ bar}$$

$$\begin{aligned} T_2 &= T_1 \left(\frac{V_1}{V_2} \right)^{\kappa-1} = 300 \times 8^{0.4} \\ &= 689.2 \text{ K.} \end{aligned}$$

Combustion equation is:

$$U_P(T_P) = -(Q_v)_s + [U_R(T_R) - U_R(T_s)] + U_P(T_s) \quad (10.30)$$

Reactants energy $[U_R(T_R) - U_R(T_s)]$ is

Constituent	CH ₄	O ₂	N ₂
$u_{689.2}$	21,883.9	15,105.9	14,587.7
u_{298}	5719.6	6032.0	6025.8
Difference	16,164.3	9073.9	8561.9
n	1	2	7.52
nu	16,164.3	18,146.4	64,385.5

$$\text{Thus } [U_R(T_R) - U_R(T_s)] = 9.8696 \times 10^4 \text{ kJ}$$

Products energy at standard temperature, $U_P(T_s)$, is

Constituent	CO ₂	H ₂ O	N ₂
u_{298}	7041.6	7223.3	6025.8
n	1	2	7.52
nu_{298}	7041.6	14,446.6	45,314.0

$$\text{Hence } U_P(T_s) = 66802.2 \text{ kJ.}$$

Substituting these values into [Eqn \(10.30\)](#), and converting the calorific value to molar terms gives

$$\begin{aligned} U_P(T_P) &= 50144 \times 16 + 9.8696 \times 10^4 + 66802.2 \\ &= 9.678 \times 10^5 \text{ kJ.} \end{aligned}$$

The value of specific internal energy for the mixture of products is

$$u_P(T_P) = \frac{U_P(T_P)}{n_P} = \frac{9.678 \times 10^5}{10.52} = 92000 \text{ kJ/kmol.}$$

An approximate value of the temperature can be obtained by assuming the exhaust products to be 70% N₂ and 30% CO₂. Using this approximation gives

T	$U_P(T_P)$
2500	76,848.7
3000	94,623.3

Hence T_P is around 3000 K. Assume $T_P = 3000$ K and evaluate $U_P(T_P)$

Constituent	CO ₂	H ₂ O	N ₂
u_{3000}	137,950.4	109,612.6	76,504.6
n	1	2	7.52
nu	137,950.4	219,225.2	575,314.6

$$\sum nu = U_P(T_P) = 932490.2 \text{ kJ.}$$

This value is less than that obtained from Eqn (10.30), and hence the temperature was underestimated.

Try $T_P = 3100$ K.

Constituent	CO ₂	H ₂ O	N ₂
u_{3100}	143,420.0	114,194.9	79,370.9
n	1	2	7.52
nu	143,420.0	228,389.8	596,869.2

$$\sum nu = 968678.9 \text{ kJ.}$$

Hence the value T_P is between 3000 and 3100 K.

Linear interpolation gives

$$T_P = 3000 + \frac{967800 - 932490.2}{968678.9 - 932490.2} \times 100 = 3097.$$

Evaluating $U_P(T_P)$ at $T_P = 3097$ K gives

Constituent	CO ₂	H ₂ O	N ₂
u_{3097}	143,255.1	114,057.5	79,285.1
n	1	2	7.52
nu	143,255.1	228,114.9	596,224

$$\sum nu = U_P(T_P) = 967594 \text{ kJ.}$$

This is within 0.0212% of the value of $U_P(T_P)$ evaluated from Eqn (10.30).

The final pressure, p_3 , can be evaluated using the perfect gas law because

$$p_3 V_3 = n_3 \Re T_3 = n_P \Re T_3$$

and

$$p_1 V_1 = n_1 \mathcal{R} T_1 = n_R \mathcal{R} T_1$$

giving

$$\begin{aligned} p_3 &= \frac{n_P \mathcal{R} T_3}{n_R \mathcal{R} T_1} \frac{V_1}{V_3} p_1 \\ &= \frac{3097}{300} \times 8 \times 1 = 82.59 \text{ bar.} \end{aligned}$$

Example 3: nonadiabatic combustion in an engine

In the previous calculation, example 2, the combustion was assumed to be adiabatic. If 10% of the energy liberated by the fuel was lost by heat transfer, calculate the final temperature and pressure after combustion.

Solution

The effect of heat transfer is to reduce the amount of energy available to raise the temperature of the products. This can be introduced in Eqn (10.30) to give Eqn (10.31).

$$U_P(T_P) = -(Q_v)_s - Q_{HT} + [U_R(T_R) - U_R(T_s)] + U_P(T_s) \quad (10.31)$$

In this case $Q_{HT} = -0.1(Q_v)_s$ and hence

$$U_P(T_P) = -0.9(Q_v)_s + [U_R(T_R) - U_R(T_s)] + U_P(T_s) \quad (10.32)$$

Substituting values gives

$$\begin{aligned} U_P(T_P) &= 0.9 \times 50144 \times 16 + 9.8696 \times 10^4 + 66802.2 \\ &= 887571.8 \text{ kJ.} \end{aligned}$$

Using a similar technique to before, the first estimate of $U_P(T_P)$ is

$$U_P(T_P) = \frac{887571.8}{10.52} = 84369.9 \text{ kJ/kmol.}$$

From the previous calculation the value of T_P lies between 2500 and 3000 K, and an estimate is

$$T_P = 2500 + \frac{84369.9 - 76848.7}{94623.3 - 76848.7} \times 500 = 2712 \text{ K.}$$

Try $T_P = 2700 \text{ K}$ to check for energy balance.

Constituent	CO ₂	H ₂ O	N ₂
u_{2700}	121,807.5	95,927.5	67,877.4
n	1	2	7.52
nu	121,807.5	191,854.9	510,438.1

$$U_P(T_P) = 823993.7 \text{ kJ.}$$

This is less than the value obtained from the energy equation and hence $T_P > 2700$ K. Try $T_P = 2800$ K.

Constituent	CO ₂	H ₂ O	N ₂
u_{2800}	127,154.9	100,470.8	70,754.1
n	1	2	7.52
nu	127,154.9	200,941.6	532,071.1

$$U_P(T_P) = 860167.6 \text{ kJ.}$$

Hence, by linear extrapolation, try

$$\begin{aligned} T_P &= 2800 + \frac{887571.8 - 860167.6}{860167.6 - 823993.7} \times 100 \\ &= 2875.8 \text{ K.} \end{aligned}$$

Constituent	CO ₂	H ₂ O	N ₂
u_{2876}	131,227.9	103,929.1	72,935
n	1	2	7.52
nu	131,227.9	207,858.1	548,471.5

$$U_P(T_P) = 887557.5 \text{ kJ.}$$

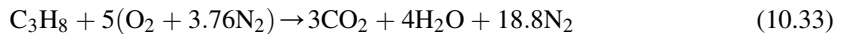
This value is within 0.0016% of the value from the energy equation.

Example 4: combustion with a weak mixture of propane

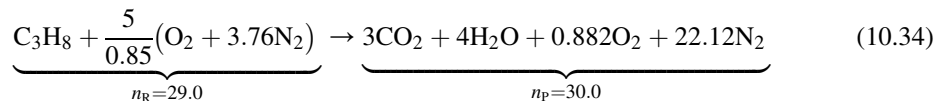
A mixture of propane and excess air is burned at constant volume in an engine with a compression ratio of 10:1. The strength of the mixture (ϕ) is 0.85 and the initial conditions at the start of the compression stroke are 1.2 bar and 127 °C. Assume the ratio of specific heats for compression is 1.4 and take the internal energy of reaction (Q_v)_s of propane as $-46,440$ kJ/kg. Evaluate the final temperature and pressure after combustion neglecting dissociation. The internal energy of propane is 12,911.7 kJ/kmol at the beginning of compression and 106,690.3 kJ/kmol at the end (before combustion).

Solution

Stoichiometric chemical equation is



Weak mixture equation is



Combustion equation is (Eqn (10.30))

$$U_P(T_P) = -(Q_v)_s + [U_R(T_R) - U_R(T_s)] + U_P(T_s).$$

Conditions at start of combustion

$$p_2 = p_1 \left(\frac{V_1}{V_2} \right)^\kappa = 1.2 \times 10^{1.4} = 30.142 \text{ bar.}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\kappa-1} = 400 \times 10^{0.4} = 1004.75 \text{ K.}$$

Reactants energy $[U_R(T_R) - U_R(T_s)]$ is

Constituent	C ₃ H ₈	O ₂	N ₂
$u_{1004.7}$	106,690.3	23,165.0	22,013.6
u_{298}	12,911.7	6032.0	6025.8
Difference	93,778.7	17,133.0	15,987.9
n	1	5.882	22.12
nu	93,778.7	100,776.1	353,651.4

$$[U_R(T_R) - U_R(T_s)] = 548206.2 \text{ kJ.}$$

Products energy at standard temperature, T_s , is

Constituent	CO ₂	H ₂ O	O ₂	N ₂
u_{298}	7041.6	7223.3	6031.7	6025.8
n	3	4	0.882	22.12
nu	21,124.8	28,893.2	5320.0	133,290.7

$$U_P(T_s) = 188628.7 \text{ kJ.}$$

$$\begin{aligned} U_P(T_P) &= 46440 \times (12 \times 3 + 8) + 548206.2 + 188628.7 \\ &= 2043360.0 + 548206.2 + 188628.7 \\ &= 2780194.9 \text{ kJ.} \end{aligned}$$

Assume $T_P = 3100 \text{ K.}$

Constituent	CO ₂	H ₂ O	O ₂	N ₂
u_{3100}	143,420.0	114,194.9	84,974.72	79,370.95
n	3	4	0.882	22.12
nu	430,260.1	456,779.6	74,947.7	1,755,685.0

$$U_P(T_P) = 2717672.4 \text{ kJ.}$$

Try $T_P = 3200$ K.

Constituent	CO ₂	H ₂ O	O ₂	N ₂
u_{3200}	148,954.8	118,773.6	88,164.1	82,226.2
n	3	4	0.882	22.12
nu	446,864.5	475,094.3	77,760.8	1,818,843

$$U_P(T_P) = 2818562.6 \text{ kJ.}$$

Interpolating linearly gives

$$T_P = 3100 + \frac{2780194.9 - 2717672.4}{2818562.6 - 2717672.4} \times 100 = 3162 \text{ K.}$$

Check solution using $T_P = 3162$ K.

Constituent	CO ₂	H ₂ O	O ₂	N ₂
u_{3162}	146,843.0	117,034.7	86,949.1	81,142.8
n	3	4	0.882	22.12
nu	440,529	468,138.7	76,689.4	1,794,878

$$U_P(T_P) = 2780234.8 \text{ kJ.}$$

This value is within 0.0014% of the value calculated from the energy equation. Hence $T_P = 3162$ K.

Pressure at the end of combustion

$$p_3 = \frac{n_P \mathcal{R} T_P}{n_R \mathcal{R} T_1} \cdot \frac{V_1}{V_3} \cdot p_1 = \frac{30}{29} \times \frac{3162}{400} \times 10 \times 1.2$$

$$= 98.13 \text{ bar.}$$

Example 5: combustion at constant pressure of a rich mixture of benzene

A rich mixture of benzene (C₆H₆) and air with an equivalence ratio, ϕ , of 1.2 is burned at constant pressure in an engine with a compression ratio of 15:1. If the initial conditions are 1 bar and 25 °C calculate the pressure, temperature and volume after combustion (Fig. 10.9). The ratio of specific heats during compression, κ , is 1.4 and the calorific value of benzene is 40,635 kJ/kg.

$$p_1 = 1 \text{ bar}$$

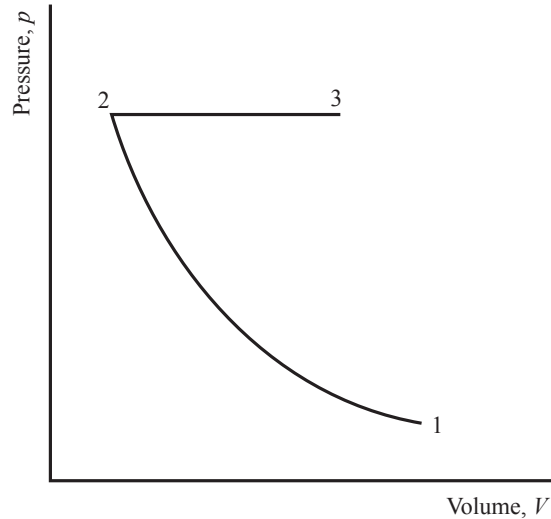
$$T_1 = 298 \text{ K}$$

$$p_2 = p_1 \left(\frac{V_1}{V_2} \right)^{1.4} = 44.31 \text{ bar}$$

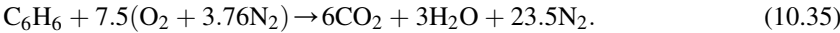
$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{0.4} = 880 \text{ K.}$$

FIGURE 10.9

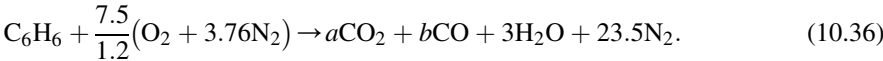
p – V diagram for constant pressure combustion.



The stoichiometric chemical equation is

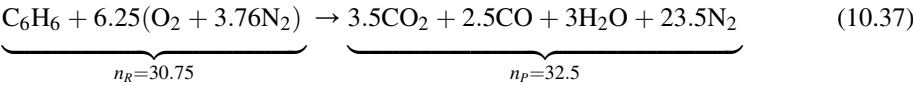


The rich mixture equation is



$$\left. \begin{array}{l} a + b = 6 \\ 2a + b + 3 = 12.5 \end{array} \right\} a = 3.5; b = 2.5$$

Hence



The energy equation, for constant pressure combustion is

$$H_P(T_P) = -(Q_p)_s + [H_R(T_R) - H_R(T_s)] + H_P(T_s). \quad (10.38)$$

Reactants energy $[H_R(T_R) - H_R(T_s)]$

Constituent	C_6H_6	O_2	N_2
h_{880}	39,936.1	27,230.9	26,342.1
h_{298}	8201.8	8509.7	8503.4
Difference	31,734.4	18,721.2	17,838.7
n	1	6.25	23.5
nh	31,734.4	117,007.5	419,209.3

$$[H_R(T_R) - H_R(T_s)] = 567951.2 \text{ kJ.}$$

Products enthalpy at standard temperature, T_s

Constituent	CO ₂	CO	H ₂ O	N ₂
h_{298}	9519.3	8489.5	9701.0	8503.4
n	3.5	2.5	3	23.5
nh	33,317.5	21,223.8	29,102.9	199,830.6

$$H_P(T_s) = 283474.8 \text{ kJ.}$$

In this case the combustion is not complete and hence the full energy available in the fuel is not released. Applying Hess's law, the energy released by a combustion process is given by

$$(Q_p)_{25} = (\Delta H_f)_P - (\Delta H_f)_R.$$

In this case

$$\begin{aligned} (Q_p)_{25} &= 3.5(\Delta h_f)_{\text{CO}_2} + 2.5(\Delta h_f)_{\text{CO}} + 3(\Delta h_f)_{\text{H}_2\text{O}} - (\Delta h_f)_{\text{C}_6\text{H}_6} \\ &= 3.5 \times -393522 + 2.5 \times -110529 + 3 \times -241827 - (82847.6) \quad (10.39) \\ &= -2461978.1 \text{ kJ.} \end{aligned}$$

This value can also be calculated from the enthalpy of reaction by subtracting the energy which is not released because of the incomplete combustion of all the carbon to carbon dioxide,

$$\begin{aligned} (Q_p)_{25} &= (Q_p)_{25,\text{total}} - 2.5\{(\Delta h_f)_{\text{CO}_2} - (\Delta h_f)_{\text{CO}}\} \\ &= -40635 \times 78 - 2.5(-393522 + 110529) \\ &= -3169530 + 707482.5 \\ &= -2462047.5 \text{ kJ.} \end{aligned}$$

These two values of enthalpy of combustion are the same within the accuracy of the data used (they differ by less than 0.003%). Hence, referring to Fig. 10.7, the *loss of energy available due to incomplete combustion* is 707,482.5 kJ/kmol C₆H₆ because not all the carbon is converted to carbon dioxide.

Thus

$$H_P(T_P) = 2462047.5 + 567888.1 + 283471.3 = 3313406.9 \text{ kJ.}$$

Assume $T_P = 2800 \text{ K.}$

Constituent	CO ₂	CO	H ₂ O	N ₂
h_{2800}	150,434.9	94,792.4	123,750.8	94,034.2
n	3.5	2.5	3	23.5
nh	526,522.2	236,981.0	371,252.5	2,209,803

$$H_P(T_P) = 3344558.7 \text{ kJ.}$$

Hence $T_P < 2800$ K.

Use $T_P = 2700$ K.

Constituent	CO ₂	CO	H ₂ O	N ₂
h_{2700}	144,256.1	91,070.2	118,376.1	90,326.0
n	3.5	2.5	3	23.5
nh	504,896.3	227,675.4	355,128.2	2,122,661

$$H_P(T_P) = 3210360.9 \text{ kJ.}$$

Interpolate linearly

$$T_P = 2700 + \frac{3313406.9 - 3210360.9}{3344558.7 - 3210360.9} \times 100 = 2776.8 \text{ K.}$$

Constituent	CO ₂	CO	H ₂ O	N ₂
h_{2777}	149,011.4	93,936.1	122,512.5	93,181.1
n	3.5	2.5	3	23.5
nh	521,540	234,840.3	367,537.5	2,189,757

$$H_P(T_P) = 3313674.8 \text{ kJ.}$$

Hence the equations balance within 0.020%.

The pressure at the end of combustion is the same as that at the end of compression i.e. $p_3 = 44.31$ bar. Hence the volume at the end of combustion, V_3 , is given by

$$V_3 = \frac{n_P \mathcal{R} T_P}{n_R \mathcal{R} T_1} \times \frac{p_1}{p_3} \times V_1 = \frac{32.5 \times 2777}{30.75 \times 298} \times \frac{1}{44.31} \times V_1 = 0.2223 V_1.$$

10.7 CONCLUDING REMARKS

A consistent method of analysing combustion has been introduced. This is suitable for use with all the phenomena encountered in combustion, including weak and rich mixtures, incomplete combustion, heat and work transfer, dissociation and rate kinetics. The method which is soundly based on the First Law of Thermodynamics ensures that energy is conserved. While the approach seems cumbersome for hand calculations it is easily implemented in computer programs.

A large number of examples of different combustion situations have been presented.

10.8 PROBLEMS

Assume that air consists of 79% N₂ and 21% O₂ by volume

- P10.1** Calculate the lower heat of reaction at constant volume for benzene C₆H₆ at 25 °C. The heats of formation at 25 °C are: benzene, (C₆H₆) 80.3 MJ/kmol; water vapour (H₂O), −242 MJ/kmol; carbon dioxide (CO₂), −394.0 MJ/kmol.
 A mixture of one part by volume of vaporised benzene to fifty parts by volume of air is ignited in a cylinder and adiabatic combustion ensues at constant volume. If the initial pressure and temperature of the mixture are 10 bar and 500 K respectively, calculate the maximum pressure and temperature after combustion neglecting dissociation. (Assume the internal energy of the fuel is 8201 kJ/kmol at 298 K and 12,998 kJ/kmol at 500 K)
 [−3170 MJ/kmol; 52.11 bar; 2580 K]
- P10.2** The heat of reaction of methane (CH₄) is determined in a constant pressure calorimeter by burning the gas as a very weak mixture. The gas flow rate is 70 L/h, and the mean gas temperature (inlet to outlet) is 25 °C. The temperature rise of the cooling water is 1.8 °C, with a water flow rate of 5 kg/min. Calculate the higher and lower heats of reaction at constant volume and constant pressure in kJ/kmol if the gas pressure at inlet is 1 bar.
 [−800,049.5 kJ/kmol; −887,952 kJ/kmol]
- P10.3** In an experiment to determine the calorific value of octane (C₈H₁₈) with a bomb calorimeter the mass of octane was 5.42195×10^{-4} kg, the water equivalent of the calorimeter including water 2.677 kg and the corrected temperature rise in the water jacket 2.333 K. Calculate the lower heat of reaction of octane, in kJ/kmol at 15 °C.
 If the initial pressure and temperature were 25 bar and 15 °C, respectively and there was 400% excess oxygen, estimate the maximum pressure and temperature reached immediately after ignition assuming no heat losses to the water jacket during this time. No air was present in the calorimeter.
 [−5,099,000 kJ/kmol; 3135 K]
- P10.4** A vessel contains a mixture of ethylene (C₂H₄) and twice as much air as that required for complete combustion. If the initial pressure and temperature are 5 bar and 440 K, calculate the adiabatic temperature rise and maximum pressure when the mixture is ignited.
 If the products of combustion are cooled until the water vapour is just about to condense, calculate the final temperature, pressure and heat loss per kmol of original mixture.
 The enthalpy of combustion of ethylene at the absolute zero is −1,325,671 kJ/kmol; and the internal energy at 440 K is 16,529 kJ/kmol.
 [1631 K; 23.53 bar; 65 °C; 3.84 bar; 47,119 kJ/kmol]
- P10.5** A gas engine is operated on a stoichiometric mixture of methane (CH₄) and air. At the end of the compression stroke the pressure and temperature are 10 bar and 500 K, respectively. If the combustion process is an adiabatic one at constant volume, calculate the maximum temperature and pressure reached.
 [59.22 bar; 2960 K]

P10.6 A gas injection system supplies a mixture of propane (C_3H_8) and air to a spark-ignition engine, in the ratio of volumes of 1:30. The mixture is trapped at 1 bar and 300 K, the volumetric compression ratio is 12:1, and the index of compression, $\kappa = 1.4$. Calculate the equivalence ratio, the maximum pressure and temperature achieved during the cycle, and also the composition (by volume) of the dry exhaust gas.
[0.79334, 119.1 bar, 2883 K; 0.8463, 0.1071, 0.0465]

P10.7 A turbocharged, intercooled compression ignition engine is operated on octane (C_8H_{18}) and achieves constant pressure combustion. The volumetric compression ratio of the engine is 20:1, and the pressure and temperature at the start of compression are 1.5 bar and 350 K, respectively. If the air-fuel ratio is 24:1 calculate maximum temperature and pressure achieved in the cycle, and the indicated mean effective pressure (imep, $\bar{p}_i$) of the cycle in bar. Assume that the index of compression, $\kappa_c = 1.4$, while that of expansion, $\kappa_e = 1.35$.
[2495 K; 99.4 bar; 20.57 bar]

P10.8 One method of reducing the maximum temperature in an engine is to run with a rich mixture. A spark-ignition engine with a compression ratio of 10:1, operating on the Otto cycle, runs on a rich mixture of octane (C_8H_{18}) and air, with an equivalence ratio of 1.2. The trapped conditions are 1 bar and 300 K, and the index of compression is 1.4. Calculate how much lower the maximum temperature is under this condition than when the engine was operated stoichiometrically. What are the major disadvantages of operating in this mode?
[208 °C]

P10.9 A gas engine with a volumetric compression ratio of 10:1 is run on a weak mixture of methane (CH_4) and air, with an equivalence ratio, $\phi = 0.9$. If the initial temperature and pressure at the commencement of compression are 60 °C and 1 bar respectively, calculate the maximum temperature and pressure reached during combustion at constant volume if compression is isentropic, and 10% of the heat released during the combustion period is lost by heat transfer.

Assume the ratio of specific heats, κ , during the compression stroke is 1.4, and the heat of reaction at constant volume for methane at 25 °C is -8.023×10^5 kJ/kmol CH_4
[2817 K; 84.59 bar].

P10.10 A jet engine burns a weak mixture ($\phi = 0.32$) of octane (C_8H_{18}) and air. The air enters the combustion chamber from the compressor at 10 bar and 500 K; assess if the temperature of the exhaust gas entering the turbine is below the limit of 1300 K. Assume that the combustion process is adiabatic and that dissociation can be neglected. The enthalpy of reaction of octane at 25 °C is $-44,880$ kJ/kg, and the enthalpy of the fuel in the reactants may be assumed to be negligible.

[Maximum temperature, $T_p = 1298$ K; value is very close to limit]

P10.11 A gas engine is run on a chemically correct mixture of methane (CH_4) and air. The compression ratio of the engine is 10:1, and the trapped temperature and pressure at inlet valve closure are 60 °C and 1 bar, respectively. Calculate the maximum temperature and pressure achieved during the cycle if:

- combustion occurs at constant volume;
- 10% of the energy added by the fuel is lost through heat transfer;
- the compression process is isentropic.

It can be assumed that the ratio of specific heats, $\kappa = 1.4$, and that the internal energy of methane in the reactants is negligible.

[2956 K; 88.77 bar]

CHEMISTRY OF COMBUSTION

11

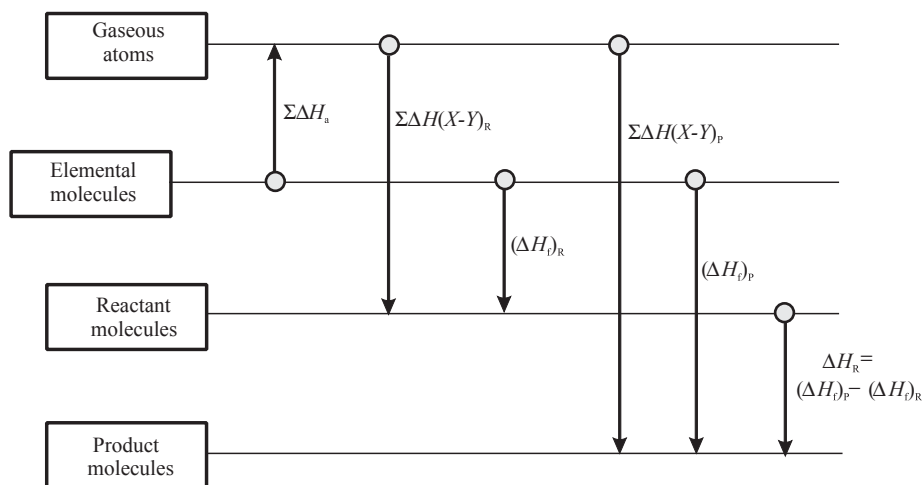
The thermodynamics of combustion were considered in Chapter 10, and it was stated that adiabatic combustion could be achieved. The concept of adiabatic combustion runs counter to the experience of many engineers, who tend to relate combustion to heat addition or heat release processes. This approach is encouraged in mechanical engineering by the application of the air standard cycle to engines to enable them to be treated as heat engines. In reality combustion is not a process of energy transfer but one of energy transformation. The energy released by combustion in a spark ignition (petrol) engine is all contained in the mixture prior to combustion, and it is released by the spark. It will be shown that the energy which causes the temperature rise in a combustion process is obtained by breaking the bonds which hold the fuel atoms together.

11.1 BOND ENERGIES AND HEAT OF FORMATION

Heats (enthalpies and internal energies) of formation can be evaluated empirically by ‘burning’ the fuel. They can also be evaluated by consideration of the chemical structure of the compound. Each compound consists of a number of elements held together by certain types of bond. The bond energy is the amount of energy required to separate a molecule into atoms; the energy of a particular type of bond is *similar* irrespective of the actual structure of the molecule.

This concept was introduced in Chapter 10, and heats of formation were used to evaluate heats of reaction (Hess’ Law). The process of breaking the chemical bonds during the combustion process can be depicted by a diagram such as Fig. 11.1. It is assumed that element molecules can be atomised (in a constant pressure process) by the addition of energy equal to ΔH_a . If these atoms are then brought together they would combine, releasing dissociation energy of $\sum \Delta H(X - Y)_R$ to form the reactants. The sum of the dissociation and atomisation energies (taking account of the signs) results in the enthalpy of formation of the reactants. In a similar way, the enthalpy of formation of the products can be evaluated. Using Hess’ Law, the enthalpy of reaction of the fuel can be evaluated as the difference between the enthalpies of formation of the products and the reactants. These energies are essentially the *bond energies* of the various molecules and some of these energies are listed in Table 11.1.

Figure 11.2 shows how the energy required to separate two atoms varies with distance: the bond energy is defined as the minimum potential energy relative to that at infinity. The point of minimum energy indicates that the molecule is in equilibrium.

**FIGURE 11.1**

Relationship between enthalpies of formation and reaction.

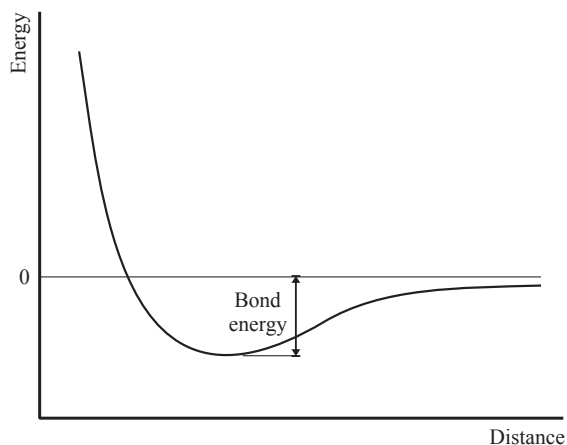
In addition to the energy associated with particular bonds there are also energies caused by the possibility of resonance or strain in a particular molecule. For example, the ring structure of benzene, which is normally considered to be three simple double bonds between carbon atoms, together with three single ones, plus six carbon/hydrogen bonds, can reform to give bonding across the cyclic structure (see Fig. 11.3).

This results in a substantially higher energy than would be estimated from the simple bond structure, and some typical values are shown in Table 11.2.

Table 11.1 Some Atomisation, Dissociation and Resonance Energies (Based on 25 °C)

Bond Atomisation (ΔH_a)	Energy MJ/kmol	Bond Dissociation ($\Delta H(X-Y)$)	Energy MJ/kmol	Resonance	Energy MJ/kmol
H–H	435.4	C–H	414.5	Benzene: C ₆ H ₆	150.4
C (graphite)	717.2	N–H	359.5	Naphthalene: C ₁₀ H ₈	255.4
(O = O) _{O₂}	498.2	O–H	428.7	Carbon dioxide: CO ₂	137.9
N≡N	946.2	H–OH	497.5	–COOH group	117.0
		C–O	351.7		
		C=O	698.1		
		C–C	347.5		
		C=C	615.5		
		C≡C	812.2		

Note: These values have been taken from different sources and may not be exactly compatible.

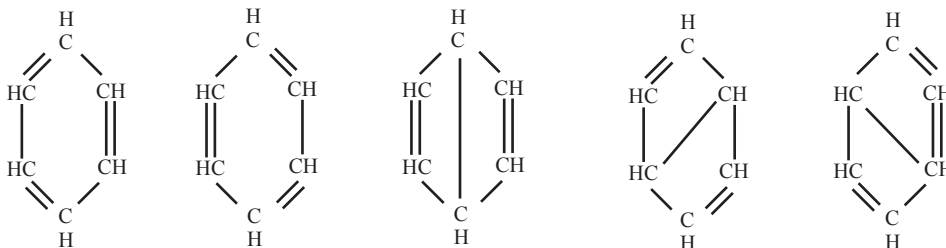
**FIGURE 11.2**

Variation of bond energy with distance between atoms.

11.2 ENERGY OF FORMATION

It will be considered in this section that the processes take place at constant pressure and the property enthalpy (h or H) will be used; if the processes were constant volume ones then internal energies (u or U) would be the appropriate properties.

A hydrocarbon fuel consists of carbon and hydrogen (and possibly another element) atoms that are held together by chemical bonds. These atoms can be considered to have been brought together by heating carbon and hydrogen (in molecular form) under conditions that encourage the resulting atoms to bond. There are two processes involved in this: first, the carbon has to be changed from solid graphite into gaseous carbon atoms and the hydrogen also has to be atomised; then, second, the atoms must be cooled to form the hydrocarbon fuel. These two processes have two energies associated with them: the first is atomisation energy (ΔH_a) and the second is dissociation energy ($\Sigma \Delta H(X - Y)_R$) required to dissociate the chemical bond in the compound C_xH_y . Figure 11.1 shows these terms, and

**FIGURE 11.3**

Bonding arrangements of benzene, showing bond resonance through delocalised electrons.

Table 11.2 Enthalpies of Formation and Reaction for Commonly Encountered Fuels and Compounds
(From Goodger (1979))

Fuel	Chemical Formula	Molecular Weight (m_w) (integrals)	Enthalpy of Formation, Δh_f (kJ/kmol)	Higher Enthalpy of Reaction, Δh_R (MJ/kmol)	Lower Enthalpy of Reaction, Δh_R		Stoichiometric Air–Fuel Ratio, ϵ_{st}
					(kJ/kg)	(MJ/kmol)	
Alkanes	C_nH_{2n+2}						
Methane	CH ₄	16	−74,898	−891	−50,047	−802.9	17.16
Ethane	C ₂ H ₆	30	−84,724	−1561	−47,519	−1428.8	16.02
Propane	C ₃ H ₈	44	−103,916	−2221	−46,387	−2045.4	15.60
Butane	C ₄ H ₁₀	58	−124,817	−2880	−45,771	−2660.2	15.38
Pentane	C ₅ H ₁₂	72	−146,538	−3538	−45,384	−3274.3	15.25
Hexane	C ₆ H ₁₄	86	−167,305	−4197	−45,134	−3889.3	15.16
Heptane	C ₇ H ₁₆	100	−187,946	−4856	−44,955	−4504.4	15.10
Octane	C ₈ H ₁₈	114	−208,586	−5515	−44,820	−5119.5	15.05
Cetane	C ₁₆ H ₃₄	226	—	−10,711	−44,000	−9963.4	14.88
Acetylenes	C_nH_{2n-2}						
Acetylene	C ₂ H ₂	26	+226,900	−1270	−48,258	−1226.4	13.20
Propyne	C ₃ H ₄	40	+185,555	−1939	−46,200	−1850.9	13.73
Aromatics							
Benzene	C ₆ H ₆	78	+82,982	−3304	−40,605	−3172	13.20
Toluene	C ₇ H ₈	92	+50,032	−3950	−40,967	−3774	13.43
Xylene	C ₈ H ₁₀	106	+18,059	−4598	−41,276	−4378	13.60
Naphthalene	C ₁₀ H ₈	128	+150,934	−5233	−39,455	−5057	12.87
Alcohols	$C_nH_{2n+1}OH$	$C_nH_{2n+2}O$					
Methanol	CH ₃ OH	32	−201,301	−764	−21,114	−676	6.44
Ethanol	C ₂ H ₅ OH	46	−235,466	−1410	−27,742	−1278	8.85
Propanol	C ₃ H ₇ OH	60	−235,107	−2069	−31,504	−1893	10.30
Mixtures							
Gasoline (petrol)	C _n H _{1.87n}	≈ 110	—	−5203	−44,000	−4840	14.6
Light diesel	C _n H _{1.8n}	≈ 170	—	−7616	−42,500	−7225	14.5
Heavy diesel	C _n H _{1.7n}	≈ 200	—	−8760	−41,400	−8280	14.4
Natural gas	C _n H _{3.8n} N _{0.1n}	≈ 18	—	−900	−45,000	−810	14.5

also indicates that the energy of formation of the fuel (ΔH_f) is the net energy required for the process, i.e.

$$\Delta H_f = \sum \Delta H_a - \sum \Delta H(X - Y)_R \quad (11.1)$$

In reality the enthalpy of formation is more complex than given above because energy can be stored in molecules in a number of ways, including resonance energies (in the benzene ring structure) and changes of phase (latent heats). A more general representation of the *enthalpy of formation* is

$$\Delta H_f = \sum \Delta H_a - \sum \Delta H(X - Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \quad (11.2)$$

Example

Evaluate the enthalpy of formation of CO_2 and H_2O from the atomisation and dissociation energies listed in Table 11.1.

Solution

Carbon dioxide (CO_2)

Carbon dioxide is formed from carbon and oxygen in the reaction.



where the (g) indicates that the element or compound is in the gaseous (vapour) phase, and (l) will be used to indicate that the element or compound is in the liquid phase.

The reaction in Eqn (11.3) is achieved by atomisation of the individual carbon (graphite) molecules and the oxygen molecules, with subsequent recombination to form carbon dioxide. Effectively the reactant molecules, which are in a metastable state, are activated above a certain energy to produce atoms which will then combine to form the stable CO_2 molecule (see Fig. 11.4).

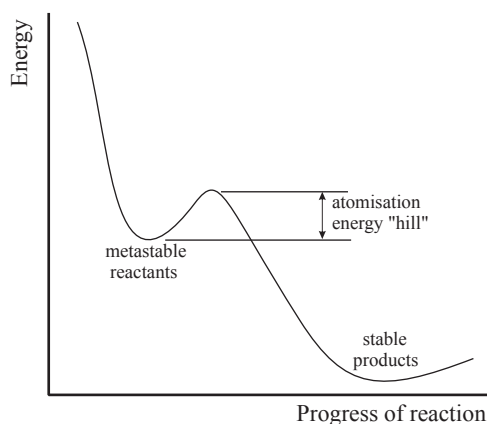


FIGURE 11.4

Gibbs energy variation during a reaction.

Hence, from Fig. 11.1,

$$(\Delta H_f)_{\text{CO}_2} = \sum \Delta H_a - \sum \Delta H(X - Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \quad (11.4)$$

In this case there is a resonance energy but the latent energy (i.e. latent heat) is zero. Then

$$\begin{aligned} (\Delta H_f)_{\text{CO}_2} &= \Delta H_a [\text{C}_{\text{graphite}}] + \Delta H_a [\text{O} = \text{O}] - 2(\text{C} = \text{O}) - \Delta H_{\text{res}} [\text{CO}_2] \\ &= 717.2 + 435.4 - 2 \times 698.1 - 137.9 \\ &= -381.5 \text{ MJ/kmol} \end{aligned} \quad (11.5)$$

The tabulated value is -393.4 MJ/kmol .

Water (H₂O)

This is formed from the hydrogen and oxygen molecules in the reaction



Thus

$$(\Delta H_f)_{\text{H}_2\text{O}} = \sum \Delta H_a - \sum \Delta H(X - Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \quad (11.7)$$

In this case $\Delta H_{\text{res}} = 0$ but ΔH_{latent} depends upon the phase of the water. First, consider the water is in vapour phase, when $\Delta H_{\text{latent}} = 0$. Then

$$\begin{aligned} (\Delta H_f)_{\text{H}_2\text{O}} &= \sum \Delta H_a - \sum \Delta H(X - Y) \\ &= \Delta H_a [\text{H} - \text{H}] + \frac{1}{2} \Delta H_a [\text{O} = \text{O}] - [\text{H} - \text{OH}] - [\text{O} - \text{H}] \\ &= 435.4 + \frac{1}{2} (498.2) - 497.5 - 428.7 \\ &= -241.7 \text{ MJ/kmol} \end{aligned} \quad (11.8)$$

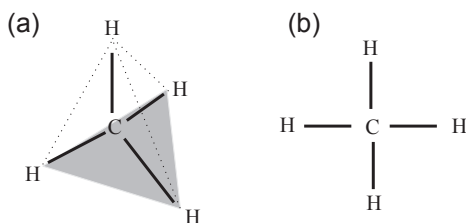
This compares well with the tabulated values of -241.6 MJ/kmol .

If the water was in liquid phase then Eqn (11.6) becomes



$$\begin{aligned} (\Delta H_f)_{\text{H}_2\text{O}(\text{l})} &= (\Delta H_f)_{\text{H}_2\text{O}(\text{g})} + (m_w)_{\text{H}_2\text{O}} h_{\text{fg}} \\ &= -241.7 - 18 \times 2441.8/1000 \\ &= -285.65 \text{ MJ/kmol} \end{aligned} \quad (11.10)$$

The tabulated value is -285.6 MJ/kmol .

**FIGURE 11.5**

Atomic arrangement of methane molecule.

Example

Evaluate the enthalpy of formation of methane, CH_4 .

Solution

The structure of methane is tetrahedral, and of the form shown in Fig. 11.5a. Methane is often depicted in planar form as shown in Fig. 11.5b.

Methane can be formed by the following reaction



Hence

$$\begin{aligned} (\Delta H_f)_{\text{CH}_4} &= \sum \Delta H_a - \sum \Delta H(X-Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \\ &= \Delta H_a [\text{C}_{\text{graphite}}] + 2\Delta H_a [\text{H}-\text{H}] - 4[\text{H}-\text{C}] \\ &= 717.2 + 2 \times 425.4 - 4 \times 414.5 \\ &= -70 \text{ MJ/kmol} \end{aligned} \quad (11.12)$$

The tabulated value is -74.78 MJ/kmol , and the difference occurs because the energy of the bonds in methane is affected by the structure of the methane molecule which results in attraction forces between molecules.

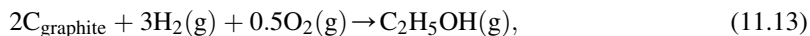
Example

Evaluate the enthalpy of formation of ethanol, $\text{C}_2\text{H}_5\text{OH}$.

Solution

The planar representation of the structure of ethanol is shown in Fig. 11.6.

Ethanol can be considered to be made up of the following processes



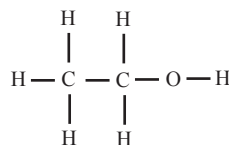


FIGURE 11.6

Structure of ethanol molecule.

giving the enthalpy of formation of ethanol as

$$(\Delta H_f)_{\text{C}_2\text{H}_5\text{OH}} = \sum \Delta H_a - \sum \Delta H(X-Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \quad (11.14)$$

This gives the following equation

$$\begin{aligned}
 & 2\text{C}_{\text{graphite}} + 3\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \\
 & \rightarrow 2\text{C}(\text{g}) - \underbrace{2 \times 717.2}_{\text{atomisation energy for C}} + 6\text{H} - \underbrace{3 \times 435.4}_{\text{atomisation energy for H}} + \text{O} + 0.5 \times 498.2 - \underbrace{5}_{\text{atomisation energy for O}} [\text{C}-\text{H}] - [\text{C}-\text{C}] - [\text{C}-\text{O}] - [\text{O}-\text{H}] \\
 & \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) + 2 \times 717.2 + 3 \times 435.4 + 0.5 \times 498.2 - 5 \times 414.5 - 347.5 - 351.7 - 428.7 \\
 & \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) - 210.7 \text{ MJ/kmol}
 \end{aligned} \quad (11.15)$$

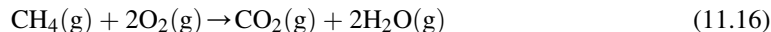
Hence the enthalpy of formation of gaseous ethanol is -210.7 MJ/kmol . This is equivalent to -5.853 MJ/kg of ethanol. The value obtained from tables is about -222.8 MJ/kmol , and the difference is attributable to the slight variations in bond energy that occur due to the three-dimensional nature of the chemical structure.

Example

Evaluate the *enthalpy of reaction* of methane, CH_4 .

Solution

This can be obtained either by using atomisation and dissociation energies, in a similar manner to that used to find the enthalpies of formation of compounds, or from the enthalpies of formation of the compounds in the reactants and products. Both methods will be used in this case. The reaction describing the combustion of methane is



The chemical structure of methane was given above. Hence the enthalpy of formation of the reactants is

$$\begin{aligned}
 (\Delta H_f)_R &= \sum \Delta H_a - \sum \Delta H(X-Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \\
 &= \Delta H_a [\text{C}_{\text{graphite}}] + 2\Delta H_a [\text{H}-\text{H}] + 2\Delta H_a [\text{O}=\text{O}] - 4[\text{H}-\text{C}] - 2[\text{O}=\text{O}]
 \end{aligned} \quad (11.17)$$

Note that the atomisation and dissociation energies of oxygen are equal ($2\Delta H_a[\text{O}=\text{O}]=2[\text{O}=\text{O}]$) and cancel out, i.e. the enthalpy of formation of oxygen is zero. This value of zero is assumed as a base level for all elements.

Thus

$$(\Delta H_f)_R = (\Delta H_f)_{\text{CH}_4} = -70 \text{ MJ/kmol} \quad (11.18)$$

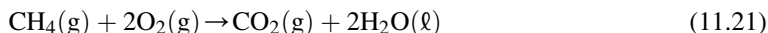
Similarly the enthalpy of formation of the products

$$\begin{aligned} (\Delta H_f)_P &= \sum \Delta H_a - \sum \Delta H(X-Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \\ &= \Delta H_a[\text{C}_{\text{graphite}}] + \Delta H_a[\text{O}=\text{O}] + 2\Delta H_a[\text{H}-\text{H}] + \Delta H_a[\text{O}=\text{O}] - 2[\text{C}=\text{O}] \\ &\quad - 2[\text{H}-\text{OH}] - 2[\text{O}-\text{H}] - \Delta H_{\text{res}}[\text{CO}_2] \\ &= (\Delta H_f)_{\text{CO}_2} + 2(\Delta H_f)_{\text{H}_2\text{O}} \\ &= -381.5 - 2 \times 241.7 \text{ MJ/kmol} \end{aligned} \quad (11.19)$$

The heat of reaction is given by

$$\begin{aligned} \Delta H_R &= (\Delta H_f)_P - (\Delta H_f)_R \\ &= -381.5 - 2 \times 241.7 - (-70) \\ &= -794.9 \text{ MJ/kmol} \end{aligned} \quad (11.20)$$

This is close to the value of -802.3 MJ/kmol quoted as the *lower* enthalpy of reaction of methane. If the higher heat of reaction of methane is required then Eqn (11.14) becomes

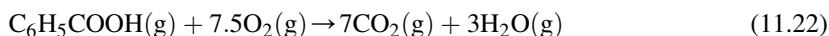


Example

Evaluate the lower enthalpy of reaction of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$). The planar diagram of its structure is shown in Fig. 11.7.

Solution

The reaction of benzoic acid with oxygen is

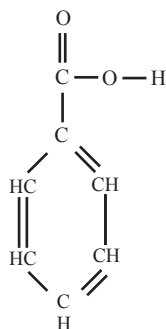


The easiest way to evaluate the enthalpy of reaction is from Eqn (11.20)

$$\Delta H_R = (\Delta H_f)_P - (\Delta H_f)_R \quad (11.23)$$

The values of H_f were calculated above for CO_2 and H_2O , and hence the only unknown quantity in Eqn (11.20) is the enthalpy of formation of the benzoic acid, which is

$$(\Delta H_f)_{\text{C}_6\text{H}_5\text{COOH}} = \sum \Delta H_a - \sum \Delta H(X-Y) - \sum \Delta H_{\text{res}} - \sum \Delta H_{\text{latent}} \quad (11.24)$$

**FIGURE 11.7**

Structure of benzoic acid molecule.

The acid is in gaseous form before the reaction, see Eqn (11.22), and thus $\Delta H_{\text{latent}} = 0$. Substituting values into Eqn (11.24) gives

$$\begin{aligned}
 (\Delta H_f)_{\text{C}_6\text{H}_5\text{COOH}} &= \sum \Delta H_a - \sum \Delta H(X-Y) - \sum \Delta H_{\text{res}} \\
 &= 7\Delta H_a[\text{C}_{\text{graphite}}] + 3\Delta H_a[\text{H}-\text{H}] + \Delta H_a[\text{O}=\text{O}] - 5[\text{H}-\text{C}] - 4[\text{C}-\text{C}] \\
 &\quad - 3[\text{C}=\text{C}] - [\text{C}=\text{O}] - [\text{C}-\text{O}] - [\text{O}-\text{H}] - [\Delta H_{\text{res}}]_{\text{C}_6\text{H}_6} - [\Delta H_{\text{res}}]_{\text{COOH}}
 \end{aligned} \tag{11.25}$$

Hence,

$$\begin{aligned}
 (\Delta H_f)_{\text{C}_6\text{H}_5\text{COOH}} &= 7 \times 717.2 + 3 \times 435.4 + 498.2 - 5 \times 414.5 - 4 \times 347.5 - 3 \times 615.5 - 698.1 \\
 &\quad - 351.7 - 428.7 - 150.4 - 117.0 \\
 &= -230.1 \text{ MJ/kmol}
 \end{aligned} \tag{11.26}$$

The enthalpy of formation of the products is

$$\begin{aligned}
 (\Delta H_f)_p &= 7(\Delta H_f)_{\text{CO}_2} + 3(\Delta H_f)_{\text{H}_2\text{O}} \\
 &= 7 \times (-381.5) + 3 \times (-241.7) \\
 &= -3395.5 \text{ MJ/kmol}
 \end{aligned} \tag{11.27}$$

Thus the enthalpy of reaction of benzoic acid is

$$(\Delta H_R)_{\text{C}_6\text{H}_5\text{COOH}} = -3395.6 - (-230.1) = -3165.5 \text{ MJ/kmol} \tag{11.28}$$

The tabulated value is -3223.2 MJ/kmol giving an inaccuracy of about 2%.

11.3 ENTHALPY OF REACTION

The enthalpies of reaction of some commonly encountered fuels are given in Table 11.2. These have been taken from a number of sources and converted to units consistent with this text where necessary. There are a number of interesting observations that can be made from this table, viz.

- the enthalpies of reaction of many of the hydrocarbon fuels on a basis of mass are very similar, and around 44,000 kJ/kg;
- the stoichiometric air–fuel ratios of many basic hydrocarbon fuels lie in the range 13:1 to 17:1;
- some of the fuels have positive enthalpies of formation;
- all of the fuels have negative enthalpies of reaction;
- the enthalpies of reaction of the alcohols are less than those of the non-oxygenated fuels, simply because the oxygen cannot provide any energy of reaction;
- the commonly used hydrocarbon fuels are usually mixtures of hydrocarbon compounds.

11.4 CONCLUDING REMARKS

It has been shown that the energy released by a fuel is contained in it by virtue of its structure, i.e. the bonds between the atoms. It is possible to assess the enthalpies of formation or reaction of a wide range of fuels by considering the chemical structure of the bonds in the compound.

A table of enthalpies of formation and reaction for common fuels has been given ([Table 11.2](#)).

CHEMICAL EQUILIBRIUM
AND DISSOCIATION

12

Up to now, this book has concentrated on combustion problems which can be solved by methods based on equilibrium but which do not require an explicit statement of the fact, e.g. complete combustion of a hydrocarbon fuel in air can be analysed by assuming that the products consist only of H_2O and CO_2 . These methods are not completely correct and a more rigorous analysis is necessary to obtain greater accuracy.

Consider the combustion of carbon monoxide (CO) with oxygen (O_2); up till now the reaction has been described by the equation



It is implied in this equation that carbon monoxide combines with oxygen to form carbon dioxide, and as soon as that has happened, the reaction ceases. This is not a true description of what happens in practice. The real process is one of dynamic equilibrium with some of the carbon dioxide breaking down into carbon monoxide and oxygen (or even more esoteric components) again, which might then recombine to form carbon dioxide. The breakdown of the CO_2 molecule is known as *dissociation*. To evaluate the amount of dissociation that occurs (the *degree of dissociation*), it is necessary to evolve new techniques.

It will be seen that the calculation of combustion with a number of degrees of freedom is quite tedious, but easily formalised into an iterative technique; this is ideal for developing into a computer program. EQUIL2 is a program that does this, and it incorporates the enthalpy coefficients used in this text; the program is available on <http://booksite.elsevier.com/9780444633736>.

12.1 GIBBS ENERGY

The concept of Gibbs energy, G , was introduced in Chapter 2. The change in the specific Gibbs energy, g , for a system of fixed composition was defined in terms of other properties as

$$dg = vdp - sdT. \quad (12.2)$$

It was also shown that for a closed system at constant temperature and pressure, performing only mechanical work, to be in equilibrium

$$dG)_{p,T} = 0 \quad (12.3)$$

Equations (12.2) and (12.3) are based on the assumption that $G = mg = mg(p, T)$, and this is quite acceptable for a single component system, or one of fixed composition. If the system has more than one component and these components can react to form other compounds, e.g. if the system contained carbon monoxide, oxygen and carbon dioxide as defined in Eqn (12.1), then it is necessary to define the Gibbs energy as $G = mg = mg(p, T, m_i)$ where m_i is the mass of component i and $m = \sum m_i$. The significance of changes of composition on the value of the Gibbs energy of a mixture will now be investigated.

If

$$G = mg = mg(p, T, m_i), \quad (12.4)$$

and if it is assumed that G is a continuous function with respect to p and T and the masses of constituents comprising the mixture, then the change of G with changes in the independent variables is

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,m} dp + \left(\frac{\partial G}{\partial T}\right)_{p,m} dT + \left(\frac{\partial G}{\partial m_1}\right)_{p,T,m_{i \neq 1}} dm_1 + \dots + \left(\frac{\partial G}{\partial m_n}\right)_{p,T,m_{i \neq n}} dm_n \quad (12.5a)$$

where $dm_1 \dots dm_n$ are changes in mass of the various constituents. A similar equation can be written in terms of amount of substance, and is

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_{i \neq 1}} dn_1 + \dots + \left(\frac{\partial G}{\partial n_n}\right)_{p,T,n_{i \neq n}} dn_n \quad (12.5b)$$

For the initial part of the development of these equations, the mass-based relationship will be used. The term $(\partial G / \partial m_1)_{p,T,m_{i \neq 1}} dm_1$ represents the ‘quantity’ of Gibbs energy introduced by the transfer of mass dm_1 of constituent 1 to the system. (This can be more readily understood by considering the change in internal energy, dU , when the term $(\partial U / \partial m_1)_{p,T,m_{i \neq 1}} dm_1$ has a more readily appreciated significance.)

The significance of the terms on the right of Eqn (12.5a) is:

1. The first term denotes the change of Gibbs energy due to a change in pressure; the temperature, total mass and composition of the system remaining constant. This is equivalent to the term derived when considering a system of constant composition and is Vdp .
2. The second term denotes the change of Gibbs energy due to a change in temperature, the pressure and total mass of the system remaining constant. This is equivalent to $-SdT$ derived previously.
3. The third term shows the change of Gibbs energy due to a change in the mass (or amount of substance if written in terms of n) of constituent m_1 , the pressure, temperature and masses of other constituents remaining constant. It is convenient to define this as

$$\mu_1 = \left(\frac{\partial G}{\partial m_1}\right) \quad (12.6)$$

4. The fourth term is a general term of the form of term (3) in Eqn (12.6).

Hence, in terms of masses

$$dG = Vdp - SdT + \sum_{i=1}^n \mu_i dm_i \quad (12.7a)$$

while in terms of amount of substance

$$dG = Vdp - SdT + \sum_{i=1}^n \mu_{m_i} dn_i \quad (12.7b)$$

12.2 CHEMICAL POTENTIAL, μ

The term μ is called the chemical potential and is defined as $\left(\frac{\partial G}{\partial m_i}\right)_{p,T,m_j \neq i}$. The significance of μ will now be examined. First, it can be considered in terms of the other derived properties.

By definition

$$dG = d(H - TS) = dH - TdS - SdT \quad (12.8)$$

Hence

$$\begin{aligned} dH &= dG + TdS + SdT \\ &= Vdp - SdT + \sum \mu_i dm_i + TdS + SdT \\ &= Vdp + TdS + \sum \mu_i dm_i \end{aligned} \quad (12.9)$$

Considering each of the terms in Eqn (12.9), then these can be interpreted as the capacity to do work brought about by a change in a particular property. The first term is the increase in capacity to do work that is achieved by an isentropic pressure rise (cf. the work done in a feed pump of a Rankine cycle) and the second term is the increased capacity to do work that occurs as a result of reversible heat transfer. The third term is also an increase in the capacity of the system to do work, but this time it is brought about by the addition of a particular component to a mixture. For example, if oxygen is added to a mixture of carbon monoxide, carbon dioxide, water and nitrogen (the products of combustion of a hydrocarbon fuel), then the mixture could further react to convert more of the carbon monoxide to carbon dioxide, and more work output could be obtained. Thus μ_i is the increase in the capacity of a system to do work when unit mass (or, in the case of μ_{m_i} , unit amount of substance) of component i is added to the system. μ_i can be considered to be a ‘chemical pressure’ because it is the driving force in bringing about reactions.

Assuming that H is a continuous function,

$$dH = \left(\frac{\partial H}{\partial p}\right)_{S,m} dp + \left(\frac{\partial H}{\partial S}\right)_{p,m} dS + \left(\frac{\partial H}{\partial m_1}\right)_{S,p,m_i \neq 1} dm_1 + \dots + \left(\frac{\partial H}{\partial m_n}\right)_{S,p,m_i \neq n} dm_n \quad (12.10)$$

By comparison of Eqns (12.9) and (12.10),

$$\mu_i = \left(\frac{\partial H}{\partial m_i}\right)_{S,p,m_j \neq i} \quad (12.11)$$

Similarly it can be shown that

$$\begin{aligned}\mu_i &= \left(\frac{\partial U}{\partial m_i} \right)_{s,v,m_j \neq i} \\ \mu_i &= \left(\frac{\partial F}{\partial m_i} \right)_{T,v,m_j \neq i}\end{aligned}\quad (12.12)$$

The following characteristics of chemical potential may be noted:

1. The chemical potential, μ , is a function of properties and hence is itself a thermodynamic property.
2. The numerical value of μ is not dependent on the property from which it is derived. (All the properties have the dimensions of energy and, hence, by the conservation of energy this is reasonable.)
3. The numerical value of μ is independent of the size of the system and is hence an *intensive* property.

For example,

$$\left(\frac{\partial U}{\partial m_i} \right)_{s,v,m_j \neq i} = \mu_i = \left(\frac{\partial(mu)}{\partial(mx_i)} \right)_{s,v,m_j \neq i} = \left(\frac{\partial u}{\partial x_i} \right)_{s,v,m_j \neq i} \quad (12.13)$$

Since μ is an intensive property, it may be compared with the other intensive properties p , T etc. By the two-property rule, this means that

$$p = p(\mu, T) \quad (12.14)$$

and similarly

$$\mu = \mu(p, T). \quad (12.15)$$

It can be shown that the chemical potential, μ , for a pure phase is equal in magnitude to the specific Gibbs energy at any given temperature and pressure
i.e.

$$\mu = g. \quad (12.16)$$

(Note: Although $\mu = g$ it is different from g inasmuch as it is an intensive property whereas g is a specific property. Suppose there is a system of mass m , then the total Gibbs energy is $G = mg$ whereas the chemical potential of the whole system is still μ (cf. p or T).)

12.3 STOICHIOMETRY

Consider the reaction



Equation (12.17) shows the stoichiometric proportions of the reactants and products. It shows that 1 mol CO and 1/2 mol O₂ could combine to form 1 mol CO₂. If the reaction proceeded to completion, no CO or O₂ would be left at the final condition.

This is the *stoichiometric* equation of the reaction and the amounts of substance in the equation give the *stoichiometric coefficients*.

The general equation for a chemical reaction is



where v is a stoichiometric coefficient and A , B , C and D are the substances involved in the reaction.

Applying Eqn (12.18) to the $\text{CO} + \frac{1}{2}\text{O}_2$ reaction gives

$$\begin{aligned} v_{\text{CO}} &= -1 \\ v_{\text{O}_2} &= -1/2 \\ v_{\text{CO}_2} &= 1. \end{aligned} \quad (12.19)$$

It is conventional in chemistry to assign negative values to the stoichiometric coefficients on the left-hand side of the equation (nominally, the reactants) and positive signs to those on the right-hand side (nominally, the products).

12.3.1 MIXTURES

Mixtures are not necessarily stoichiometric and the following terms were introduced in Chapter 10 to describe the proportions of a mixture.

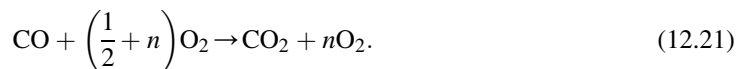
1. If the reactants occur in proportion to the stoichiometric coefficients then the mixture is said to be *chemically correct* or *stoichiometric*.
2. If the reactants have a greater proportion of fuel than the correct mixture then it is said to be *rich*.
3. If the reactants have a lesser proportion of fuel than the correct mixture then it is said to be *weak*.

For example, the chemically correct mixture is $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$

Rich mixture (excess of fuel)



Weak mixture (excess of oxidant)



N.B. Equations (12.20) and (12.21) have been written neglecting dissociation.

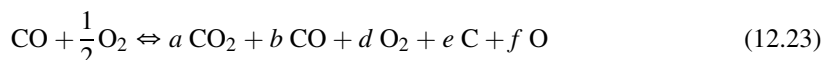
12.4 DISSOCIATION

The basis of dissociation is the atomic model that all mixtures of gases are in a state of dynamic equilibrium. Molecules of the compounds are being created whilst existing ones are breaking down into simpler compounds or elements (dissociating). In the equilibrium situation the rates of creation

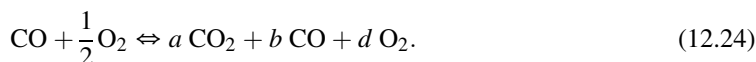
and destruction of molecules of any compounds are equal. This means that macroscopic measuring techniques do not sense the changes but give the impression that the system is in a state of ‘static’ equilibrium. The effect of this is that the reactions can no longer be said to be unidirectional but must be shown as



On a molecular basis the above reaction can go either way. It is now necessary to consider a technique which will define the *net* direction of change for a collection of molecules. First, consider the general equation for the $\text{CO} + \frac{1}{2} \text{O}_2$ reaction, neglecting particularly esoteric and rare compounds.



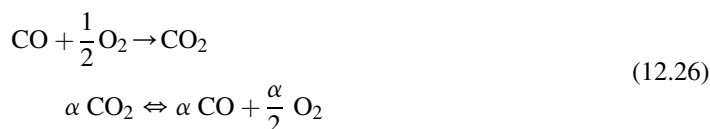
where, the carbon (C) and atomic oxygen (O) are formed by the breakdown of the reactants. Experience shows that in the ranges normally encountered in practice, the C and O atoms have a negligible effect. This allows the general reaction to be simplified to



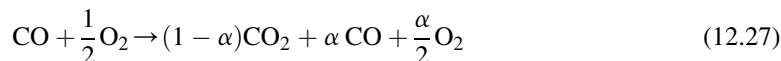
It is possible to write this equation in a slightly different form by considering the amount of CO_2 which has dissociated. This can be defined as $\alpha = (1-a)$, and the equation for the dissociation of CO_2 is



By considering the stoichiometric equation (Eqn (12.22)) and the dissociation equation (Eqn (12.25)), a general equation may be constructed in terms of α :



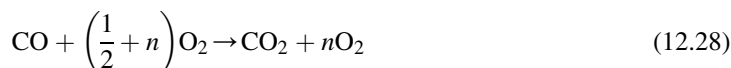
Adding Eqn (12.26) gives



In Eqn (12.27), α is known as the *degree of dissociation*. This equation shows the effect of dissociation on a chemically correct mixture. Before discussing methods of evaluating α , the effect of dissociation on nonstoichiometric mixtures will be shown, first using the carbon monoxide reaction and then a general hydrocarbon fuel.

12.4.1 WEAK MIXTURE WITH DISSOCIATION

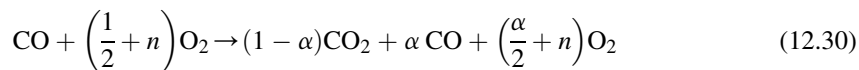
Equation without dissociation



Dissociation of CO₂



Adding Eqns (12.28) and (12.29) gives

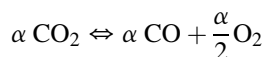


12.4.2 RICH MIXTURE WITH DISSOCIATION

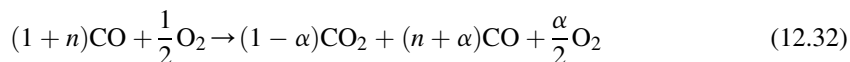
Equation without dissociation



Dissociation of CO₂ (Eqn (12.29))

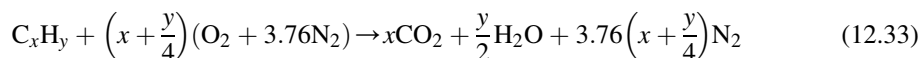


Total reaction



12.4.3 GENERAL HYDROCARBON REACTION WITH DISSOCIATION

A general hydrocarbon fuel can be defined as C_xH_y, and this will react with the stoichiometric quantity of air as shown in the following equation.



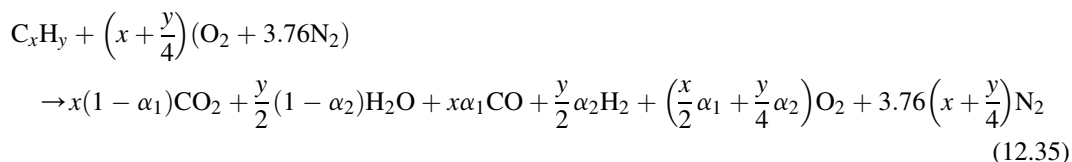
The dissociation of the CO₂ and H₂O can be added in to this equation as



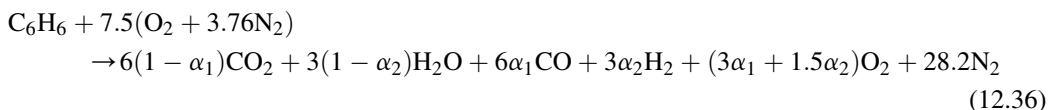
and



which gives a general equation with dissociation



If the fuel was benzene (C_6H_6), then Eqn (12.35) would become



If the mixture were not stoichiometric, then Eqn (12.33) would be modified to take account of the air–fuel ratio and Eqns (12.35) and (12.36) would also be modified. These equations are returned to in the later examples. In Eqn (12.36), the potential combination of nitrogen and oxygen has been neglected. In many combustion processes the oxygen and nitrogen join together at high temperatures to form compounds of these elements; one of these compounds is nitric oxide (NO) and the equations can be extended to include this reaction. This will be introduced later.

12.4.4 GENERAL OBSERVATION

As a result of dissociation there is always some oxidant in the products, hence dissociation always reduces the effect of the desired reaction, e.g. if the reaction is exothermic then dissociation reduces the energy released (see Fig. 12.1).

Having introduced the concept of dissociation it is necessary to evolve a method which allows the value of the degree of dissociation, α , to be calculated. This method will be developed in the following sections.

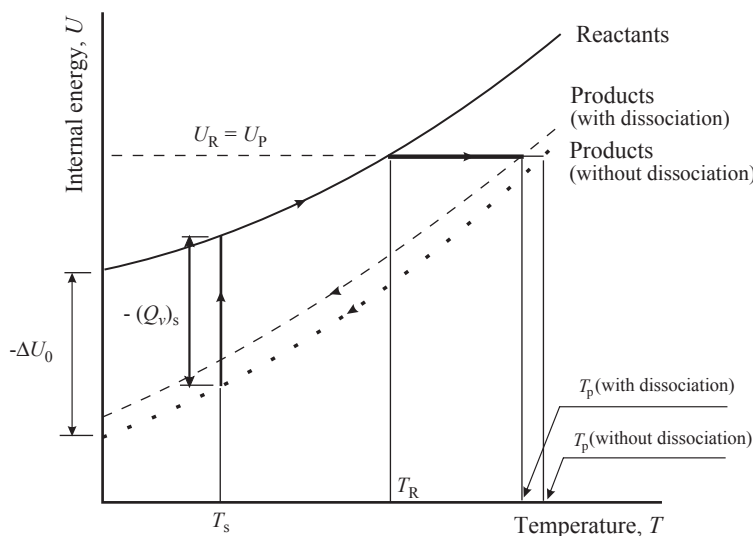


FIGURE 12.1

Effect of dissociation on combustion.

12.5 CALCULATION OF CHEMICAL EQUILIBRIUM AND THE LAW OF MASS ACTION

General relationships will be derived, and the particular case of the $\text{CO} + \frac{1}{2}\text{O}_2$ reaction will be shown in brackets { }.

It was previously shown that for a system at constant pressure and temperature to be in an equilibrium state, it must have a minimum value of Gibbs energy, i.e. $dG_{p,T} = 0$.

But, by definition, for a system at constant pressure and temperature

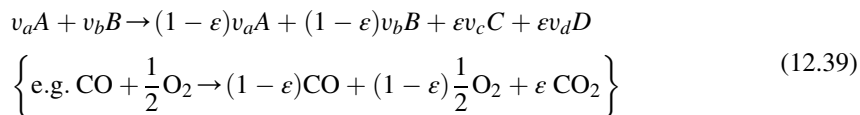
$$dg)_{p,T} = \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n. \quad (12.37)$$

where $m_1, m_2, \dots m_n$ are the masses (or amounts) of the *possible* constituents of the mixture.

Only four constituents will be considered during this discussion, two reactants and two products, but the theory can be extended to any number of constituents. The equilibrium equation for the *complete* reaction is:



At some intermediate stage in the reaction the state may be represented as:



where stoichiometric coefficients equal to unity are implicit.

ε is known as the *fraction of reaction* and is an *instantaneous* value during the reaction as opposed to α , the degree of dissociation, which is a final *equilibrium* value. The use of ε allows the changes in Gibbs energy to be considered as the reaction progresses.

For the purposes of evaluating the dissociation phenomena it is possible to consider the reaction to occur at constant temperature and pressure (equal to values obtained by other means or calculated by an implicit iterative technique). The Gibbs energy of the system may be described by the following equation.

$$\begin{aligned} G &= (1 - \varepsilon)v_a \mu_a + (1 - \varepsilon)v_b \mu_b + \varepsilon v_c \mu_c + \varepsilon v_d \mu_d \\ \left\{ G &= (1 - \varepsilon)\mu_{\text{CO}} + \frac{1}{2}(1 - \varepsilon)\mu_{\text{O}_2} + \varepsilon \mu_{\text{CO}_2} \right\}. \end{aligned} \quad (12.40)$$

To find the equilibrium condition while maintaining p and T constant, this function has to be minimised with respect to ε , i.e. it is necessary to locate when

$$\left. \frac{\partial G}{\partial \varepsilon} \right)_{p,T} = 0.$$

Now

$$dG = Vdp - SdT + \sum \mu_i dm_i \quad (12.41)$$

and

$$dG)_{p,T} = \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n. \quad (12.42)$$

From here on the mass form of the equation (Eqn (12.5a)) will be replaced by the mole form of the equation (Eqn (12.5b)), because this is more appropriate for chemical reactions. It is possible to relate the amount of substance of each constituent in terms of ε , viz.

$$\begin{aligned} n_a &= (1 - \varepsilon)v_a + A \\ n_b &= (1 - \varepsilon)v_b + B \\ n_c &= \varepsilon v_c + C \\ n_d &= \varepsilon v_d + D \end{aligned} \quad (12.43)$$

where A , B , C and D allow for the excess amount of substance in nonstoichiometric mixtures.

Hence

$$dn_a = -v_a d\varepsilon \quad (12.44)$$

and applying similar techniques

$$-\frac{dn_a}{v_a} = -\frac{dn_b}{v_b} = \frac{dn_c}{v_c} = \frac{dn_d}{v_d} = d\varepsilon. \quad (12.45)$$

This is known as the *equation of constraint* because it states that the changes of amount of substance (or mass) must be related to the stoichiometric equation (i.e. changes are *constrained* by the stoichiometry).

Hence

$$dG)_{p,T} = -\mu_a v_a d\varepsilon - \mu_b v_b d\varepsilon + \mu_c v_c d\varepsilon + \mu_d v_d d\varepsilon \quad (12.46)$$

giving

$$\begin{aligned} \left(\frac{\partial G}{\partial \varepsilon} \right)_{p,T} &= -\mu_a v_a - \mu_b v_b + \mu_c v_c + \mu_d v_d \\ &= 0, \text{ for equilibrium.} \end{aligned} \quad (12.47)$$

Therefore at equilibrium

$$\mu_a v_a + \mu_b v_b = \mu_c v_c + \mu_d v_d. \quad (12.48)$$

Since μ is numerically equal to g , it is possible to describe μ in a similar way to g , see Chapter 9 Section 9.2.4.

viz.

$$\mu = \mu^0 + \Re T \ln p_r \quad (12.49)$$

where

$$\mu^0 = \mu_0 + \mu(T) \quad (12.50)$$

and this is the value of μ at temperature, T , and the datum pressure, p_0 .

The value of pressure to be used in Eqn (12.49) is the ratio of the *partial* pressure of the individual constituent to the datum pressure.

Substituting for μ in the equilibrium equation, Eqn (12.48):

$$v_a(\mu_a^0 + \Re T \ln p_{r_a}) + v_b(\mu_b^0 + \Re T \ln p_{r_b}) = v_c(\mu_c^0 + \Re T \ln p_{r_c}) + v_d(\mu_d^0 + \Re T \ln p_{r_d}) \quad (12.51)$$

which can be rearranged to give

$$(v_a\mu_a^0 + v_b\mu_b^0 - v_c\mu_c^0 - v_d\mu_d^0) + \Re T(v_a \ln p_{r_a} + v_b \ln p_{r_b} - v_c \ln p_{r_c} - v_d \ln p_{r_d}) = 0 \quad (12.52)$$

Hence

$$\begin{aligned} -(v_a\mu_a^0 + v_b\mu_b^0 - v_c\mu_c^0 - v_d\mu_d^0) &= \Re T \ln \left\{ \frac{p_{r_a}^{v_a} p_{r_b}^{v_b}}{p_{r_c}^{v_c} p_{r_d}^{v_d}} \right\} = \Re T \ln \left[\left\{ \frac{p_a^{v_a} p_b^{v_b}}{p_c^{v_c} p_d^{v_d}} \right\} p_0^{(v_c + v_d - v_a - v_b)} \right] \\ &= -\Re T \ln \left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} = -\Re T \ln \left[\left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} p_0^{(v_a + v_b - v_c - v_d)} \right] \end{aligned} \quad (12.53)$$

The left-hand side of Eqn (12.53) is the difference in the standard chemical potentials at the reference pressure, p_0 , of 1 bar or 1 atm. This is defined as

$$-\Delta G_T^0 = v_a\mu_a^0 + v_b\mu_b^0 - v_c\mu_c^0 - v_d\mu_d^0 \quad (12.54)$$

Hence

$$-\frac{\Delta G_T^0}{\Re T} = \ln \left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} = \ln \left[\left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} p_0^{(v_a + v_b - v_c - v_d)} \right] = \ln K_{p_r} \quad (12.55)$$

giving

$$K_{p_r} = \left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} = \left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} p_0^{(v_a + v_b - v_c - v_d)} \quad (12.56)$$

K_{p_r} is called the *equilibrium constant*, and is a dimensionless value. Sometimes the equilibrium constant is defined as

$$K_p = \left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} \quad (12.57)$$

i.e.

$$K_{p_r} = K_p p_0^{(v_a + v_b - v_c - v_d)} \text{ or } K_p = K_{p_r} / p_0^{(v_a + v_b - v_c - v_d)} \quad (12.58)$$

K_p has the dimensions of pressure to the power of the sum of the stoichiometric coefficients, i.e. $p^{\Sigma v}$. The nondimensional equilibrium constant is defined as

$$\ln K_{p_r} = -\frac{\Delta G_T^0}{\Re T} \quad (12.59)$$

Now ΔG_T^0 is a function of T alone (having been defined at a standard pressure, p_0), therefore $K_{p_r} = f(T)$.

Equation (12.56) shows that the numerical value of K_{p_r} is related to the datum pressure used to define μ^0 . If the amounts of substance of reactants and products are the same then the value of K_p is not affected by the datum pressure (because $v_a + v_b - v_c - v_d = 0$). However, if the amounts of substance of products and reactants are not equal, as is the case for the $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ reaction, then the value of K_p will be dependent on the units of pressure. Hence the value of equilibrium constant, K_p , is the same for the water gas reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) in both SI and imperial units because K_p is dimensionless in this case.

12.5.1 K_p DEFINED IN TERMS OF MOLE FRACTION

The definition of partial pressure is

$$p_a = x_a p \quad (12.60)$$

Hence replacing the terms for partial pressure in Eqn (12.57) by the definition in Eqn (12.60) gives:

$$\Re T \ln \left\{ \frac{p_c^{v_c} p_d^{v_d}}{p_a^{v_a} p_b^{v_b}} \right\} = \Re T \left[\ln \left(\frac{x_c^{v_c} x_d^{v_d}}{x_a^{v_a} x_b^{v_b}} \right) p^{(v_c + v_d - v_a - v_b)} \right] \quad (12.61)$$

which results in the following expression for K_p in terms of mole fraction

$$K_p = \left(\frac{x_c^{v_c} x_d^{v_d}}{x_a^{v_a} x_b^{v_b}} \right) p^{(v_c + v_d - v_a - v_b)} \quad (12.62)$$

The above expressions are known as the *law of mass action*.

12.6 VARIATION OF GIBBS ENERGY WITH COMPOSITION

Equations (12.57) and (12.62) show that the equilibrium composition of a mixture is defined by the equilibrium constant that can be defined in terms of the partial pressures or mole fractions of the constituents of the mixture: the equilibrium constant was evaluated by equating the change of Gibbs energy at constant pressure and temperature to zero, i.e. $dG)_{p,T} = 0$. It is instructive to examine how the Gibbs energy of a mixture varies with composition at constant temperature and pressure. Assume that two components of a mixture, A and B , can combine chemically to produce compound C . This is a slightly simplified form of Eqns (12.38) and (12.39). If the chemical equation is



then at some point in the reaction, defined by the fraction of reaction, ε , the chemical composition is

$$(1 - \varepsilon)A + (1 - \varepsilon)B + 2\varepsilon C \quad (12.64)$$

and the Gibbs energy is

$$G = (1 - \varepsilon)\mu_a + (1 - \varepsilon)\mu_b + 2\varepsilon\mu_c \quad (12.65)$$

This can be written, by substituting for μ from Eqns (12.49) and (12.50), as

$$\begin{aligned} G &= (1 - \varepsilon) \left(\mu_a^0 + \mathcal{R}T \ln p_{r_a} \right) + (1 - \varepsilon) \left(\mu_b^0 + \mathcal{R}T \ln p_{r_b} \right) + 2\varepsilon \left(\mu_c^0 + \mathcal{R}T \ln p_{r_c} \right) \\ &= \left[(1 - \varepsilon) \mu_a^0 + (1 - \varepsilon) \mu_b^0 + 2\varepsilon \mu_c^0 \right] + \mathcal{R}T \left[(1 - \varepsilon) \ln p_{r_a} + (1 - \varepsilon) \ln p_{r_b} + 2\varepsilon \ln p_{r_c} \right] \end{aligned} \quad (12.66)$$

The partial pressures are defined by Eqn (12.60) as $p_i = x_i p$ and the mole fractions of the constituents are

$$x_a = \frac{1 - \varepsilon}{2}; \quad x_b = \frac{1 - \varepsilon}{2}; \quad x_c = \frac{2\varepsilon}{2} = \varepsilon. \quad (12.67)$$

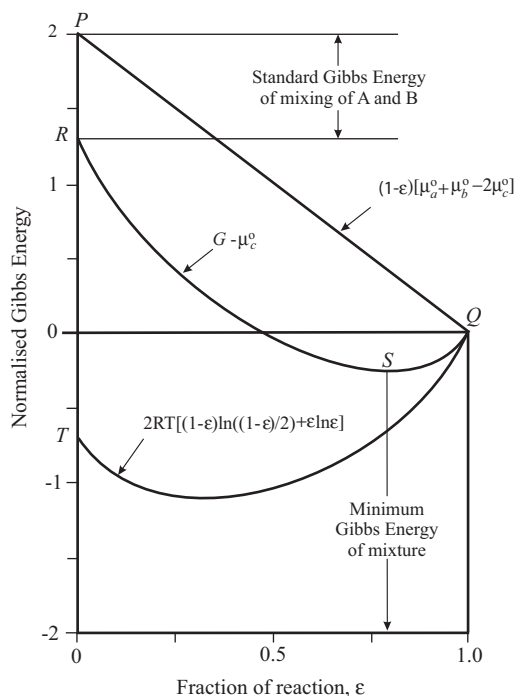
Substituting these terms in Eqn (12.66) gives

$$\begin{aligned} G &= \left[(1 - \varepsilon) \mu_a^0 + (1 - \varepsilon) \mu_b^0 + 2\varepsilon \mu_c^0 \right] + \mathcal{R}T \left[(1 - \varepsilon) \ln \left(\frac{1 - \varepsilon}{2} \right) p_r + (1 - \varepsilon) \ln \left(\frac{1 - \varepsilon}{2} \right) p_r + 2\varepsilon \ln \varepsilon p_r \right] \\ &= \left[(1 - \varepsilon) \mu_a^0 + (1 - \varepsilon) \mu_b^0 + 2\varepsilon \mu_c^0 \right] + \mathcal{R}T \left[(1 - \varepsilon) + (1 - \varepsilon) + 2\varepsilon \right] \ln p_r \\ &\quad + \mathcal{R}T \left[(1 - \varepsilon) \ln \left(\frac{1 - \varepsilon}{2} \right) + (1 - \varepsilon) \ln \left(\frac{1 - \varepsilon}{2} \right) + 2\varepsilon \ln \varepsilon \right] \end{aligned} \quad (12.68)$$

Equation (12.68) can be rearranged to show the variation of the Gibbs energy of the mixture as the reaction progresses from the reactants *A* and *B* to the product *C* by subtracting $2\mu_c^0$ from the left-hand side, giving

$$G - 2\mu_c^0 = (1 - \varepsilon) \left[\mu_a^0 + \mu_b^0 - 2\mu_c^0 \right] + 2\mathcal{R}T \ln p_r + 2\mathcal{R}T \left[(1 - \varepsilon) \ln \left(\frac{1 - \varepsilon}{2} \right) + \varepsilon \ln \varepsilon \right] \quad (12.69)$$

Equation (12.69) consists of three terms; the second one simply shows the effect of pressure and will be neglected in the following discussion. The first term is the difference between the standard chemical potentials of the separate components ($\mu_a^0 + \mu_b^0$) before any reaction has occurred and the standard chemical potential of the mixture ($2\mu_c^0$) after the reaction is complete. Since the standard chemical potentials are constant throughout this isothermal process, this term varies linearly with the fraction of reaction, ε . The third term defines the change in chemical potential due to mixing and is a function of the way in which the *entropy of the mixture* (not the specific entropy) varies as the reaction progresses. The manner in which the first and third terms might vary is shown in Fig. 12.2 and the sum of the terms is also shown. It can be seen that for this example, the equilibrium composition is at $\varepsilon = 0.78$. This figure illustrates that the Gibbs energy of the mixture initially reduces as the composition of the mixture goes from *A* + *B* to *C*. The standard chemical potential of compound *C* is less than the sum of the standard chemical potentials of *A* and *B*, and hence the reaction will tend to go in the direction shown in Eqn (12.63). If the standard chemical potentials were the only parameters of importance in the reaction then the reactants *A* and *B* would be completely transformed to the product, *C*. However, as the reaction progresses the term based on the mole fractions varies non-monotonically, as shown by the line labelled $\mathcal{R}T \left[(1 - \varepsilon) \ln \left(\frac{1 - \varepsilon}{2} \right) + 2\varepsilon \ln \varepsilon \right]$, and this affects the composition of the mixture which obeys the law of mass action. If the two terms are added together then the variation of

**FIGURE 12.2**

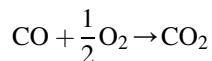
Variation of the Gibbs energy of a mixture.

$G - 2\mu_c^0$ with ϵ is obtained. It can be seen that the larger the difference between the standard chemical potentials (i.e. the steeper the slope of the line PQ), then the larger is the fraction of reaction to achieve an equilibrium composition. This is to be expected because the driving force for the reaction has been increased. Some examples of dissociation are given later and these can be more readily understood if this section is borne in mind.

12.7 EXAMPLES OF SIGNIFICANCE OF K_p

12.7.1 EXAMPLE 1

Consider the reaction in Eqn (12.1).

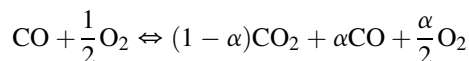


$$v_{\text{CO}} = -1, v_{\text{O}_2} = -1/2, v_{\text{CO}_2} = 1.$$

Hence

$$K_{p_r} = \frac{p_{\text{rCO}_2}}{p_{\text{rCO}} \sqrt{p_{\text{rO}_2}}}. \quad (12.70)$$

Thus, if K_{p_r} is known, the ratio of the partial pressures in the equilibrium state is known. It would be convenient to manipulate this expression into a more useful form. Consider the general reaction equation for the carbon monoxide and oxygen reaction (eqn (12.27))



then

$$\begin{aligned} p_{\text{rCO}_2} &= \frac{n_{\text{CO}_2}}{n_p} \frac{p}{p_0} = \frac{1 - \alpha}{1 + \alpha/2} \frac{p}{p_0} \\ p_{\text{rCO}} &= \frac{n_{\text{CO}}}{n_p} \frac{p}{p_0} = \frac{\alpha}{1 + \alpha/2} \frac{p}{p_0} \\ p_{\text{rO}_2} &= \frac{n_{\text{O}_2}}{n_p} \frac{p}{p_0} = \frac{\alpha/2}{1 + \alpha/2} \frac{p}{p_0} \end{aligned} \quad (12.71)$$

Hence, the value of K_{p_r} can be related to the degree of dissociation, α , through the following equation

$$K_{p_r} = \frac{1 - \alpha}{1 + \alpha/2} \frac{1 + \alpha/2}{\alpha} \sqrt{\frac{1 + \alpha/2}{\alpha/2}} \frac{\sqrt{p_0}}{\sqrt{p}} = \frac{1 - \alpha}{\alpha} \sqrt{\frac{1 + \alpha/2}{\alpha/2}} \frac{\sqrt{p_0}}{\sqrt{p}}. \quad (12.72a)$$

and

$$K_p = \frac{1 - \alpha}{\alpha} \sqrt{\frac{1 + \alpha/2}{\alpha/2}} \frac{1}{\sqrt{p}} = \frac{K_{p_r}}{\sqrt{p_0}} \quad (12.72b)$$

The relationship between K_{p_r} and α allows the degree of dissociation, α , to be evaluated if K_p is known. Equation (12.72) shows that, for this reaction, the value of K_p is a function of the degree of dissociation and also the pressure of the mixture. This is because the amount of substance of products is not equal to the amount of substance of reactants.

12.7.2 EXAMPLE 2

Consider the water–gas reaction:



By the law of mass action

$$\begin{aligned} K_{p_r} &= \frac{p_{\text{rCO}} p_{\text{rH}_2\text{O}}}{p_{\text{rCO}_2} p_{\text{rH}_2}} \\ &= \left(\frac{x_{\text{CO}} x_{\text{H}_2\text{O}}}{x_{\text{CO}_2} x_{\text{H}_2}} \right) p^{1+1-1-1} = \left(\frac{x_{\text{CO}} x_{\text{H}_2\text{O}}}{x_{\text{CO}_2} x_{\text{H}_2}} \right) = K_p \end{aligned} \quad (12.74)$$

In this reaction, the amount of substance in the products is equal to the amount of substance in the reactants and there is no effect of pressure in the dissociation equation. Comparing the results for the carbon monoxide (Eqn (12.1)) and the water gas reactions (Eqn (12.73)), it can be seen that if a mixture of products of the reaction in Eqn (12.1) was subjected to a change in pressure the chemical composition of the mixture would change, whereas the chemical composition of the products of the water–gas reaction would be the same at any pressure.

These points are returned to later in this section.

12.7.3 EXAMPLE 3: A ONE DEGREE OF DISSOCIATION EXAMPLE

A spark-ignition engine operates on a 10% rich mixture of carbon monoxide and air. The conditions at the end of compression are 8.5 bar and 600 K, and it can be assumed that the combustion is adiabatic at constant volume. Calculate the maximum pressure and temperature achieved if dissociation occurs.

(There are two different approaches for solving this type of problem; both of these will be outlined below. The first approach, which develops the chemical equations from the degrees of dissociation, is often the easier method for hand calculations because it is usually possible to estimate the degree of dissociation with reasonable accuracy, and it can also be assumed that the degree of dissociation of the water vapour is less than that of the carbon dioxide. The second approach is more appropriate for computer programs because it enables a set of simultaneous (usually nonlinear) equations to be defined.)

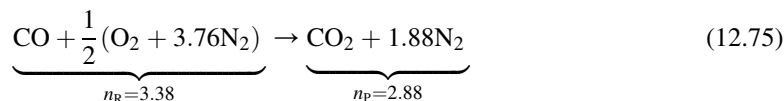
General considerations

The products of combustion with dissociation have to obey all of the laws which define the conditions of the products of combustion without dissociation, described in Chapter 10, plus the ratios of constituents defined by the equilibrium constant, K_p . This means that the problem becomes one with two iterative loops: it is necessary to evaluate the degree of dissociation from the chemical equation and the equilibrium constant, and to then ensure that this obeys the energy equation (i.e. the First Law of Thermodynamics). The following examples show how this can be achieved.

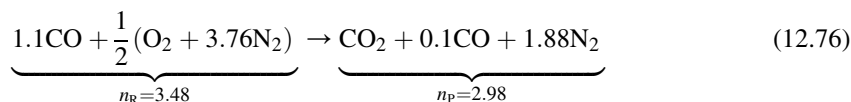
Solution:

Note that there is only one reaction involved in this problem, and that the carbon monoxide converts to carbon dioxide in a single step. Most combustion processes have more than one chemical reaction.

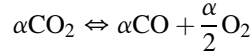
Stoichiometric combustion equation



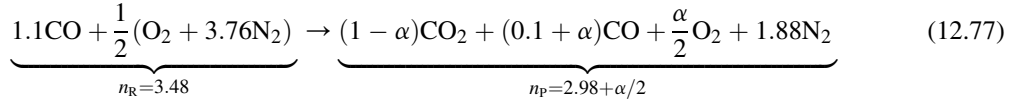
Rich combustion equation



Dissociation of CO_2 (Eqn (12.29))



Total combustion equation with dissociation



The equilibrium constant, K_{p_r} , is given by Eqn (12.70):

$$K_{p_r} = \frac{(p/p_0)_{\text{CO}_2}}{(p/p_0)_{\text{CO}}(p/p_0)_{\text{O}_2}^{1/2}}$$

The values of partial pressures in the products are

$$\frac{p_{\text{CO}_2}}{p_0} = x_{\text{CO}_2} \frac{p_2}{p_0} = \frac{1-\alpha}{n_P} \frac{p_2}{p_0}; \quad \frac{p_{\text{CO}}}{p_0} = x_{\text{CO}} \frac{p_2}{p_0} = \frac{0.1+\alpha}{n_P} \frac{p_2}{p_0}; \quad \frac{p_{\text{O}_2}}{p_0} = x_{\text{O}_2} \frac{p_2}{p_0} = \frac{\alpha}{2n_P} \frac{p_2}{p_0}. \quad (12.78)$$

Also, from the ideal gas law

$$p_2 V_2 = n_2 \mathfrak{R} T_2, \text{ and } p_1 V_1 = n_1 \mathfrak{R} T_1. \quad (12.79)$$

Thus

$$\frac{n_P}{p_2} = \frac{n_1 T_1}{p_1 T_2} = \frac{245.65}{T_2}. \quad (12.80)$$

Hence, substituting these values in Eqn (12.70) gives

$$K_{p_r} = \frac{(1-\alpha)}{(0.1+\alpha)} \left(\frac{2n_P}{\alpha} \frac{p_0}{p_2} \right)^{1/2}, \text{ giving } K_{p_r}^2 = \frac{(1-\alpha)^2}{(0.1+\alpha)^2} \left(\frac{2 \times 245.65}{\alpha T_2} p_0 \right) \quad (12.81)$$

This is an implicit equation in the products temperature, T_2 , because $K_p = f(T_2)$. Writing K_p^2 as X gives

$$X(0.1+\alpha)^2 \alpha T_2 = (1-\alpha)^2 \times 2 \times 245.65 p_0 = (1-\alpha)^2 \times 2 \times 245.65 \times 1.01325 \quad (12.82)$$

Expanding Eqn (12.82) gives

$$0 = 497.77 - \alpha(995.54 + 0.01XT_2) + \alpha^2(497.77 - 0.2XT_2) - \alpha^3XT_2 \quad (12.83)$$

The term XT_2 can be evaluated for various temperatures because $XT_2 = K_{p_r}^2 T_2$

T_2 (K)	K_p	XT_2
2800	6.582	121303
2900	4.392	55940
3000	3.013	27234

Solving for α at each temperature gives

T_P	α
2800	0.090625
2900	0.1218125
3000	0.171875

These values of α all obey the chemical equation, i.e. *dissociation*, but they do not all obey the energy equation. It is necessary to consider the energy equation now to check which value of T_2 balances an equation of the form

$$U_P(T_P) = -(Q_v)_s + [U_R(T_R) - U_R(T_s)] + U_P(T_s)$$

This energy equation, based on the internal energy of reaction at $T = 0$, may be rewritten

$$0 = -\Delta U_0 - U_P(T_P) + U_R(T_R) \quad (12.84)$$

Now $U_R(T_R)$ is constant and is given by

Constituent	CO	O ₂	N ₂
u_{600}	12626.2	12939.6	12571.7
n	1.1	0.5	1.88

$$U_R(T_R) = 43993.4 \text{ kJ}$$

Hence,

$$U_P(T_P) = (1 - \alpha) \times 279523 + 43993 \quad (12.85)$$

It can be seen that the value of U_P is a function of α : the reason for this is because the combustion of the fuel (CO) is not complete when dissociation occurs. In a simple, single degree of freedom reaction like this the reduction in energy released is directly related to the progress of the reaction.

T_P	α	$U_P(T_P)$
2800	0.090625	298184
2900	0.1218125	289467
3000	0.171875	275473

Evaluating the energy which is contained in the products at 2900 and 3000 K, allowing for the variation in α as the temperature changes, gives.

$$T_p = 2900 \text{ K}$$

Constituent	CO ₂	CO	O ₂	N ₂
u_{2900}	131933.3	74388.9	78706.6	73597.5
n	0.871875	0.2281	0.0641	1.88

$$U_p(T_p) = 275405 \text{ kJ}$$

$$T_p = 3000 \text{ K}$$

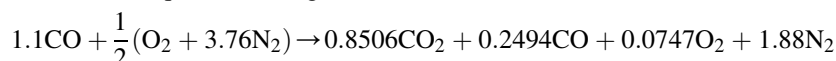
Constituent	CO ₂	CO	O ₂	N ₂
u_{3000}	137320	77277	81863	76468
n	0.8281	0.2719	0.08594	1.88

$$U_p(T_p) = 285521 \text{ kJ}$$

These values are plotted in Fig. 12.3, and it can be seen that, if the variation of the energy terms was linear with temperature, the temperature of the products after dissociation would be 2958 K. The calculation will be repeated to show how well this result satisfies both the energy and dissociation equations.

First, it is necessary to evaluate the degree of dissociation which will occur at this products' temperature. At $T_p = 2950 \text{ K}$, $K_p = 3.62613$ and this can be substituted into Eqn (12.78) to give $\alpha = 0.1494$.

Hence, the chemical equation, taking account of dissociation, is



Applying the energy equation, the energy released by the combustion process gives a products energy of

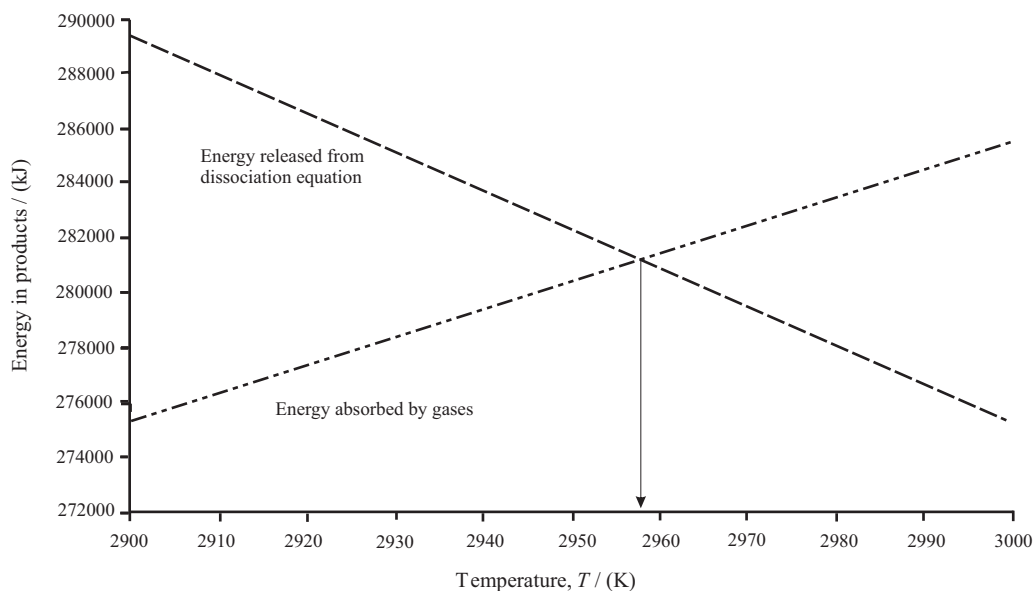
$$U_p(T_p) = (1 - \alpha) \times 279523 + 43993 = 281755 \text{ kJ}$$

This energy is contained in the products as shown in the following table.

Constituent	CO ₂	CO	O ₂	N ₂
u_{2958}	135670	76079	80488	75299
n	0.8506	0.2494	0.0747	1.88

$$U_p(T_p) = 281947 \text{ kJ}$$

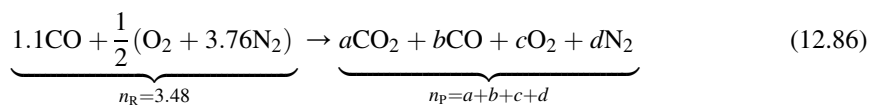
The equations are balanced to within 0.068% and this is close enough for this example.

**FIGURE 12.3**

Energy contained in products based on Eqn (12.80) and the tables of energies.

Alternative method

In this approach, the degree of dissociation, α , will not be introduced explicitly. The chemical equation which was written in terms of α in Eqn (12.77) can be written as



Considering the atomic balances

$$\text{Carbon:} \quad 1.1 = a + b \quad \text{giving} \quad b = 1.1 - a \quad (12.87a)$$

$$\text{Oxygen:} \quad 2.1 = 2a + b + 2c \quad \text{giving} \quad c = 0.5(1 - a) \quad (12.87b)$$

$$\text{Nitrogen:} \quad 1.88 = d \quad (12.87c)$$

Total amount of substance in the products

$$n_P = a + b + c + d \quad (12.88)$$

The ratios of the amounts of substance in the equilibrium products are defined by the equilibrium constant,

$$K_{p_r} = \frac{(p/p_0)_{\text{CO}_2}}{(p/p_0)_{\text{CO}}(p/p_0)_{\text{O}_2}^{1/2}} = \frac{an_{\text{P}}^{1/2}p_0^{1/2}}{bc^{1/2}p_{\text{P}}^{1/2}}. \quad (12.89)$$

Hence,

$$b^2c \frac{p_{\text{P}}}{p_0 n_{\text{P}}} K_{p_r}^2 = a^2, \quad (12.90)$$

and, from the atomic balances, this can be written in terms of a as

$$(1.1 - a)^2 \frac{1}{2} (1 - a) \frac{p_{\text{P}}}{p_0 n_{\text{P}}} K_{p_r}^2 = a^2 \quad (12.91)$$

The previous calculations showed that the temperature of the products which satisfies the governing equations is $T_{\text{P}} = 2950$ K, which gives a value of $K_{p_r} = 13.1488$. These values will be used to demonstrate this example. Then

$$\left\{ 1.21 - 2.2a + a^2 - (1.21a - 2.2a^2 + a^3) \right\} \frac{p_{\text{P}}}{p_0 n_{\text{P}}} \times \frac{13.1488}{2} = a^2. \quad (12.92)$$

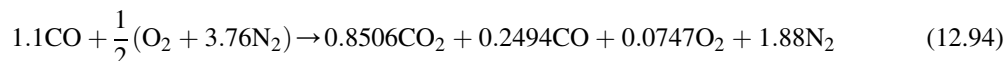
It is possible to evaluate the ratio $p_{\text{P}}/p_0 n_{\text{P}}$ from the perfect gas relationship, giving

$$\frac{p_{\text{P}}}{p_0 n_{\text{P}}} = \frac{p_{\text{R}} T_{\text{P}}}{n_{\text{R}} T_{\text{R}}} = \frac{8.5 \times 2950}{3.48 \times 600} = 12.009$$

This enables a cubic equation in a to be obtained

$$95.532 - 269.23a + 251.65a^2 - 78.953a^3 = 0 \quad (12.93)$$

The solution to this equation is $a = 0.8506$, and hence the chemical equation becomes



which is the same as that obtained previously. The advantage of this approach is that it is possible to derive a set of simultaneous equations which define the equilibrium state, and these can be easily solved by a computer program. The disadvantage is that it is not possible to use the intuition that most engineers can adopt to simplify the solution technique. It must be recognised that the full range of iteration was not used in this demonstration, and the solution obtained from the original method was simply used for the first 'iteration'.

12.8 THE VAN'T HOFF RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT AND HEAT OF REACTION

It has been shown that, [Eqn \(12.54\)](#)

$$\ln K_{p_r} = \frac{1}{RT} (v_a \mu_a^0 + v_b \mu_b^0 - v_c \mu_c^0 - v_d \mu_d^0). \quad (12.95)$$

Thus

$$\begin{aligned}\frac{d}{dT} \ln K_{p_r} &= \frac{d}{dT} \left\{ \frac{1}{\Re T} \left(v_a \mu_a^0 + v_b \mu_b^0 - v_c \mu_c^0 - v_d \mu_d^0 \right) \right\} \\ &= \frac{d}{dT} \left\{ \frac{1}{\Re T} \left([v\mu^0]_R - [v\mu^0]_P \right) \right\}\end{aligned}\quad (12.96)$$

Consider definition of μ^0

$$\begin{aligned}\mu^0 &= h_0 + h(T) - T\{s_0 + s(T)\} \\ &= h_0 + h(T) - Ts_0 - T \int \frac{dh}{T}.\end{aligned}\quad (12.97)$$

Consider the terms

$$h(T) - T \int \frac{dh}{T} = T \left\{ \frac{h(T)}{T} - \int \frac{dh}{T} \right\} \quad (12.98)$$

Let

$$\begin{aligned}v &= h(T) & dv &= dh \\ u &= \frac{1}{T} & du &= -\frac{dT}{T^2}\end{aligned}$$

Integrating by parts gives

$$T \left\{ \frac{h(T)}{T} - \int \frac{dh(T)}{T} \right\} = -T \int \frac{h(T) dT}{T^2}. \quad (12.99)$$

Thus

$$\frac{d}{dT} \ln K_{p_r} = - \sum \frac{v}{\Re} \frac{h(T)}{T^2} = - \sum \frac{vh(T)}{\Re T^2} \quad (12.100)$$

Although Σ has been used as a shorthand form it does include both positive and negative signs; these must be taken into account when evaluating the significance of the term.

Thus

$$\begin{aligned}\frac{d}{dT} (\ln K_{p_r}) &= -\frac{1}{\Re T^2} (v_a h_a + v_b h_b - v_c h_c - v_d h_d) \\ &= -\frac{1}{\Re T^2} ([vh]_R - [vh]_P)\end{aligned}\quad (12.101)$$

But, by definition

$$Q_p = (v_c h_c + v_d h_d) - (v_a h_a + v_b h_b) \quad (12.102)$$

Hence

$$\frac{d}{dT} (\ln K_{p_r}) = \frac{Q_p}{\Re T^2}. \quad (12.103)$$

Equation (12.103) is known as the *Van't Hoff equation*. It is useful for evaluating the heat of reaction for any particular reaction since

$$Q_p = -\frac{\Re d(\ln K_{p_r})}{d(1/T)}.$$

The value of $d(\ln K_p)/d(1/T)$ may be obtained by plotting a graph of $\ln K_p$ against $1/T$.

The values of K_p have been calculated using Eqn (12.95) and are listed in Table 12.3 (at the end of this chapter) for four reactions. The values have also been depicted as a graph in Fig. 12.4 and it can be seen that over a small range of temperature $\ln K_p \approx A - \frac{B}{T}$, where T is the temperature in K; this is to be expected from Eqn (12.95).

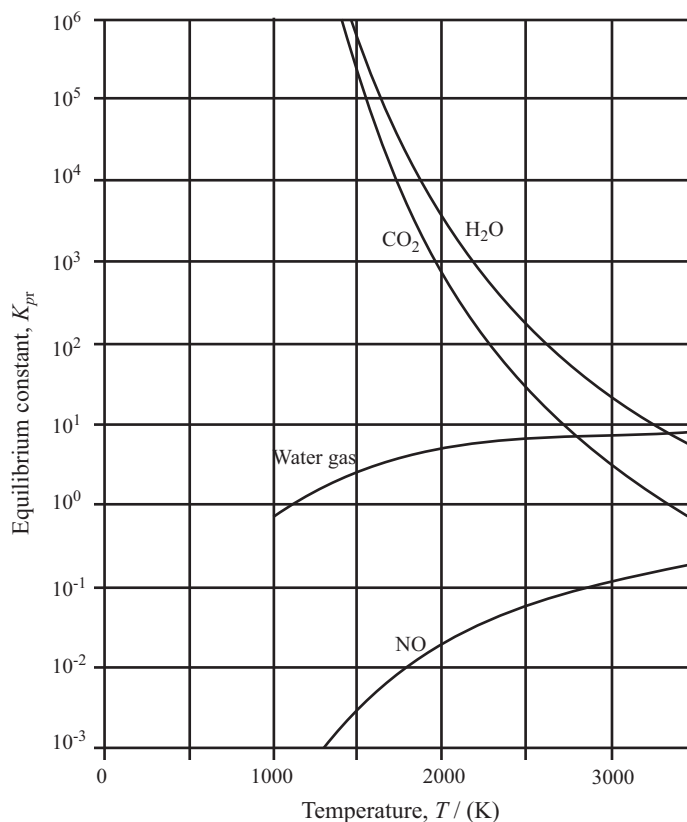
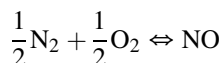
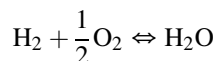
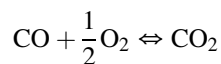


FIGURE 12.4

Variation of equilibrium constant, K_p , at a standard pressure, $p_0 = 1$ bar, with temperature for the reactions.



12.9 THE EFFECT OF PRESSURE AND TEMPERATURE ON DEGREE OF DISSOCIATION

12.9.1 THE EFFECT OF PRESSURE

The effect of pressure on the degree of dissociation is defined by Eqn (12.62), viz.

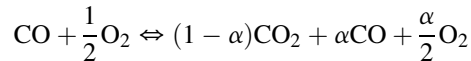
$$K_{p_r} = \left(\frac{x_c^{v_c} x_d^{v_d}}{x_a^{v_a} x_b^{v_b}} \right) p_r^{(v_c + v_d - v_a - v_b)}$$

It can be seen that the ratio of the amounts of substance is given by

$$\frac{x_a^{v_a} x_b^{v_b}}{x_c^{v_c} x_d^{v_d}} = \frac{p_r^{(v_c + v_d - v_a - v_b)}}{K_{p_r}} \quad (12.104)$$

This can be interpreted in the following way. If $v_c + v_d - v_a - v_b = 0$ then the mole fractions of the products will not be a function of pressure. However, if $v_c + v_d - v_a - v_b > 0$ then the species on the left-hand side of the chemical equation (i.e. the reactants) increase, whereas if $v_c + v_d - v_a - v_b < 0$ then the species on the right-hand side of the equation (i.e. the products) increase. The basic rule is that the effect of increasing the pressure is to shift the equilibrium to reduce the total amount of substance.

Considering the two reactions introduced previously. The equation for the carbon monoxide reaction (12.27) was

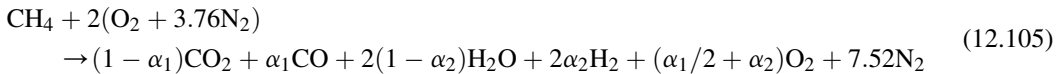


and the equilibrium Eqn (12.72) was

$$K_{p_r} = \frac{1 - \alpha}{1 + \alpha/2} \frac{1 + \alpha/2}{\alpha} \sqrt{\frac{1 + \alpha/2}{\alpha/2}} \frac{1}{\sqrt{p_r}} = \frac{1 - \alpha}{\alpha} \sqrt{\frac{1 + \alpha/2}{\alpha/2}} \frac{1}{\sqrt{p_r}}$$

This means that $v_c + v_d - v_a - v_b < 0$, and this would result in the constituents on the ‘products’ side of the equation increasing. This is in agreement with the previous statement because the total amounts of reactants in Eqn (12.27) is 1.5, whilst the total amounts of products is $1 + \alpha/2$, where α is less than 1.0.

A similar calculation for the combustion and dissociation of a stoichiometric methane (CH_4) and air mixture, performed using a computer program entitled EQUIL2¹ gave the results in Table 12.1. The chemical equation for this reaction is

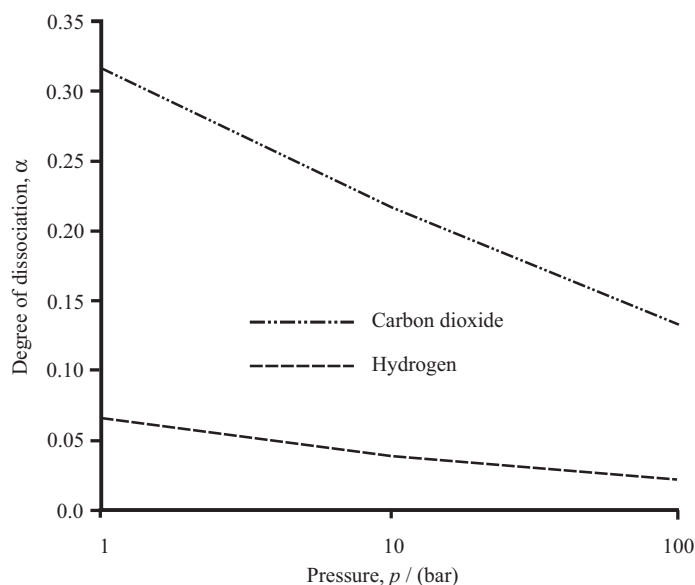


¹An executable version of EQUIL2 is available at <http://booksite.elsevier.com/9780444633736>.

Table 12.1 Amount of Products for Constant Pressure Combustion of Methane in Air Initial Temperature = 1000 K; Equivalence Ratio = 1.00

Pressure (bar)	No Dissociation	1	10	100
Amount of CO ₂	1	0.6823	0.7829	0.8665
Amount of CO	0	0.3170	0.2170	0.1335
Amount of H ₂ O	2	1.8654	1.920	1.9558
Amount of H ₂	0	0.1343	0.0801	0.0444
Amount of O ₂	0	0.2258	0.1485	0.0889
Amount of N ₂	7.52	7.52	7.52	7.52
Total amount of substance	10.52	10.7448	10.6685	10.6091

where α_1 is the degree of dissociation of the CO₂ reaction and α_2 is the degree of dissociation of the H₂O reaction. It can be seen that dissociation tends to increase the amount of substance of products, and hence the effect of pressure should be to reduce the degree of dissociation. This effect can be seen quite clearly in Table 12.1, where the amount of substance of products is compared under four sets of conditions: no dissociation, dissociation at $p = 1$ bar, dissociation at $p = 10$ bar and dissociation at $p = 100$ bar. The minimum total amount of substance occurs when there is no dissociation, with the maximum amount of substance then occurring at the lowest pressure. Figure 12.5 shows how the degrees of dissociation for the carbon dioxide and water reactions vary with pressure.

**FIGURE 12.5**

Effect of pressure on degree of dissociation.

Table 12.2 Amount of Products for Constant Pressure Combustion of Methane in Air Pressure = 1 bar; Equivalence ratio = 1

Temperature (K)	No Dissociation	$T = 1000\text{ K}$	$T = 1500\text{ K}$	$T = 2000\text{ K}$
Amount of CO_2	1	0.6823	0.4814	0.3031
Amount of CO	0	0.3170	0.5186	0.6969
Amount of H_2O	2	1.8654	1.7320	1.5258
Amount of H_2	0	0.1343	0.2679	0.4741
Amount of O_2	0	0.2258	0.3933	0.5855
Amount of N_2	7.52	7.52	7.52	7.52
Total amount of substance	10.52	10.7448	10.9132	11.1055

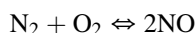
12.9.2 THE EFFECT OF TEMPERATURE

The effect of temperature can be considered in a similar way to the effect of pressure. Basically it should be remembered that the changes in composition that take place during dissociation do so to achieve the minimum value of Gibbs energy for the mixture. The Gibbs energy of each constituent is made up of three components, the Gibbs energy at absolute zero (g_0), the Gibbs energy as a function of temperature ($g(T)$) and that related to partial pressure. The equilibrium point is achieved when the sum of these values for all the constituents is a minimum. This means that, as the temperature rises, the constituents with the most positive heats of formation are favoured. These constituents include O_2 ($g_0 = 0$), H_2 ($g_0 = 0$) and CO ($g_0 = -113\text{ MJ/kmol}$). Both water and carbon dioxide have larger (negative) values of g_0 . This effect can be seen from the results in Table 12.2, which have been calculated for the combustion of methane in air. Another way of considering this effect is simply to study Eqn (12.54), and to realise that for gases with negative heats of formation an increase in temperature leads to a *decrease* in the value of K_p . This means that the numerator of Eqn (12.55) must get smaller relative to the denominator, which pushes the reaction backwards towards the reactants. This is borne out in Table 12.2; the degrees of dissociation for this reaction increase with temperature and these are shown in Fig. 12.6.

Finally, it should be noted that in all the cases shown, the degree of dissociation in the hydrogen reaction is much less than that for the carbon reaction. This supports the assumption made in previous work that the hydrogen will be favoured in the oxidation process.

12.10 DISSOCIATION CALCULATIONS FOR THE EVALUATION OF NITRIC OXIDE

If it is necessary to evaluate the formation of nitric oxide in a combustion chamber, then the equations have to be extended to include many more species. While it is possible to add the calculation of NO to a simple dissociation problem, as is done in Example 5 below, this does not result in an accurate estimate of the quantity of NO formed. The reason for this is that NO is formed by a chain of reactions which are more complex than simply.



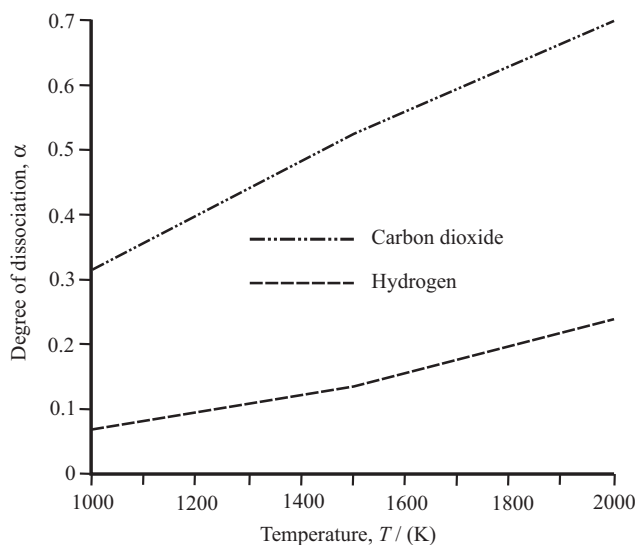
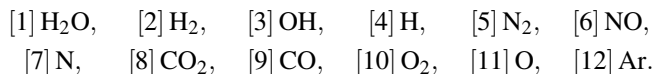


FIGURE 12.6

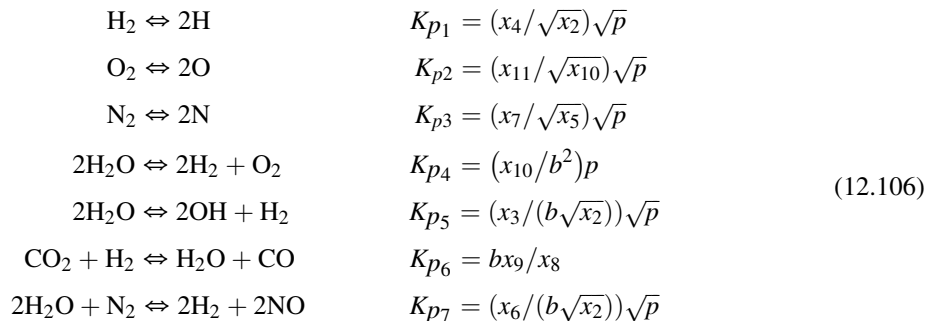
Effect of temperature on degree of dissociation.

This chain of reactions has to include the formation of atomic oxygen and nitrogen and also the OH radical. To obtain an accurate prediction of the NO concentration a total of 12 species have been considered.



The numbers in [] will be used to identify the species in later equations.

The formation and breakdown of these species are defined by the following set of equations.



where $b = x_1/x_2$

A numerical method for solving these equations is given in Horlock and Winterbone (1986), based on the original paper by Lavoie et al. (1970).

Figure 12.7 shows the results of performing such calculations using a simple computer program. The coefficients in the program were evaluated using the data presented in Table 9.3 in Chapter 9, but with the addition of OH and N. The three diagrams are based on combustion of octane in air at a constant pressure of 30 bar, and show the effect of varying equivalence ratio, ϕ , at different temperatures. The conditions are the same as quoted in Heywood (1988). Figure 12.7(a) shows the results for the lowest temperature of 1750 K, and it can be seen that the graph contains no atomic nitrogen (N) or atomic oxygen (O) because these are at very low concentrations ($<10^{-4}$). When the mixture is weak some OH is produced. It is apparent from this diagram that there is not much dissociation of the carbon dioxide or water because the concentration of oxygen drops to very low values above $\phi = 1$. Some nitric oxide is formed in the weak region ($x_{\text{NO}} = 3 \times 10^{-3}$ at the weakest mixture), but this rapidly reduces to a very low value at stoichiometric simply because there is no oxygen available to combine with the nitrogen. Figure 12.7(b) shows similar graphs for a temperature of 2250 K, and it can be seen that the NO level has increased by almost a factor of 10. There is also some NO formed by combustion with rich mixtures; this is because, by this temperature, the carbon dioxide and water are dissociating, as is indicated by the increase in the CO and the OH radical in the weak mixture region. By the time 2750 K is reached, shown in Fig. 12.7(c), there is a further tripling of the NO production and CO is prevalent throughout the weak mixture zone. There are also significant amounts of OH and oxygen over the whole range of equivalence ratio.

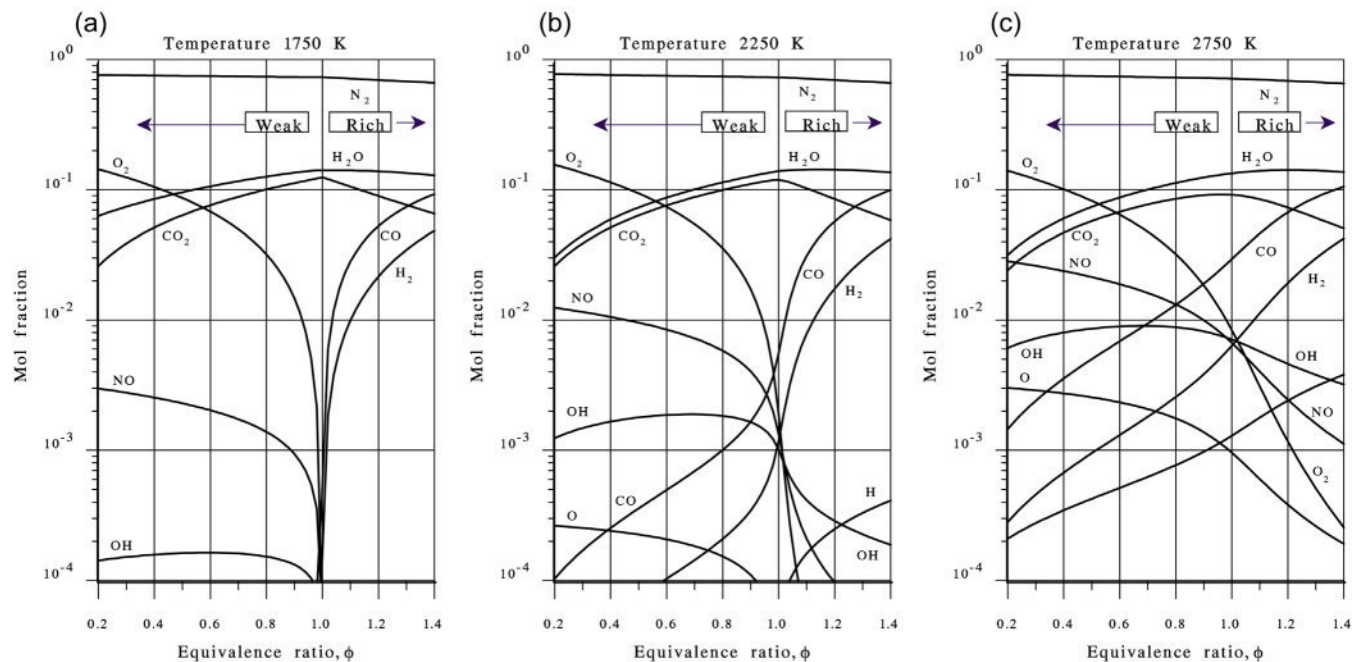
The diagrams shown in Fig. 12.7 are relatively contrived because they do not depict real combustion situations. However, they do allow the parameters which control the production of the products of combustion to be decoupled to show the effects of changing the parameters independently of each other. The equilibrium concentrations depicted in Fig. 12.7 are the values which drive the formation of the exhaust constituents through the chemical kinetics equations.

12.11 DISSOCIATION PROBLEMS WITH TWO, OR MORE, DEGREES OF DISSOCIATION

The previous example, Example 3, which considered the dissociation of carbon monoxide, shows the fundamental techniques involved in calculating dissociation but it is an unrealistic example because rarely are single component fuels burned. Even if a single component fuel such as hydrogen was burned in an engine, it would be necessary to consider other ‘dissociation’ reactions because it is likely that nitric oxide will be formed from the combination of the oxygen and nitrogen in the combustion chamber. These more complex examples will be considered here.

12.11.1 EXAMPLE 4: COMBUSTION OF A TYPICAL HYDROCARBON FUEL

A weak mixture of octane (C_8H_{18}) and air, with an equivalence ratio of 0.9, is ignited at 10 bar and 500 K and burns at constant volume. Assuming the combustion is adiabatic, calculate the conditions at

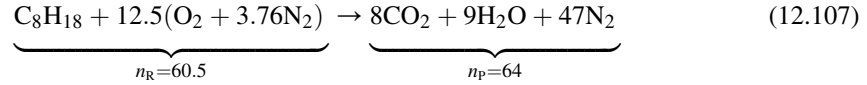
**FIGURE 12.7**

Variation of products of combustion with temperature and equivalence ratio for octane and air at 30 bar (based on Heywood (1988))
 (a) temperature 1750 K (b) temperature 2250 K (c) temperature 2750 K.

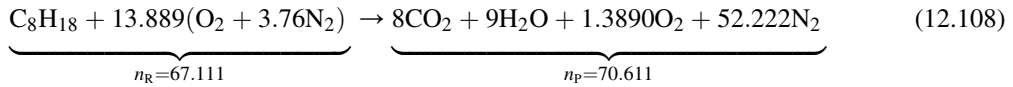
the end of combustion allowing for dissociation of the carbon dioxide and water, but neglecting any formation of NO.

Solution:

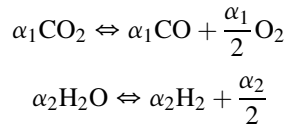
Stoichiometric equation neglecting dissociation



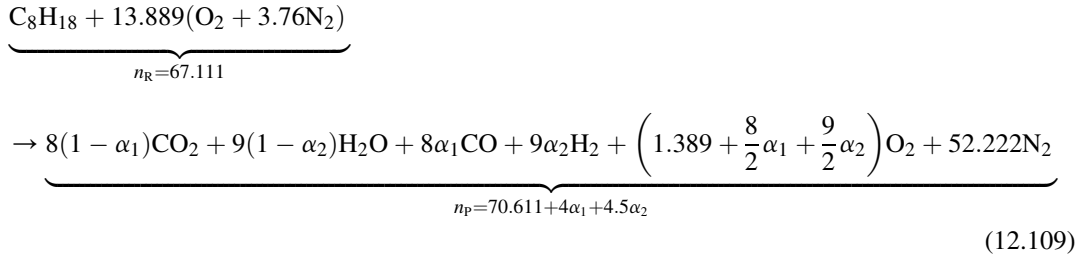
Weak mixture neglecting dissociation



Dissociation [Eqns \(12.25\) and \(12.34\)](#)



Weak mixture including dissociation is



The temperature and pressure calculated for combustion without dissociation are 2874 K and 60.481 bar respectively. Dissociation will lower the final temperature; assume that $T_P = 2800$ K.

The equilibrium constants from [Table 12.3](#) at 2800 K are

$$K_{p_{r1}} = \frac{p_{r\text{CO}_2}}{p_{r\text{CO}}p_{r\text{O}_2}^{1/2}} = 6.58152$$

$$K_{p_{r2}} = \frac{p_{r\text{CO}}p_{r\text{H}_2\text{O}}}{p_{r\text{CO}_2}p_{r\text{H}_2}} = 6.8295 \quad (12.110)$$

From Eqn (12.109), the partial pressures of the constituents are

$$\begin{aligned} p_{\text{rCO}_2} &= \frac{8(1 - \alpha_1)}{n_P} \frac{p}{p_0} \\ p_{\text{rCO}} &= \frac{8\alpha_1}{n_P} \frac{p}{p_0} & p_{\text{rH}_2\text{O}} &= \frac{9(1 - \alpha_2)}{n_P} \frac{p}{p_0} \\ p_{\text{rO}_2} &= \frac{(1.389 + 4\alpha_1 + 4.5\alpha_2)}{n_P} \frac{p}{p_0} & p_{\text{rH}_2} &= \frac{9\alpha_2}{n_P} \frac{p}{p_0} \end{aligned}$$

Hence

$$K_{p_{\text{r}}}^2 = 43.3164 = \frac{[8(1 - \alpha_1)]^2}{[8\alpha_1]^2} \frac{n_P}{(1.389 + 4\alpha_1 + 4.5\alpha_2)} \frac{p_0}{p} \quad (12.111)$$

and

$$K_{p_{\text{r}}} = \frac{9(1 - \alpha_2)}{9\alpha_2} \frac{8\alpha_1}{8(1 - \alpha_1)} = \frac{(1 - \alpha_2)}{\alpha_2} \frac{\alpha_1}{(1 - \alpha_1)} \quad (12.112)$$

The $K_{p_{\text{r}}}$ equation (Eqn (12.111)) contains a pressure term, but this can be replaced by the temperature of the products by applying the perfect gas law to the mixture. Then

$$\begin{aligned} p_P V_P &= n_P \mathfrak{R} T_P \\ p_R V_R &= n_R \mathfrak{R} T_R \end{aligned} \quad (12.113)$$

Thus

$$\frac{n_P}{p_P} = \frac{n_R \mathfrak{R} T_R}{p_R \mathfrak{R} T_P} = \frac{n_R T_R}{p_R T_P} \quad (12.114)$$

Substituting gives

$$K_{p_{\text{r}}}^2 = 43.3164 = \frac{(1 - \alpha_1)^2}{\alpha_1^2} \frac{n_R T_R}{(1.389 + 4\alpha_1 + 4.5\alpha_2) p_R T_P} p_0 \quad (12.115)$$

Inserting values for these parameters gives

$$\frac{43.3164 \times 10 \times 2800}{67.111 \times 500} = \frac{(1 - \alpha_1)^2}{\alpha_1^2 (1.389 + 4\alpha_1 + 4.5\alpha_2)} \quad (12.116)$$

which can be expanded to give

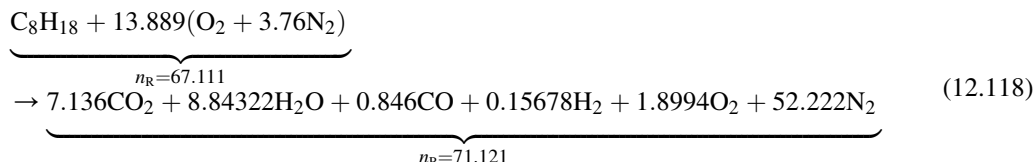
$$144.58\alpha_1^3 + \alpha_1^2(49.2052 + 162.652\alpha_2) + 2\alpha_1 - 1 = 0 \quad (12.117)$$

This equation contains both α_1 and α_2 . If it is assumed that $\alpha_1 \gg \alpha_2$ then Eqn (12.117) is a cubic equation in α_1 . Based on this assumption the value of α_1 is approximately 0.11. Substituting this value in Eqn (12.112) gives $\alpha_2 = 0.017776$, which vindicates the original assumption. Recalculation around this loop gives

$$\alpha_1 = 0.108$$

$$\alpha_2 = 0.01742$$

These values are close enough solutions for the dissociation coefficients and for the chemical equation (Eqn (12.109) which becomes



This equation satisfies the equilibrium constraints and the chemistry of the problem, *but it still has to be checked to see if it meets the First Law*. The First Law is defined by the equation

$$U_P(T_P) - U_P(T_s) = -(Q_v)_s + [U_R(T_R) - U_R(T_s)] \quad (12.119)$$

Note two things about this equation. First, it is more convenient to evaluate the difference between the internal energies of the products because now the composition of the products is also a function of temperature and hence $U_P(T_s)$ is not a constant. Second, with dissociation, $(Q_v)_s$ is not the full value of the internal energy of reaction of octane because not all the octane has been oxidised fully to CO_2 and water. The value of $(Q_v)_s$ in this case is given by

$$\begin{aligned} (\tilde{Q}_v)_s &= (Q_v)_s - 0.108 \times 8 \times (-283000) - 0.01742 \times 9 \times (-241827) \\ &= -5116320 + 244512 + 37913.6 \\ &= -4833894 \text{ kJ/kmol octane} \end{aligned} \quad (12.120)$$

ALTERNATIVE METHOD FOR CALCULATING THE ENERGY RELEASED BY COMBUSTION

The energy released from partial combustion can be calculated using Hess' law. In this case, from Table 9.4,

$$\begin{aligned} \Delta \tilde{U}_0 &= \sum_{\text{Products}} \Delta U_0 - \sum_{\text{Reactants}} \Delta U_0 \\ &= 7.136(\Delta U_0)_{\text{CO}_2} + 8.84322(\Delta U_0)_{\text{H}_2\text{O}} + 0.846(\Delta U_0)_{\text{CO}} - (\Delta U_0)_{\text{C}_8\text{H}_{18}} \\ &= 7.136 \times (-393405) + 8.84322 \times (-239082) + 0.846 \times (-113882) - (-74897)^* \\ &= -4943040 \text{ kJ/kmol C}_8\text{H}_{18} \text{ burned} \end{aligned} \quad (12.121)$$

This value can be related to the energy released at the standard temperature of 25°C by the following equation (*note, the fuel properties have been based on methane because those of octane were not available).

$$\begin{aligned}
-(\tilde{Q}_v)_s &= -\Delta\tilde{U}_0 + [U_P(T_s) - U_P(T_0)] - [U_R(T_s) - U_R(T_0)] \\
&= -4943040 + 7.136 \times 7041.6 + 8.84322 \times 7223.3 + 0.846 \times 6011.8 \\
&\quad + 0.15678 \times 6043.1 + 1.8994 \times 6032.0 + 52.222 \times 6025.8 \\
&\quad - (5779 + 13.889 \times [6032.0 + 3.76 \times 6025.8]) \\
&= -4895205 \text{ kJ/kmol C}_8\text{H}_{18} \text{ burned}
\end{aligned} \tag{12.122}$$

This is within 1.25% of that calculated from the internal energy of reaction and the difference is because data were taken from different sources.

Evaluating the energy terms for the reactants gives

$$[U_R(T_R) - U_R(T_s)] = 335014 \text{ kJ}$$

Constituent	C ₈ H ₁₈	O ₂	N ₂
u_{500}	45783	10574.8	10356.1
u_{298}	0	6032.0	6025.8
Difference	45783	4542.8	4330.3
n	1.0	13.889	52.222

Hence, the energy of the products, based on the evaluated degrees of dissociation, must be

$$\begin{aligned}
U_P(T_P) - U_P(T_s) &= -(\tilde{Q}_v)_s + [U_R(T_R) - U_R(T_s)] \\
&= 4833894 + 335014 \\
&= 5168908 \text{ kJ}
\end{aligned} \tag{12.123}$$

Evaluating the energy contained in the products at 2800 K gives

$$U_P(T_P) - U_P(T_s) = 5260072.5 \text{ kJ}$$

Constituent	CO ₂	H ₂ O	CO	H ₂	O ₂	N ₂
u_{2800}	127154.9	100470.8	71512.4	66383.6	75548.1	70754.1
u_{298}	7041.6	7223.3	6011.8	6043.1	6032.0	6025.8
Difference	120113.3	93247.5	65500.5	60340.5	69516.1	64728.4
n	7.1360	8.84322	0.864	0.15678	1.8994	52.222

This shows that the products at 2800 K contain more energy than was available from the energy released by the fuel and hence the energy equation has not been satisfied. It is necessary to repeat the whole calculation with a lower temperature guessed for the products. Rather than do a number of

iterations the value obtained from a computer program will be used immediately, and it will be shown that this gives good agreement in the energy equation; $T_P = 2772$ K will be used.

At $T_P = 2772$ K, the values of equilibrium constant can be obtained from the tables by linear interpolation.

$$\begin{aligned} K_{p_{r1}} &= 8.14828 + \frac{22}{50} \times (6.58152 - 8.14828) = 7.4589 \\ K_{p_{r2}} &= 6.72829 + \frac{22}{50} \times (6.82925 - 6.72829) = 6.7727 \end{aligned} \quad (12.124)$$

Substituting these values gives

$$\frac{55.6352 \times 10 \times 2772}{67.111 \times 500} = \frac{(1 - \alpha_1)^2}{\alpha_1^2 (1.389 + 4\alpha_1 + 4.5\alpha_2)} \quad (12.125)$$

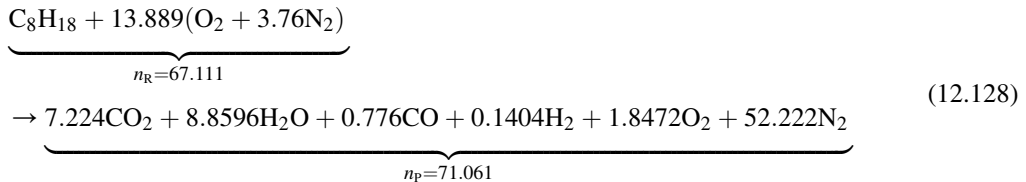
and hence

$$183.84\alpha_1^3 + \alpha_1^2(62.838 + 206.82\alpha_2) + 2\alpha_1 - 1 = 0 \quad (12.126)$$

Assuming $\alpha_2 = 0$ for the initial iteration gives $\alpha_1 = 0.099$. Recalculation around the loop results in the values

$$\begin{aligned} \alpha_1 &= 0.097 \\ \alpha_2 &= 0.0156 \end{aligned} \quad (12.127)$$

which give a chemical equation of



The energy released by the fuel becomes

$$\begin{aligned} (\tilde{Q}_v)_s &= (Q_v)_s - 0.097 \times 8 \times (-283000) - 0.0156 \times 9 \times (-241827) \\ &= -5116320 + 219608 + 33952.5 \\ &= -4862759.5 \text{ kJ/kmol octane} \end{aligned} \quad (12.129)$$

Hence, the energy of the products, based on the evaluated degrees of dissociation, must be

$$\begin{aligned} U_P(T_P) - U_P(T_s) &= -(Q_v)_s + [U_R(T_R) - U_R(T_s)] \\ &= 4862599.5 + 335014 \\ &= 5197613.5 \text{ kJ} \end{aligned} \quad (12.130)$$

Evaluating the energy contained in the products at 2772 K gives

$$U_P(T_P) - U_P(T_s) = 5195240 \text{ kJ}$$

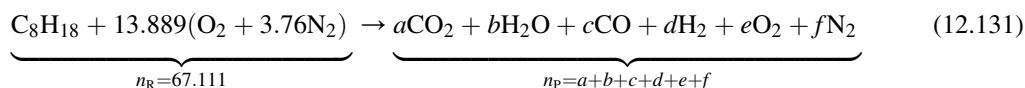
Constituent	CO ₂	H ₂ O	CO	H ₂	O ₂	N ₂
u_{2772}	125654.9	99196.2	70702.8	65594.3	74678.0	69948.5
u_{298}	7041.6	7223.3	6011.8	6043.1	6032.0	6025.8
Difference	118613.3	91972.9	64690.8	59551.2	68646.0	63922.7
n	7.2240	8.8596	0.776	0.1404	1.8472	52.222

These values are within 0.05% and hence satisfy the energy equation.

ALTERNATIVE METHOD FOR CALCULATING THE CHEMICAL EQUATION

The approach used above to calculate the coefficients in the chemical equation was based on the degrees of dissociation of the two reactions occurring in this example. It was shown previously that this approach is often the best for manual solution, but that a more general approach, in which a system of simultaneous equations is developed, is better for computer solution. This second method will be outlined below for one of the steps in the previous example.

First, Eqn (12.109) can be replaced by



If the first iteration of the previous approach is used, then $T_P = 2800 \text{ K}$ and, as given in Eqn (12.110),

$$K_{p_{r1}} = \frac{p_{\text{rCO}_2}}{p_{\text{rCO}} p_{\text{rO}_2}^{1/2}} = 6.58152$$

$$K_{p_{r2}} = \frac{p_{\text{rCO}} p_{\text{rH}_2\text{O}}}{p_{\text{rCO}_2} p_{\text{rH}_2}} = 6.8295$$

Now, by definition,

$$K_{p_{r1}} = \frac{p_{\text{rCO}_2}}{p_{\text{rCO}} p_{\text{rO}_2}^{1/2}} = \frac{a}{c e^{1/2}} \frac{n_P^{1/2}}{p_P^{1/2}} p_0^{1/2} \quad (12.132)$$

which gives

$$K_{p_{r1}}^2 = \frac{a^2}{c^2 e} \frac{n_P}{p_P} p_0 \quad (12.133)$$

For the water gas reaction

$$K_{p_{r2}} = \frac{p_{\text{rCO}} p_{\text{rH}_2\text{O}}}{p_{\text{rCO}_2} p_{\text{rH}_2}} = 6.8295 = \frac{cb}{ad} \quad (12.134)$$

and the total amount of substance in the products is

$$n_P = a + b + c + d + e + f \quad (12.135)$$

Considering the atom balances gives

$$\text{Carbon:} \quad 8 = a + c \text{ giving } c = 8 - a \quad (12.136a)$$

$$\text{Hydrogen:} \quad 18 = 2b + 2d \text{ giving } b = 9 - d \quad (12.136b)$$

$$\begin{aligned} \text{Oxygen:} \quad 27.778 &= 2a + b + c + 2e \\ \text{giving } e &= 13.889 - a - (b + c)/2 \end{aligned} \quad (12.136c)$$

$$\text{Nitrogen:} \quad f = 52.223 \quad (12.136d)$$

From the perfect gas law

$$\frac{n_P}{p_P} = \frac{n_R T_R}{p_R T_P}, \quad (12.137)$$

giving Eqn (12.133) as

$$K_{p_1}^2 = 43.3164 = \frac{a^2}{c^2 e} \frac{n_R T_R}{p_R T_P} p_0 \quad (12.138)$$

Equation (12.138) is a member of a nonlinear set of equations in the coefficients of the chemical equation. One way to solve this is to make an assumption about the relative magnitude of d and the other parameters. If it is assumed that d is small compared to the other parameters in Eqn (12.131), then Eqn (12.138) becomes a cubic equation in a . This is equivalent to assuming that α_2 is small compared to α_1 , as was assumed in the previous calculation. If Eqns (12.136(a)–(c)) are substituted into Eqn (12.138), with the assumption that $d = 0$, then Eqn (12.138) becomes

$$(8 - a)^2 (5.389 - a/2) = \frac{a^2}{K_{p_1}^2} \frac{n_R T_R}{p_R T_P} p_0 = \frac{a^2}{43.3164} \frac{67.111 \times 500}{10 \times 2800} \times 1 = 0.027667 a^2, \quad (12.139)$$

giving

$$344.896 - 118.224a + 13.3613a^2 - a^3/2 = 0 \quad (12.140)$$

The solution to Eqn (12.140) relevant to this problem is $a = 7.125$; giving $c = 8 - a = 0.875$ and $b = 9$. It is now possible to check if this result satisfies the equilibrium condition for the water gas reaction, viz. Equations (12.134), which gives

$$d = \frac{cb}{aK_{p_2}} = \frac{0.875 \times 9}{7.125 \times 6.89295} = 0.16184. \quad (12.141)$$

The calculation should now be performed again based on the new value of d given in Eqn (12.141). This produces a new cubic equation in a , similar to that in Eqn (12.140) but with the following coefficients.

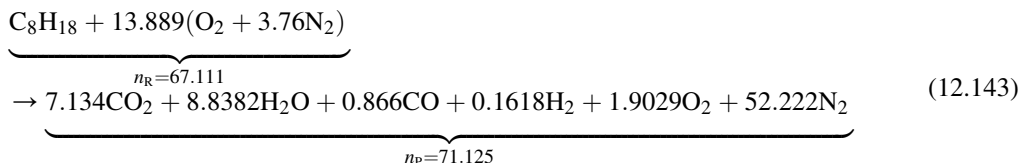
$$350.07 - 119.519a + 13.442a^2 - a^3/2 = 0.$$

The new value of a is 7.134, which is close enough to the actual solution because the value of d compatible with this is

$$d = \frac{cb}{aK_{p_{r2}}} = \frac{0.866 \times 8.8382}{7.134 \times 6.89295} = 0.1556, \quad (12.142)$$

and it can be seen that the change in d will have a small effect on subsequent values of the coefficients.

Hence, the chemical equation is



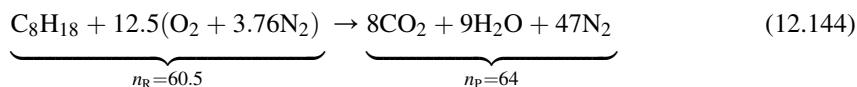
Equation (12.143), which has been calculated from the general equation (Eqn (12.131)), is almost the same as that calculated using the degrees of dissociation in Eqn (12.109). This is to be expected because both approaches are exactly equivalent. This solution requires further iterations to satisfy the energy equation as done in the previous approach.

EXAMPLE 5: A RICH MIXTURE

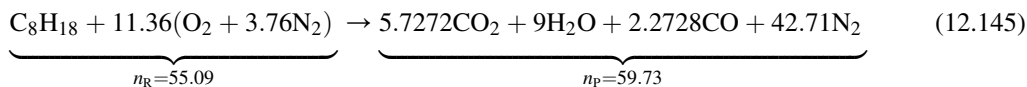
A rich mixture of octane (C_8H_{18}) and air, with an equivalence ratio of 1.1, is ignited at 10 bar and 500 K and burns at constant volume. Assuming the combustion is adiabatic, calculate the conditions at the end of combustion allowing for dissociation of the carbon dioxide and water, but neglecting any formation of NO.

Solution:

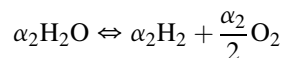
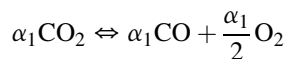
Stoichiometric equation neglecting dissociation



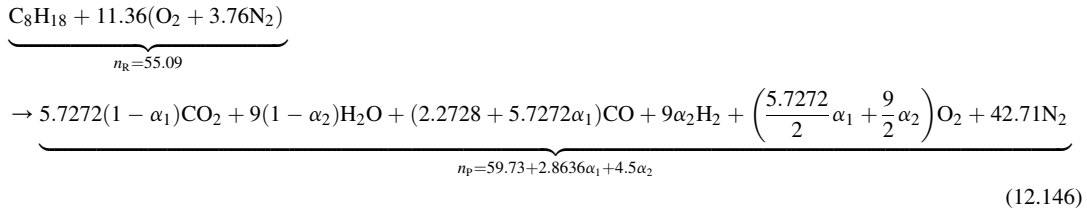
Rich mixture neglecting dissociation



Dissociation equations (Eqns (12.25) and (12.34))



Rich mixture including dissociation is



It can be seen that this is a significantly more complex equation than for the weak mixture. Application of a computer program gives the final temperature and pressure, *without dissociation*, as 2958.6 K and 64.15 bar respectively. The equilibrium constants are

$$K_{p_{r1}} = 6.58152 = \frac{p_{\text{rCO}_2}}{p_{\text{rCO}} p_{\text{rO}_2}^{1/2}} \quad (12.147)$$

$$K_{p_{r2}} = 6.82925 = \frac{p_{\text{rCO}} p_{\text{rH}_2\text{O}}}{p_{\text{rCO}_2} p_{\text{rH}_2}}$$

Substituting for the mole fractions gives

$$p_{\text{CO}_2} = \frac{5.7272(1-\alpha_1)}{n_P} p; \quad p_{\text{CO}} = \frac{(2.2728 + 5.7272\alpha_1)}{n_P} p; \quad p_{\text{O}_2} = \frac{(2.8636\alpha_1 + 4.5\alpha_2)}{n_P} p \quad (12.148)$$

Hence

$$K_{p_{r1}}^2 = 43.3164 = \frac{5.7272^2(1-\alpha_1)^2 n_P}{(2.2728 + 5.7272\alpha_1)^2 (2.8636\alpha_1 + 4.5\alpha_2)} \frac{p_0}{p} \quad (12.149)$$

Similarly

$$p_{\text{H}_2\text{O}} = \frac{9(1-\alpha_2)}{n_P} p; \quad p_{\text{H}_2} = \frac{9\alpha_2}{n_P} p \quad (12.150)$$

and

$$K_{p_{r2}} = \frac{(2.2728 + 5.7272\alpha_1) \times 9 \times (1-\alpha_2)}{9\alpha_2 \times 5.7272(1-\alpha_1)} = \frac{1-\alpha_2}{\alpha_2} \times \frac{(2.2728 + 5.7272\alpha_1)}{5.7272(1-\alpha_1)} \quad (12.151)$$

The $K_{p_{r1}}$ and $K_{p_{r2}}$ equations (Eqns (12.149) and (12.151)) are again nonlinear equations in α_1 and α_2 , and they can be solved in the same manner as before.

The solution to this problem, allowing for dissociation is a final temperature of 2891 K and a final pressure of 62.99 bar. This results in the following degrees of dissociation: $\alpha_1 = 0.0096$, $\alpha_2 = 0.05540$. It is left to the reader to prove these values are correct.

EXAMPLE 6: THE FORMATION OF NITRIC OXIDE

When a mixture of oxygen and nitrogen is heated above about 2000 K, these two elements will join together to form nitric oxide. The elements combine in this way because the energy of formation of

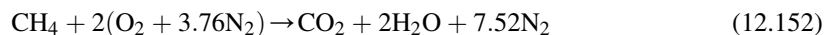
nitric oxide is positive, i.e. the reaction which forms it is endothermic, and hence combination of nitrogen and oxygen tends to reduce the Gibbs energy of the mixture. Note that other compounds tend to dissociate at high temperature because their energies of formation are negative, i.e. the reactions which form them are exothermic.

Example

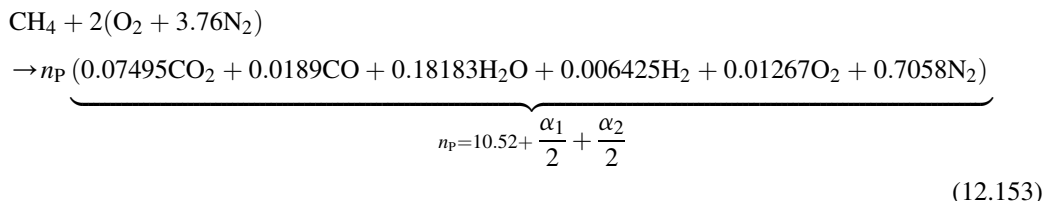
Methane is burned with a stoichiometric quantity of air and achieves a pressure of 99.82 bar and a temperature of 2957 K after combustion, if dissociation of the carbon dioxide and water vapour are taken into account. The mole fractions of the constituents are 7.495% CO₂, 1.890% CO, 18.183% H₂O, 0.6425% H₂, 1.267% O₂ and 70.58% N₂. Calculate the amount of nitric oxide formed at this temperature, neglecting the effect of the NO formation on the dissociation of carbon monoxide and water. Estimate the effect of the NO formation on the temperature of the products. The energy of the reactants, $U_R(T_R) = 179377$ kJ.

Solution:

Chemical equation without dissociation



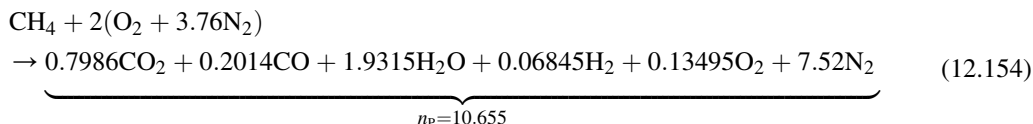
Chemical equation with dissociation



It is possible to evaluate the total amount of substance in the products as follows.

$$0.07495 = \frac{1 - \alpha_1}{n_P}, \text{ and } 0.0189 = \frac{\alpha_1}{n_P}, \text{ giving } n_P = 10.655.$$

and hence



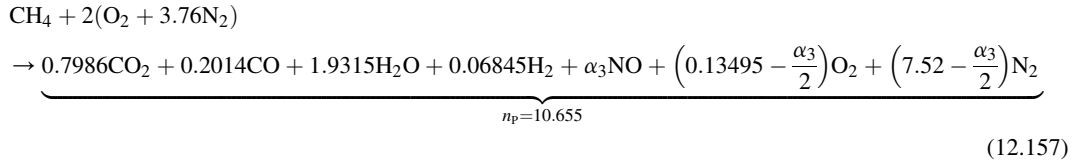
Assume that combination of the nitrogen and oxygen occurs to form nitric oxide.



The temperature of the products is $T_P = 2956$ K, giving

$$K_{p_{r3}} \approx 0.11279 = \frac{P_{r\text{NO}}}{P_{r\text{O}_2}^{1/2} P_{r\text{N}_2}^{1/2}}. \quad (12.156)$$

Adding in the NO equation to the chemical equation gives



The partial pressures of the nitrogen constituents are

$$p_{\text{NO}} = \frac{\alpha_3}{n_p} p; \quad p_{\text{N}_2} = \frac{(7.52 - \alpha_3/2)}{n_p} p; \quad p_{\text{O}_2} = \frac{(0.13495 - \alpha_3/2)}{n_p} p. \quad (12.158)$$

and hence

$$\frac{\alpha_3}{(7.52 - \alpha_3/2)^{1/2}(0.13495 - \alpha_3/2)^{1/2}} = 0.11279 \quad (12.159)$$

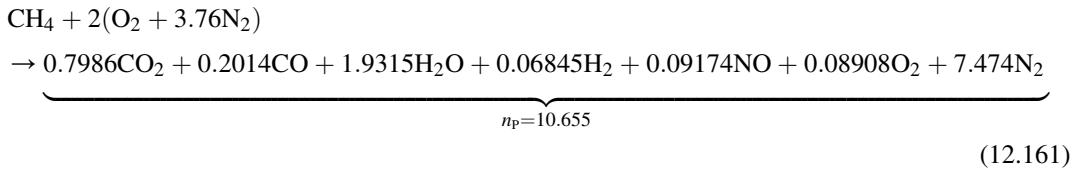
Squaring gives

$$1.00318\alpha_3^2 + 0.04869\alpha_3 - 0.01291 = 0, \quad (12.160)$$

which gives

$$\alpha_3 = 0.09174.$$

Hence, the chemical equation is



It can be seen that the effect of the NO formation is to reduce the amount of oxygen in the products. The effect of this is to upset the equilibrium of the carbon dioxide and water reactions, and the values of α_1 and α_2 will be changed. This will be considered later. First, the effect of the formation on the energy equation will be considered. This effect has already been shown in Fig. 12.7, but a more complex set of reactions was used. It is not possible to demonstrate the more complex calculation in a hand calculation.

The energy released by the original reaction, i.e. neglecting the NO reaction, can be evaluated by considering Hess' equation.

$$\begin{aligned} \Delta \tilde{U}_0 &= \sum_{\text{Products}} U_f - \sum_{\text{Reactants}} U_f \\ &= 0.7985 \times (-393405) + 0.2014 \times (-113882) + 1.9316 \times (-239082) - (-66930) \\ &= -731927 \text{ kJ/kmol CH}_4 \end{aligned}$$

(12.162)

The effect of the formation of NO is to reduce $\Delta\tilde{U}_0$ in the following manner.

$$\begin{aligned}\Delta\tilde{U}_0 &= \sum_{\text{Products}} U_f - \sum_{\text{Reactants}} U_f \\ &= 0.7985 \times (-393405) + 0.2014 \times (-113882) + 1.9316 \times (-239082) + \underbrace{0.09174 \times 89915}_{\text{Formation of NO}} - (-66930) \\ &= -723678 \text{ kJ/kmol CH}_4\end{aligned}\quad (12.163)$$

The energy equation based on 0 K is

$$-\Delta U_0 + [U_R(T_R) - U_R(0)] - [U_P(T_P) - U_P(0)] = 0 \quad (12.164)$$

giving

$$U_P(T_P) = -\Delta U_0 + U_R(T_R) \quad (12.165)$$

Applying the energy equation to the chemical equation neglecting dissociation of NO gives

$$U_P(T_P) = -(-731927) + 179377 = 911304 \text{ kJ} \quad (12.166)$$

Substituting the value of T_P given in the question, viz., 2957 K gives

$$U_P(T_P) = 913268 \text{ kJ}$$

Constituent	CO ₂	H ₂ O	CO	H ₂	O ₂	N ₂
u_{2957}	135615	107643	76050	70837	80457	75270
n	0.7986	1.9315	0.2014	0.06845	0.13495	7.52

This satisfies the energy equation within 0.2%.

Now, consider the case with NO formation. First, the energy of the products is less than in the previous case because the formation of NO has reduced the energy released by combustion. In this case,

$$U_P(T_P) = -(-723678) + 179377 = 903055 \text{ kJ}$$

If it is assumed that the temperature is reduced by the ratio 903055/911304, then a first approximation of the products temperature is 2930 K. In addition, it is necessary to include NO in the products and this is introduced in the table below.

$$U_P(T_P) = 903567 \text{ kJ}$$

Constituent	CO ₂	H ₂ O	CO	H ₂	O ₂	NO	N ₂
u_{2930}	134153	106407	75271	70068	79609	77304	74494
n	0.7986	1.9315	0.2014	0.06845	0.08908	0.09174	7.474

This value of products' energy obviously satisfies the energy equation, and shows that the effect of the formation of NO has been to reduce the products temperature, in this case by about 30 K.

Table 12.3 Equilibrium Constants

Equilibrium Constant K_{pr} Temperature (K)	$\frac{(p/p_0)_{\text{CO}_2}}{(p/p_0)_{\text{CO}}(p/p_0)_{\text{O}_2}^{1/2}}$	$\frac{(p/p_0)_{\text{H}_2\text{O}}}{(p/p_0)_{\text{H}_2}(p/p_0)_{\text{O}_2}^{1/2}}$	$\frac{(p/p_0)_{\text{CO}}(p/p_0)_{\text{H}_2\text{O}}}{(p/p_0)_{\text{CO}_2}(p/p_0)_{\text{H}_2}}$	$\frac{(p/p_0)_{\text{NO}}}{(p/p_0)_{\text{N}_2}^{1/2}(p/p_0)_{\text{O}_2}^{1/2}}$
500	1.06909E+25	7.90482E+22	0.00739	1.5710E-09
550	2.16076E+22	3.78788E+20	0.01753	1.1361E-08
600	1.22648E+20	4.38630E+18	0.03576	5.9112E-08
650	1.54176E+18	1.00209E+17	0.06500	2.3872E-07
700	3.62178E+16	3.90700E+15	0.10788	7.8997E-07
750	1.40361E+15	2.33722E+14	0.16651	2.2291E-06
800	8.17249E+13	1.98055E+13	0.24234	5.5257E-06
850	6.65502E+12	2.23642E+12	0.33605	1.2311E-05
900	7.16841E+11	3.20880E+11	0.44763	2.5096E-05
950	9.77343E+10	5.63412E+10	0.57647	4.7465E-05
1000	1.62821E+10	1.17472E+10	0.72148	8.4233E-05
1050	3.22109E+09	2.83842E+09	0.88120	1.4154E-04
1100	7.39213E+08	7.79082E+08	1.05393	2.2687E-04
1150	1.93024E+08	2.38939E+08	1.23787	3.4904E-04
1200	5.64323E+07	8.07620E+07	1.43113	5.1806E-04
1250	1.82234E+07	2.97385E+07	1.63189	7.4501E-04
1300	6.42591E+06	1.18132E+07	1.83837	1.0419E-03
1350	2.45016E+06	5.02025E+06	2.04895	1.4212E-03
1400	1.00177E+06	2.26609E+06	2.26209	1.8962E-03
1450	4.36021E+05	1.07979E+06	2.47646	2.4800E-03
1500	2.00768E+05	5.40233E+05	2.69084	3.1860E-03
1550	9.72637E+04	2.82471E+05	2.90418	4.0274E-03
1600	4.93402E+04	1.53723E+05	3.11558	5.0168E-03
1650	2.60986E+04	8.67587E+04	3.32426	6.1666E-03
1700	1.43413E+04	5.06191E+04	3.52960	7.4884E-03
1750	8.15991E+03	3.04452E+04	3.73107	8.9931E-03
1800	4.79334E+03	1.88294E+04	3.92824	1.0691E-02
1850	2.89945E+03	1.19480E+04	4.12080	1.2590E-02
1900	1.80179E+03	7.76297E+03	4.30849	1.4700E-02
1950	1.14787E+03	5.15523E+03	4.49113	1.7028E-02
2000	7.48280E+02	3.49343E+03	4.66861	1.9579E-02
2050	4.98289E+02	2.41215E+03	4.84087	2.2359E-02
2100	3.38436E+02	1.69484E+03	5.00786	2.5373E-02
2150	2.34122E+02	1.21032E+03	5.16961	2.8624E-02
2200	1.64752E+02	8.77496E+02	5.32615	3.2115E-02
2250	1.17799E+02	6.45249E+02	5.47753	3.5847E-02
2300	8.54906E+01	4.80785E+02	5.62384	3.9822E-02
2350	6.29132E+01	3.62704E+02	5.76515	4.4039E-02
2400	4.69061E+01	2.76820E+02	5.90158	4.8498E-02

Table 12.3 Equilibrium Constants—cont'd

Equilibrium Constant K_{pr} Temperature (K)	$\frac{(p/p_0)_{\text{CO}_2}}{(p/p_0)_{\text{CO}}(p/p_0)_{\text{O}_2}^{1/2}}$	$\frac{(p/p_0)_{\text{H}_2\text{O}}}{(p/p_0)_{\text{H}_2}(p/p_0)_{\text{O}_2}^{1/2}}$	$\frac{(p/p_0)_{\text{CO}}(p/p_0)_{\text{H}_2\text{O}}}{(p/p_0)_{\text{CO}_2}(p/p_0)_{\text{H}_2}}$	$\frac{(p/p_0)_{\text{NO}}}{(p/p_0)_{\text{N}_2}^{1/2}(p/p_0)_{\text{O}_2}^{1/2}}$
2450	3.54023E+01	2.13590E+02	6.03322	5.3198E-02
2500	2.70287E+01	1.66502E+02	6.16017	5.8137E-02
2550	2.08601E+01	1.31054E+02	6.28255	6.3312E-02
2600	1.62640E+01	1.04097E+02	6.40045	6.8721E-02
2650	1.28029E+01	8.33978E+01	6.51398	7.4361E-02
2700	1.01701E+01	6.73591E+01	6.62323	8.0227E-02
2750	8.14828E+00	5.48240E+01	6.72829	8.6315E-02
2800	6.58152E+00	4.49468E+01	6.82925	9.2620E-02
2850	5.35700E+00	3.71035E+01	6.92618	9.9138E-02
2900	4.39219E+00	3.08294E+01	7.01914	1.0586E-01
2950	3.62613E+00	2.57753E+01	7.10821	1.1279E-01
3000	3.01343E+00	2.89620E+01	7.19343	1.1992E-01
3050	2.51997E+00	2.47329E+01	7.27483	1.2723E-01
3100	2.11989E+00	2.12369E+01	7.35247	1.3473E-01
3150	1.79349E+00	1.83304E+01	7.42636	1.4240E-01
3200	1.52559E+00	1.59006E+01	7.49651	1.5025E-01
3250	1.30444E+00	1.38587E+01	7.56295	1.5826E-01
3300	1.12089E+00	1.21342E+01	7.62566	1.6643E-01
3350	9.67731E-01	1.06707E+01	7.68464	1.7476E-01
3400	8.39304E-01	9.42300E+00	7.73988	1.8322E-01
3450	7.31095E-01	8.35460E+00	7.79136	1.9183E-01
3500	6.39503E-01	7.43587E+00	7.83905	2.0057E-01

12.12 CONCLUDING REMARKS

It has been shown that dissociation is an equilibrium process which seeks to minimise the Gibbs energy of the mixture. In a combustion process, dissociation always reduces the temperatures and pressures achieved (except for very rich mixtures, see Chapter 13), and hence reduces the work output and efficiency of a device.

The thermodynamic theory of dissociation has been rigorously developed, and it will be seen later that this applies to fuel cells also (see Chapter 21).

Dissociation usually tends to break product molecules into intermediate reactant molecules (e.g. CO_2 and H_2O become CO , H_2 and O_2). However, the same theory shows that at high temperatures nitrogen and oxygen will combine to form oxides of nitrogen – a major pollutant.

A wide range of examples has been presented, covering most situations which will be encountered in respect of combustion.

12.13 PROBLEMS

Assume that air consists of 79% N₂ and 21% O₂ by volume.

- P12.1.** A cylinder contains 1 kg carbon dioxide, and this is compressed adiabatically. Show the pressure, temperature and specific volume are related by the equation

$$\frac{1 - \alpha}{\alpha} \sqrt{\frac{(2 + \alpha)}{\alpha}} = K_{p_i} \sqrt{\frac{p}{1.01325}}$$

and

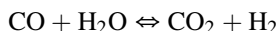
$$pv = \frac{\Re(2 + \alpha)T}{88},$$

where α = degree of dissociation.

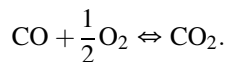
Note that the equilibrium constant for the reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$ is given by

$$K_{p_i} = \frac{(p_{\text{CO}_2}/p_0)}{(p_{\text{CO}}/p_0)(p_{\text{O}_2}/p_0)^{1/2}}, \text{ where } p_0 \text{ is the datum pressure of 1 atm.}$$

- P12.2.** (a) Calculate the equilibrium constant, K_p , at 2000 K at the reference pressure of 1 atm for the reaction



- (b) Calculate the equilibrium constant, K_p , at 2500 K at the reference pressure of 1 atm for the reaction



Also calculate the equilibrium constant at 2500 K and a pressure of 1 bar.

[(a) 4.6686; (b) 27.028 atm^{-1/2}; 27.206 bar^{-1/2}]

- P12.3.** If it is assumed that the enthalpy of reaction, Q_p , is a constant, show that the value of K_p is given by

$$K_p = e^{-Q_p/\Re T + k}$$

where k is a constant.

For a particular reaction $Q_p = -277346$ kJ/kmol and $K_p = 748.7$ at $T = 2000$ K. Evaluate K_p at the temperature of 2500 K.

[26.64]

- P12.4.** A stoichiometric mixture of propane (C₃H₈) and air is burned in a constant volume bomb. The conditions just prior to combustion are 10 bar and 600 K. Evaluate the composition of the products allowing for dissociation if the peak temperature achieved is 2900 K and show that the combustion process is adiabatic (i.e. the heat transfer is small).

The equilibrium constant for the CO_2 reaction at 2900 K is $K_{p_r} = \frac{p_{\text{CO}_2}}{p_{\text{CO}} p_{\text{O}_2}^{1/2}} = 4.50$, and it can be assumed that the degree of dissociation for the water reaction is one quarter of that for the carbon dioxide one. Indicate the processes, including a heat transfer process, on the U - T diagram. The internal energy of propane at 25 °C is 12,380 kJ/kmol, and the internal energies of formation for the various compounds are

$$\text{CO}_2 \quad -391032; \quad \text{H}_2\text{O} \quad -239342; \quad \text{CO} \quad -108052 \text{ kJ/kmol}$$

[0.0916; 0.0229; 0.1450; 0.0076; 0.01527; 0.7176]

P12.5. Methane (CH_4) is burned with 50% excess air. The equilibrium products at a pressure of 10 bar and a temperature of 1600 K contain CO_2 , CO , H_2O , H_2 , O_2 and N_2 . Calculate the partial pressures of these gases, assuming that the partial pressures of CO and H_2 are small. [0.6545; 1.6383×10^{-5} ; 1.3089; 1.0524×10^{-5} ; 0.6545; 7.3822]

P12.6. The exhaust gas of a furnace burning a hydrocarbon fuel in air is sampled and found to be 13.45% CO_2 ; 1.04% CO ; 2.58% O_2 ; 7.25% H_2O ; 75.68% N_2 and a negligible amount of H_2 . If the temperature of the exhaust gas is 2500 K, calculate

- the carbon/hydrogen ratio of the fuel;
- the equivalence ratio;
- the equilibrium constant for the dissociation of CO_2 (show this as a function of pressure) and
- the pressure of the exhaust gas.

[1.0; 0.898; $80.52/p^{1/2}$; 8.874]

P12.7. A weak mixture of propane (C_3H_8) and 50% excess air is ignited in a constant volume combustion chamber. The initial conditions were 1 bar and 300 K and the final composition was 7.87% CO_2 , 0.081% CO , 10.58% H_2O , 0.02% H_2 , 6.67% O_2 and 74.76% N_2 by volume. Evaluate the final temperature and pressure of the products. Prove that the temperature obeys the conservation of energy, if the calorific value of propane is 46440 kJ/kg at 300 K.

The equilibrium constant for the carbon dioxide reaction is given by

$$K_p = \frac{(p_{\text{CO}})^2 p_{\text{O}_2}}{(p_{\text{CO}_2})^2} \quad \text{where} \quad \log_{10} K_p = 8.46 - \frac{28600}{T}, \quad \text{and} \quad T = \text{temperature in K.}$$

The specific heats at constant volume ($c_{v,m}$) of the constituents, in kJ/kmol K, may be taken as

CO_2	$12.7 + 22 \times 10^{-3} T$	H_2O	$22.7 + 8.3 \times 10^{-3} T$
CO	$19.7 + 2.5 \times 10^{-3} T$	N_2	$17.7 + 6.4 \times 10^{-3} T$
O_2	$20.7 + 4.4 \times 10^{-3} T$	H_2	$17.0 + 4.0 \times 10^{-3} T$

C_3H_8 neglect the internal energy in the reactants

The internal energies of formation of the constituents at 300 K are

$$\text{CO}_2 \quad -393 \times 10^3; \quad \text{H}_2\text{O} \quad -241 \times 10^3; \quad \text{CO} \quad -112 \times 10^3 \text{ kJ/kmol}$$

[2250 K; 7.695 bar]

- P12.8.** A mixture of propane and air with an equivalence ratio 0.9 (i.e. a weak mixture) is contained in a rigid vessel with a volume of 0.5 m^3 at a pressure of 1 bar and 300 K. It is ignited and after combustion the products are at a temperature of 2600 K and a pressure of 9.06 bar. Calculate
- the amount of substance in the reactants;
 - the amount of substance in the products and
 - the amount of substance in the products per unit amount of substance supplied in the fuel. [0.02005; 0.02096; 0.0932; 0.1368; 0.01138; 0.00261; 0.02792; 0.7281]
- P12.9.** A stoichiometric mixture of carbon monoxide and air reacts in a combustion chamber, forms exhaust products at 3000 K and 1 bar. If the products are in chemical equilibrium, but no reactions occur between the nitrogen and the oxygen, show that the molar fraction of carbon monoxide is approximately 0.169. The products of combustion now enter a heat exchanger where the temperature is reduced to 1000 K. Calculate the heat transfer from the products per amount of substance of CO_2 in the gases leaving the heat exchanger if dissociation can be neglected at the lower temperature. [−399.3 MJ/kmol CO_2]
- P12.10.** A mixture containing hydrogen and oxygen in the ratio of 2:1 by volume is contained in a rigid vessel. This is ignited at 60°C and a pressure of 1 atm (1.013 bar), and after some time the temperature is 2227°C . Calculate the pressure and the molar composition of the mixture. [5.13 bar; 96.5%; 2.36%; 1.18%]
- P12.11.** A vessel is filled with hydrogen and carbon dioxide in equal parts by volume and the mixture is ignited. If the initial pressure and temperature are 2 bar and 60°C respectively and the maximum pressure is 11.8 bar, estimate
- the maximum temperature;
 - the equilibrium constant, K_p and
 - the volumetric analysis of the products at the maximum temperature.
- Use

$$\log_{10} K_p = 1.3573 - \frac{1354}{T},$$

$$\text{where } K_p = \frac{p_{\text{H}_2\text{O}} p_{\text{CO}}}{p_{\text{H}_2} p_{\text{CO}_2}},$$

and T = temperature in kelvin.

[1965; 4.6573; 0.3417; 0.3417; 0.1583; 0.1583]

- P12.12.** A stoichiometric mixture of hydrogen and air is compressed to 18.63 bar and 845°C . It burns adiabatically at constant volume. Show that the final equilibrium temperature is 3300 K and the degree of dissociation is 8.85%. Calculate the final pressure after combustion. Show the process, including the effect of dissociation, on a U – T diagram. The equilibrium constant is

$$K_{p_r} = \frac{(p_{\text{H}_2\text{O}}/p_0)}{(p_{\text{H}_2}/p_0)(p_{\text{O}_2}/p_0)^{1/2}} = 12.1389$$

at $T = 3300 \text{ K}$.

Use the following internal energies

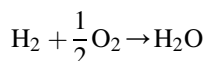
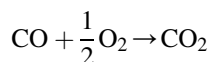
	Internal Energy/(kJ/kmol)			
<i>T</i> (K)	Oxygen, O ₂	Hydrogen, H ₂	Nitrogen, N ₂	Water, H ₂ O
0	0	0	0	−239081.7
1100	25700.3	23065.3	24341.8	
1150	27047.4	24187.6	25579.1	
3300	91379.8	80633.5	85109.6	142527.4

[47.58 bar]

- P12.13.** A mixture containing equal volumes of carbon dioxide (CO₂) and hydrogen (H₂) is contained in a rigid vessel. It is ignited at 60 °C and a pressure of 1 atm, and after some time the temperature is 2227 °C. Calculate the pressure and the molar composition of the mixture.

[7.508 atm; 35.6%; 35.6%; 14.4%; 14.4%]

- P12.14.** A gas turbine combustion chamber receives air at 6 bar and 500 K. It is fuelled using octane (C₈H₁₈) at an equivalence ratio of 0.8 (i.e. weak), which burns at constant pressure. The amount of carbon dioxide and water in the products are 9.993% and 11.37% by volume respectively. Calculate the maximum temperature achieved after combustion and evaluate the degrees of dissociation for each of the following reactions.



Assume the octane is in liquid form in the reactants and neglect its enthalpy; use an enthalpy of reaction of octane at 300 K of −44820 kJ/kg.

[0.0139; 0.00269; 2200 K]

- P12.15.** A mixture of one part by volume of vapourised benzene to 50 parts by volume of air is ignited in a cylinder and adiabatic combustion ensues at constant volume. If the initial pressure and temperature of the mixture are 10 bar and 500 K respectively, calculate the maximum pressure and temperature after combustion (see Chapter 10, P10.1).
- [51.67 bar; 2554 K]
- P12.16.** A gas engine is operated on a stoichiometric mixture of methane (CH₄) and air. At the end of the compression stroke, the pressure and temperature are 10 bar and 500 K respectively. If the combustion process is an adiabatic one at constant volume, calculate the maximum temperature and pressure reached. What has been the effect of dissociation? (See Chapter 10, P10.5.)
- [59.22 bar; 2960 K]
- P12.17.** A gas injection system supplies a mixture of propane (C₃H₈) and air to a spark-ignition engine, in the ratio of volumes of 1:30. The mixture is trapped at 1 bar and 300 K, the volumetric compression ratio is 12:1 and the index of compression, $\kappa = 1.4$. Calculate the equivalence ratio, the maximum pressure and temperature achieved during the cycle, and

also the composition (by volume) of the dry exhaust gas. What has been the effect of dissociation? (See Chapter 10, P10.6.)

[0.79334, 119.1 bar, 2883 K; 0.8463, 0.1071, 0.0465]

- P12.18.** A 10% rich mixture of heptane (C_7H_{16}) and air is trapped in the cylinder of an engine at a pressure of 1 bar and temperature of 400 K. This is compressed and ignited, and at a particular instant during the expansion stroke, when the volume is 20% of the trapped volume, the pressure is 27.06 bar. Assuming that the mixture is in chemical equilibrium and contains only CO_2 , CO , H_2O , H_2 and N_2 , find the temperature and molar fractions of the constituents. This solution presupposes that there is no O_2 in the products; use your results to confirm this.

[2000 K; 0.1037; 0.0293; 0.1434; 0.00868; 0.7148]

- P12.19.** A turbocharged, intercooled compression ignition engine is operated on octane (C_8H_{18}) and achieves constant pressure combustion. The volumetric compression ratio of the engine is 20:1 and the pressure and temperature at the start of compression are 1.5 bar and 350 K respectively. If the air–fuel ratio is 24:1, calculate maximum temperature and pressure achieved in the cycle, taking into account the dissociation of the carbon dioxide and water vapour. Assuming that the combustion gases do not change composition during the expansion stroke, calculate the indicated mean effective pressure ($imep$, $\bar{p}_i$) of the cycle in bar. What has been the effect of dissociation on the power output of the engine? Assume that the index of compression, $\kappa_c = 1.4$, while that of expansion, $\kappa_e = 1.35$ (see Chapter 10, P10.7).

[2487 K; 99.4 bar; 15.10 bar]

- P12.20.** One method of reducing the maximum temperature in an engine is to run with a rich mixture. A spark-ignition engine with a compression ratio of 10:1, operating on the Otto cycle, runs on a rich mixture of octane and air, with an equivalence ratio of 1.2. The trapped conditions are 1 bar and 300 K and the index of compression is 1.4. Calculate, taking into account dissociation of the carbon dioxide and water vapour, how much lower the maximum temperature is under this condition than when the engine was operated stoichiometrically. How has dissociation affected the products of combustion? What are the major disadvantages of operating in this mode? (See Chapter 10, P10.8.)

[3020 K; 3029 K]

- P12.21.** A gas engine with a volumetric compression ratio of 10:1 is run on a weak mixture of methane (CH_4) and air, with $\phi = 0.9$. If the initial temperature and pressure at the commencement of compression are 60 °C and 1 bar respectively, calculate the maximum temperature and pressure reached during combustion at constant volume, taking into account dissociation of the carbon dioxide and water vapour, under the following assumptions

- that 10% of the heat released is lost during the combustion period and
- that compression is isentropic.

Assume the ratio of specific heat, κ , when the compression stroke is 1.4, and the heat of reaction at constant volume for methane is -8.023×10^5 kJ/kmol CH_4 (see Chapter 10, P10.9).

[2737 K; 71.57 bar].

EFFECT OF DISSOCIATION ON
COMBUSTION PARAMETERS

13

Dissociation is an equilibrium process by which the products of combustion achieve the minimum Gibbs energy for the mixture (see Chapter 12). The effect is to cause the products that would be obtained from complete combustion to break down partially into the original reactants, and other compounds or radicals. This can be depicted on a U – T diagram as shown in Fig. 13.1.

It can be seen from Fig. 13.1 that the effect of dissociation is to reduce the temperature of the products after combustion. This, in turn, reduces the amount of energy that can be drawn from the combustion process and reduces the work output of engines.

The other effect of dissociation is to form pollutants. This is particularly true in combustion in engines, when carbon monoxide (CO) can be formed even when the mixture is weak – that is, there is more than sufficient oxygen in the air to completely oxidise both the carbon and hydrogen in the fuel. If chemical kinetics are considered (see Chapter 14), i.e. account is taken of the finite rate by which equilibrium is achieved, then it is possible to show how some of the major pollutants are formed in the quantities measured at the exit from engines. Chemical kinetic effects and dissociation are the sole

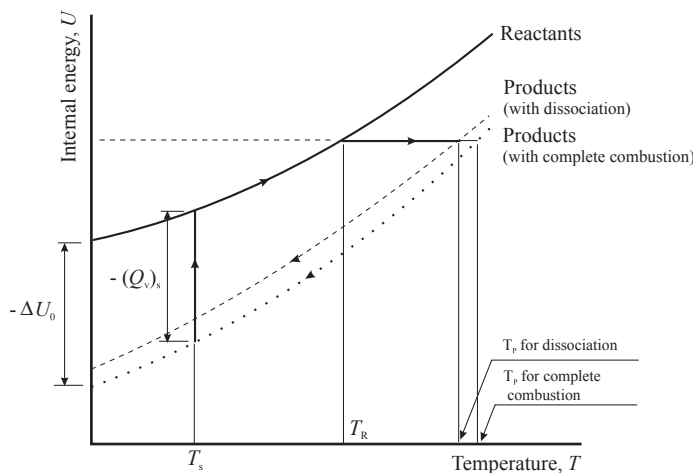


FIGURE 13.1

Internal energy–temperature diagram for combustion both with and without dissociation.

causes of the production of NO_x from fuels which do not contain nitrogen (through the combining of the nitrogen and oxygen in the air), and they also increase the amount of CO during weak and slightly rich combustion. Processes which include chemical kinetics are *not equilibrium processes*, but they attempt to reach equilibrium if there is sufficient time. The results in this chapter do not include the effects of rate kinetics: these are introduced in Chapter 14.

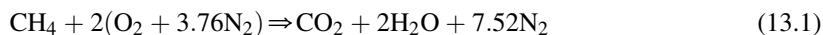
13.1 CALCULATION OF COMBUSTION BOTH WITH AND WITHOUT DISSOCIATION

It is possible for the pressure, temperature and *equilibrium composition* (i.e. neglecting rate kinetics) of various mixtures to be calculated using computer programs, based on the principles outlined in Chapter 12. A computer program, called EQUIL2, based on the enthalpy coefficients given in Chapter 9 has been used to evaluate the results presented in this chapter. The program, which has a range of fuels programmed into it, can be run in a dissociation and non-dissociation mode: it can be accessed by visiting <http://booksite.elsevier.com/9780444633736>. A series of calculations was undertaken using octane (C_8H_{18}) and methane (CH_4) as the fuels. The equivalence ratio was varied from a weak value of $\phi = 0.5$ to a rich one of $\phi = 1.25$. It was assumed that the initial pressure and temperature at entry to the combustion chamber were 1 bar and 300 K respectively, and that the fluid was compressed through a volumetric compression ratio of 12, with an index of compression ($\kappa = c_p/c_v$) of 1.4. Combustion then took place at *constant volume*. This is essentially similar to the combustion that would take place in a reciprocating engine with constant volume combustion at top dead centre (tdc): which is an ‘Otto cycle’ in which the heat addition process associated with the air-standard cycle is replaced by a realistic combustion process. Combustion in this Otto cycle is adiabatic and occurs at constant volume: this is a constant internal energy process, as shown on Fig. 13.1. The principles introduced here can be developed to study the effect of equilibrium on a realistic (finite rate of combustion) cycle, and this is done in Chapter 16.

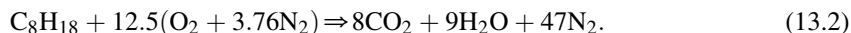
The computer program was written in a manner that enabled it to also be used for constant pressure combustion, e.g. like that occurring in a gas turbine combustion chamber. In this case the enthalpy of both the reactants and products would be equal.

13.2 THE BASIC REACTIONS

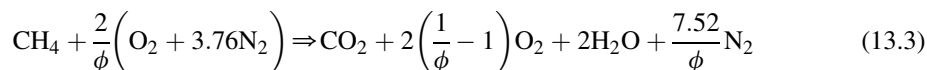
The stoichiometric combustion of methane is defined by the chemical equation:



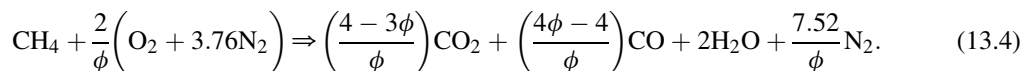
while that for octane is



If the mixture is weak, i.e. there is more oxygen than required for complete combustion of the fuel, then the equation for methane becomes



ϕ is called the equivalence ratio: in this case $\phi \leq 1.0$. For a rich mixture, $\phi \geq 1.0$, if it is assumed that the hydrogen has preferential use of the oxygen, then the equation becomes



(note: Eqn (13.4) is only valid for $1.0 \leq \phi \leq 1.333'$)

It will be assumed for the initial examples that the only dissociation is of the products, carbon dioxide and water, which dissociate according to the equations



and



These equations (Eqns (13.5) and (13.6)) have to be added into the basic equations to evaluate the chemical equation with dissociation. The program does this automatically and evaluates the mole fractions of the products. The approach adopted by the program is the same as that introduced in Chapter 12, when the products of combustion are defined by a set of simultaneous equations. Later in the chapter the dissociation of other compounds will be introduced to give a total of 11 species in the products. The method of solving for these species is outlined by Baruah (Chapter 14) in Horlock and Winterbone (1986).

13.3 THE EFFECT OF DISSOCIATION ON PEAK PRESSURE

In general, dissociation will tend to decrease the pressure achieved during the combustion process (when it occurs in a closed system) because it reduces the temperature of the products. This reduction in pressure is always evident with stoichiometric and lean mixtures, although an increase in pressure over the equivalent situation without dissociation can occur in rich mixtures due to the increase in the amount of substance in the products. Figures 13.2 and 13.3 show that the peak pressure is reduced by

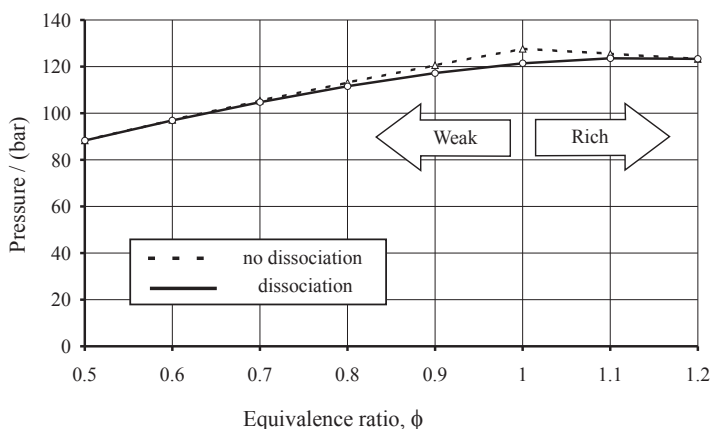


FIGURE 13.2

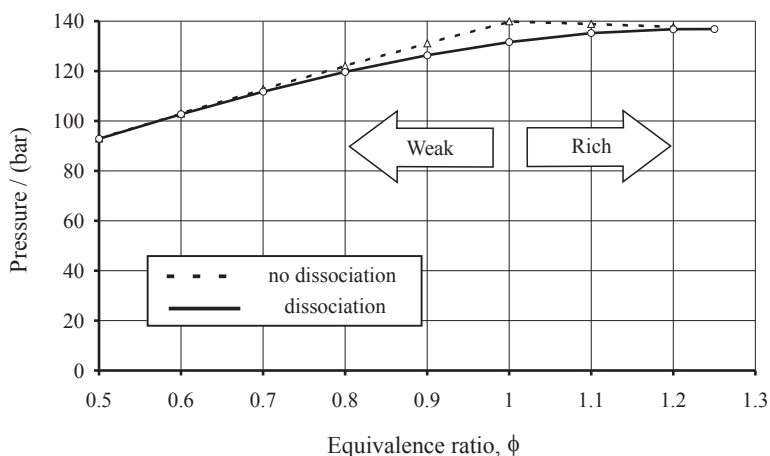
Variation of pressure with equivalence ratio for combustion of methane.

Initial pressure: 1 bar

Initial temperature: 300 K

Compression ratio, r : 12

Compression index, κ : 1.4

**FIGURE 13.3**

Variation of pressure with equivalence ratio for combustion of octane. Initial pressure: 1 bar, Initial temperature: 300 K, Compression ratio: 12, Compression index: 1.4.

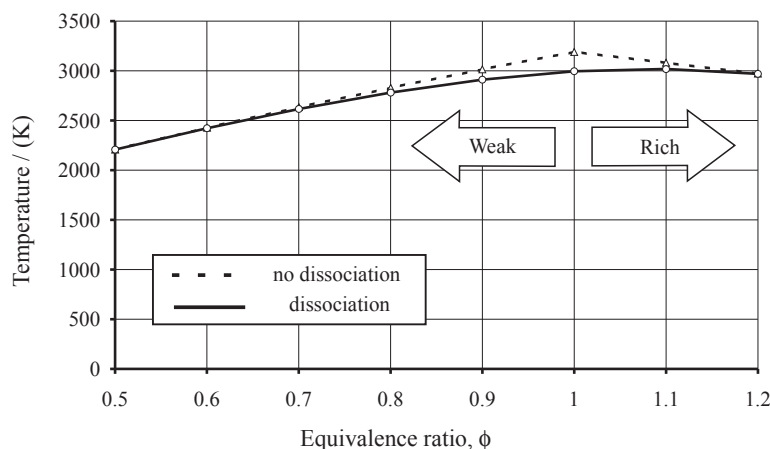
about 8 bar at the stoichiometric air–fuel ratio ($\phi = 1$) with both methane and octane. Dissociation also changes the equivalence ratio at which the peak pressure is achieved. If there is no dissociation then the peak pressure is always reached at the stoichiometric ratio ($\phi = 1$). However, when dissociation occurs the equivalence ratio at which the peak pressure occurs is moved into the rich region ($\phi > 1$). This is because dissociation tends to increase the amount of substance (n_p) in the products, compared to the non-dissociating case. The peak pressure with dissociation occurs at around $\phi = 1.1$ for methane, and around $\phi = 1.25$ for octane. It is interesting to note from the octane results (Fig. 13.3) that the peak pressure achieved both with and without dissociation is almost the same – except it occurs at a different equivalence ratio.

13.4 THE EFFECT OF DISSOCIATION ON PEAK TEMPERATURE

Figures 13.4 and 13.5 show the variation of the peak temperature, produced by an adiabatic combustion process, with equivalence ratio, both with and without dissociation. Dissociation lowers the temperature for both fuels, and moves the point at which the maximum temperature is achieved. In the case of methane the maximum temperature reduces from 3192 K (at stoichiometric) to 3019 K (at about $\phi = 1.1$ – rich), while for octane the values are 3306–3096 K (at $\phi = 1.2$). The effect of such a reduction in temperature is to lower the efficiency of an engine cycle.

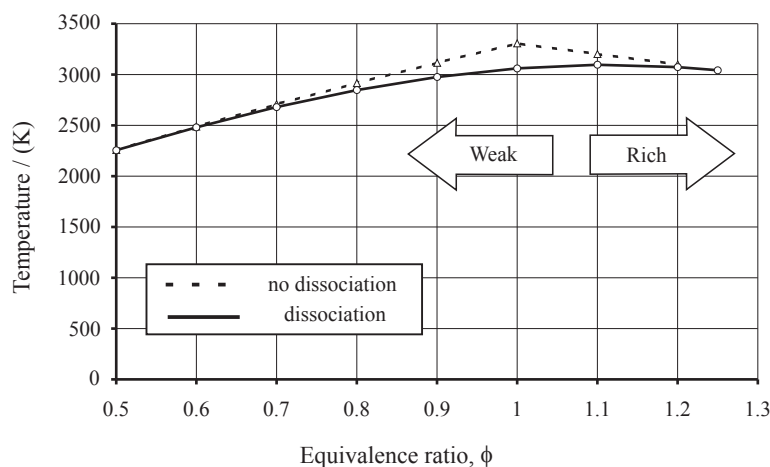
13.5 THE EFFECT OF DISSOCIATION ON THE COMPOSITION OF THE PRODUCTS

The composition of the fuel affects the composition of the products due to the different stoichiometric air–fuel ratios and the different carbon/hydrogen ratios. The stoichiometric air–fuel ratio (by weight) for methane is 17.16, whilst it is 15.05 for octane. The stoichiometric air–fuel ratio remains in the region 14–15 for most of the higher straight hydrocarbon fuels.

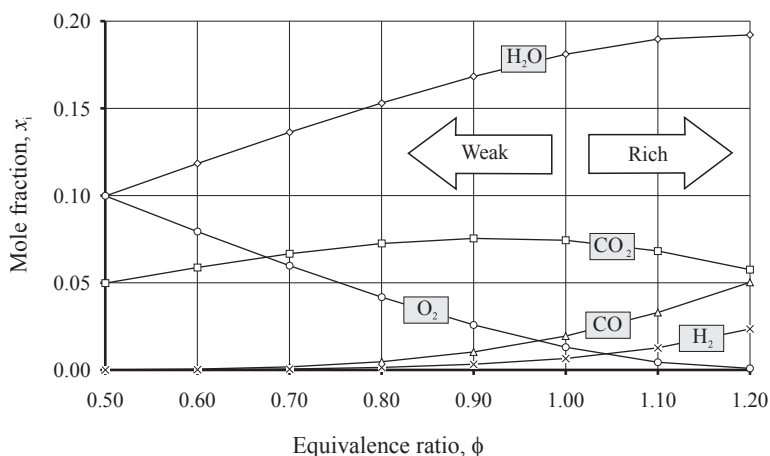
**FIGURE 13.4**

Variation of temperature with equivalence ratio for combustion of methane. Initial pressure: 1 bar, Initial temperature: 300 K, Compression ratio: 12, Compression index: 1.4.

The carbon/hydrogen ratio varies from 0.25 to 0.44 for methane and octane respectively, and this affects the composition of the products, both with and without dissociation. The mole fractions of the products for the combustion of methane (taking account of dissociation) are shown in Fig. 13.6. It can be seen that the largest mole fraction is that of water, which is more than twice that of carbon dioxide: this reflects the greater proportion of hydrogen atoms in the fuel. (Note: the mole fraction of nitrogen,

**FIGURE 13.5**

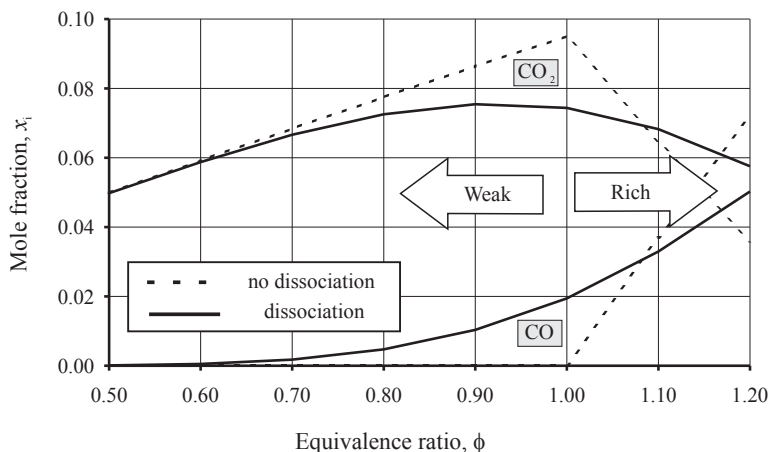
Variation of temperature with equivalence ratio for combustion of octane. Initial pressure: 1 bar, Initial temperature: 300 K, Compression ratio: 12, Compression index: 1.4.

**FIGURE 13.6**

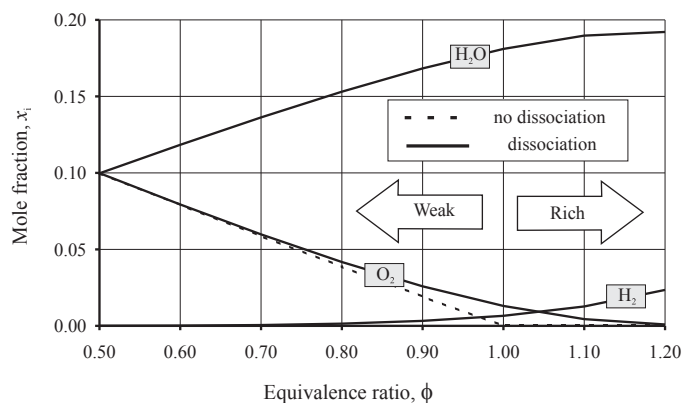
Variation of composition of products with equivalence ratio for combustion of methane. Initial pressure: 1 bar, Initial temperature: 300 K, Compression ratio: 12, Compression index: 1.4.

N₂, has been omitted from Figs 13.6–13.9 because it dominates the composition of the products. The mole fraction remains around 0.79 in all cases.)

The mixture is weak at equivalence ratios of less than unity, and there is excess oxygen for complete combustion up to an equivalence ratio of unity. This can be seen in Figs 13.7 and 13.8, where the composition of the products, both with and without dissociation, has been plotted. It can be seen from Fig. 13.8, which includes the mole fraction of oxygen, that there is no oxygen in the products at

**FIGURE 13.7**

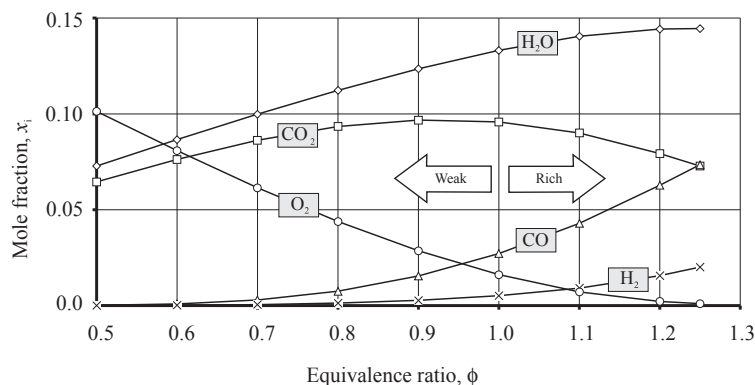
Variation of carbon reactions, with and without dissociation for combustion of methane.

**FIGURE 13.8**

Variations of hydrogen reactions, with and without dissociation for combustion of methane.

equivalence ratios of greater than unity *if there is no dissociation*. However, when there is dissociation the quantity of oxygen in the products is increased, simply due to the reverse reaction. This reverse reaction also produces some unreacted hydrogen, and dissociation causes this to be produced even with weak mixtures. It should be noted that it was assumed that the hydrogen would be oxidised in preference to the carbon in the reactions without dissociation, and this explains the absence of hydrogen in those cases.

The carbon related reactions are shown in Fig. 13.7. When dissociation is neglected the carbon is completely oxidised to carbon dioxide in the weak and stoichiometric mixtures, with no carbon monoxide being formed. After the mixture becomes rich, the level of carbon monoxide increases linearly with equivalence ratio. When dissociation is considered carbon monoxide is formed even in

**FIGURE 13.9**

Variation of composition of products with equivalence ratio for combustion of octane. Initial pressure: 1 bar, Initial temperature: 300 K, Compression ratio: 12, Compression index: 1.4.

the weak mixture region, but surprisingly there is a lower level of carbon monoxide in the rich region than when there is no dissociation. The explanation of this is that the dissociation of the water releases some oxygen that is then taken up by the carbon. The production of carbon monoxide in lean mixtures is the reason for carbon monoxide in the untreated exhaust gas from internal combustion engines even when they are operating stoichiometrically or lean.

Considering the carbon dioxide, it can be seen that this peaks at an equivalence ratio of unity ($\phi = 1$) without dissociation. However, it peaks at an equivalence ratio of around $\phi = 0.9$ – 1.0 (i.e. weak) when there is dissociation, when the peak level of carbon dioxide is only about 75% of that without dissociation.

The mole fractions of products for the combustion of octane are shown in Fig. 13.9. The trends are similar to those for the combustion of methane. The carbon dioxide fraction maximises on the lean side of stoichiometric, at ϕ of about 0.9. It is also noticeable that the mole fractions of water and carbon dioxide are much closer with octane than methane, which simply reflects the higher carbon/hydrogen ratio of octane.

13.6 THE EFFECT OF FUEL ON COMPOSITION OF THE PRODUCTS

Two different fuels were used in the previous analysis of the effect of dissociation on combustion products. Both are paraffinic hydrocarbons, with a generic structure of C_nH_{2n+2} : for methane the value of $n = 1$, while for octane $n = 8$. This means that the carbon/hydrogen ratio varies from 0.25 to 0.44. This has an effect on the amount of CO_2 produced for each unit of energy released (i.e. kg CO_2 /kJ, or more likely kg CO_2 /kWh). The effect of this ratio can be seen in Figs 13.6 and 13.9. The maximum mole fraction of CO_2 released with octane is almost 10%, whilst it peaks at around 7.5% with methane: the energy released per unit mass of mixture is almost the same for both fuels, as shown by the similarity of temperatures achieved (see Figs 13.4 and 13.5). Hence, if it is required to reduce the amount of carbon dioxide released into the atmosphere, it is better to burn fuels with a low carbon/hydrogen ratio. This explains, in part, why natural gas is a popular fuel at this time.

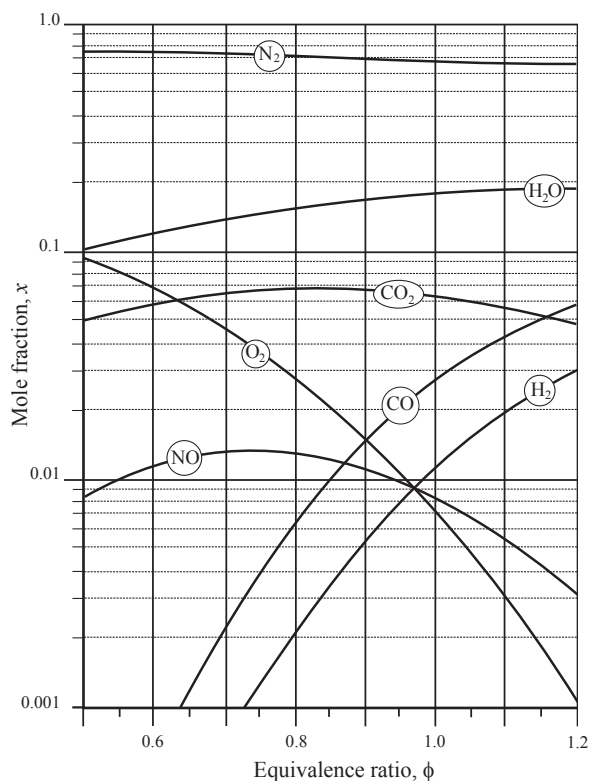
13.7 THE FORMATION OF OXIDES OF NITROGEN

It was shown in Chapter 12 that when air is taken up to high temperatures the nitrogen and oxygen will combine to form oxides of nitrogen, and in particular nitric oxide, NO. It was also stated that it is not enough to simply add the equation



but a chain of reactions including 11 species has to be introduced. This is necessary because the formation of atomic oxygen and nitrogen, and the radical OH play a significant part in the amount of NO produced in the equilibrium mixture.

These equations representing equilibrium of the 11 species have been used to analyse the equilibrium constituents of the products of combustion for the cases considered above, i.e. the combustion of methane and octane in an engine operating on an ‘Otto’ cycle. The results are shown in Figs 13.10 and 13.11. It should be noted that the ordinate axis is in logarithmic form to enable all the important constituents to be shown on a single graph: the numerical results for carbon monoxide, carbon dioxide

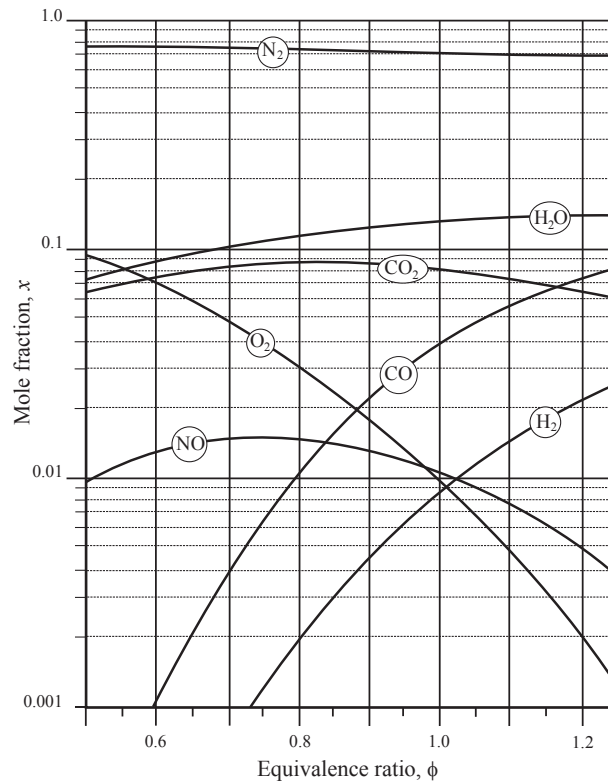
**FIGURE 13.10**

Products of combustion at top dead centre for the combustion of methane in an Otto cycle.

and water are similar to those in Figs 13.8 and 13.9; it is simply the change in scales which has changed the apparent shapes. These results will now be analysed.

Considering Fig. 13.10 first, this shows the equilibrium constituents of the mixture at tdc after adiabatic combustion of methane. The temperatures and pressures achieved by this combustion process are similar to those shown in Figs 13.2 and 13.4, although there will have been a slight reduction in both parameters because the dissociation processes all absorb energy. It can be seen that the maximum values of the mole fraction of both water (≈ 0.19) and carbon dioxide (≈ 0.07) have not been significantly changed by the extra dissociation processes, and the CO_2 still peaks in the vicinity of $\phi = 0.8$ – 0.9 . However, detailed examination shows that the levels of CO_2 and CO have been changed in the rich region, and in this case the mole fraction of CO exceeds that of CO_2 at $\phi = 1.2$. This is because more reactions are competing for the available oxygen, and the carbon is the loser.

Now considering the formation of nitric oxide: it was shown in Chapter 12 that nitrogen and oxygen will tend to combine at high temperatures to produce nitric oxide because the enthalpy of formation of nitric oxide is positive: this combination process will be referred to under the general heading of dissociation, although strictly speaking it is the opposite. This example is different from that shown in Chapter 12, when the variation in the amount of NO with equivalence ratio *at*

**FIGURE 13.11**

Products of combustion at top dead centre for the combustion of octane in an Otto cycle.

constant pressure and temperature was depicted. In this case the peak pressure and temperature achieved in the combustion process are functions of the equivalence ratio, and the variations are shown in Figs 13.2 and 13.4. In fact, the peak temperature increases from about 2200 K at $\phi = 0.5$ –3000 K at $\phi \approx 1.1$; the peak pressure goes from about 87 bar to 122 bar over the same range of equivalence ratio. The increase in temperature will tend to increase dissociation effects in all cases, whereas an increase in pressure will tend to decrease the dissociation effects in cases where dissociation increases the total amount of substance (e.g. the CO_2 reaction): this was discussed in Chapter 12. Hence, the changes occurring in the conditions in the cycle tend to run counter to each other to some extent, although the effect of temperature dominates. The value of mole fraction of NO peaks at around $\phi = 0.7$ –0.8, and obviously does not occur at the highest temperature. This is because the reaction which creates NO is dependent on the amounts of nitrogen (N_2) and oxygen (O_2) present in the mixture, as well as the temperature of the products. At low equivalence ratios there is an abundance of components to react but the temperature is low, whilst at high temperatures the driving force to react is high but there is a deficiency of oxygen. In fact, the nitrogen has to compete with the carbon monoxide and hydrogen for any oxygen that becomes available, and it gains most of the oxygen from the carbon reactions. The maximum level of NO attained is a mole fraction

of about 0.13, and this is equivalent to about 13,000 ppm (parts per million [by mass]): this level is typical of that which would be achieved *at equilibrium conditions* in an engine.

Before considering the effect of the rate of reactions on the actual levels of NO achieved, it is worthwhile seeing the effect of fuel on the level of exhaust constituents. The additional reactions do not have a major effect on the exhaust composition with octane as a fuel, and the CO₂ level is still significantly higher than with methane, as would be expected. However, the general level of NO is higher with octane than methane because of the slightly higher temperatures achieved with this fuel, and the larger proportion of CO₂ which can be ‘robbed’ for oxygen. The maximum levels of NO again occur around $\phi = 0.7$ to 0.8, and result in about 14,000 ppm.

The levels of NO in the exhaust gas of an engine are significantly lower than those calculated above for a number of reasons. First, the reactions occurring in the cylinder are not instantaneous, but are restricted by the rate at which reacting molecules meet: this is known as chemical kinetics or rate kinetics, and is the subject of Chapter 14. The effect of these kinetics is that the instantaneous level of NO in the cylinder does not achieve the equilibrium level, and lags it when it is increasing as shown in Fig. 14.1. When the equilibrium concentration is decreasing the actual level of NO still cannot maintain pace with it, and again lags the level while it decreases down the expansion stroke of the engine, as shown qualitatively in Fig. 14.1; in fact these reactions tend to ‘freeze’ at around 2000 K, and this level then dominates the exhaust value. Second, the combustion process does not take place instantaneously at tdc as shown here, but is spread over a significant period of the cycle and the pressures and temperatures are lower than those attained in the ‘Otto’ cycle: this will reduce the peak equilibrium level of NO.

It is shown on Figs 13.10 and 13.11 that the peak level of NO at equilibrium occurs at around $\phi = 0.7$ –0.8, but experience shows that the maximum values of NO in engine exhaust systems (around 2000–5000 ppm) occur at about $\phi = 0.9$. This can be explained by considering the effect of rate kinetics. It will be shown in Chapter 14 that the rate at which a reaction occurs is exponentially related to temperature. Hence, while the equilibrium level of NO is maximum at $\phi = 0.7$ –0.8 the lower temperature at this equivalence ratio limits the amount of NO produced by the reaction. The peak value of NO occurs at $\phi = 0.9$ because the driving force (the equilibrium concentration) and the rate of reaction combine at this equivalence ratio to maximise production of this pollutant.

13.8 CONCLUDING REMARKS

This chapter has laid the foundation for considering the production of emissions from combustion systems. It delivers essential information for the evaluation of rate kinetics, which is considered in Chapter 14.

The chapter has shown that the composition of typical gas mixtures found in engines at tdc is very dependent on the fuel, equivalence ratio, the temperature and pressure achieved during the process. The early sections, which neglect NO_x, show how the proportions of CO, CO₂, H₂O and H₂ vary with equivalence ratio, and the particular carbon/hydrogen ratio of the fuel used. The effect of dissociation on the peak temperatures and pressures achieved is also discussed.

The final section considered the dissociation processes that produced NO, and showed that the maximum equilibrium concentration of NO was found at relatively weak mixtures, when there was an abundance of ‘free’ oxygen.

CHEMICAL KINETICS

14

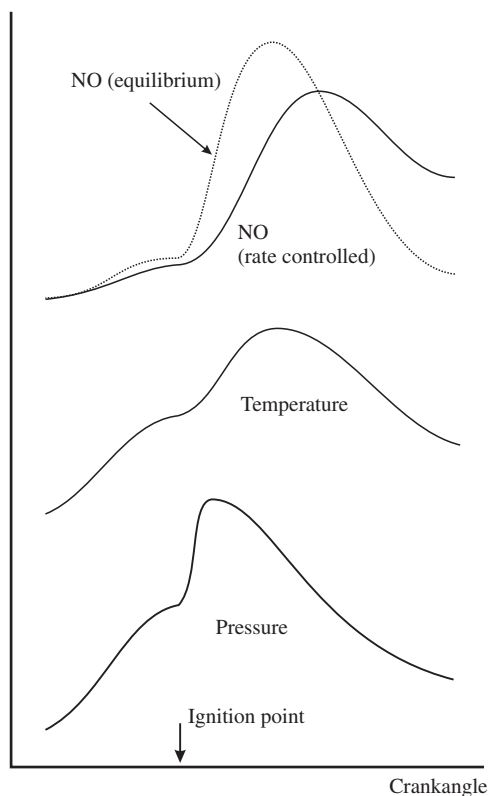
14.1 INTRODUCTION

Up till now it has been assumed that chemical reactions take place very rapidly, and that the equilibrium conditions are reached instantaneously. While most combustion processes are extremely fast, often their speed is not such that combustion can be considered to be instantaneous compared to the physical processes surrounding them. For example, the combustion in a reciprocating engine running at 6000 rev/min has to be completed in about 5 ms if the engine is to be efficient. Likewise combustion in the combustion chamber of a gas turbine has to be rapid enough to be completed before the gas leaves the chamber. Such short times mean that it is not possible for all the gases in the combustion chamber to achieve equilibrium – they will be governed by the *chemical kinetics* of the reactions.

Chemical kinetics play a major role in the formation of pollutants from combustion processes. For example, oxygen and nitrogen will coexist in a stable state at atmospheric conditions and the level of oxides of nitrogen (NO_x) will be negligible. However, if the oxygen and nitrogen are involved in a combustion process then they will join together at the high temperature to form NO_x which might well be *frozen* into the products as the temperature drops. This NO_x is a pollutant which is limited by legislation because of its irritant effects. NO_x is formed in all combustion processes, including boilers, gas turbines, diesel and petrol engines: it can be removed in some cases by the use of catalytic converters.

It was shown in Chapters 12 and 13 that significant dissociation of the normal products of combustion, carbon dioxide and water, can occur at high temperature. The values shown were based on the equilibrium amounts of the substances, and would only be achieved after infinite time; however, the rates at which chemical reactions occur are usually fast and hence some reactions get close to equilibrium even in the short time the gases are in the combustion zone. An analysis of the kinetics of reactions will now be presented.

The effect of chemical, or rate, kinetics can be assessed by considering a simple example. Imagine a spark-ignition engine in which the mixture is compressed prior to ignition by a spark. If the compression temperature is not too high it can be assumed that the reactants do not react before ignition. After ignition the reactants burn to form products at a high temperature, and these are initially compressed further (as the piston continues to rise to top dead centre, and the combustion process continues) before being expanded when the piston moves down and extracts work from the gases. As the pressure increases the temperature of the gas also increases and the products tend to dissociate: they attempt to achieve an equilibrium composition but the speed of the engine is too rapid for this. The effect can be seen in Fig. 14.1, which depicts the way in which the actual level of pollutants attempts to follow the equilibrium level, but lags the equilibrium values. This lag means that the maximum level of

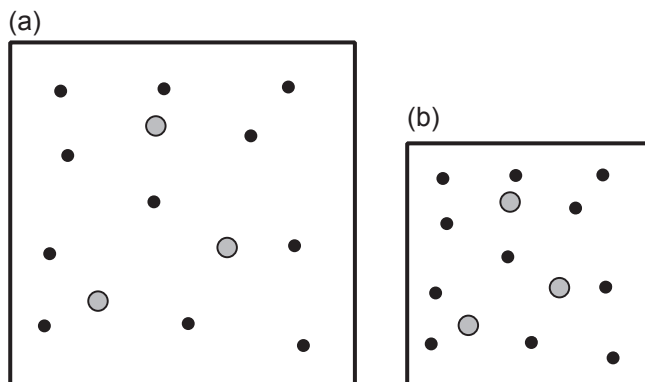
**FIGURE 14.1**

Production of pollutants in equilibrium and chemical kinetically controlled processes.

pollutant (e.g. NO_x) formed does not achieve the maximum equilibrium value, but it also means that the rate of reduction of the pollutants is slower than that of the equilibrium species and the NO_x is usually *frozen* at a level above the equilibrium value of the exhaust gas from the combustion chamber, boiler, gas turbine, diesel engine, etc.

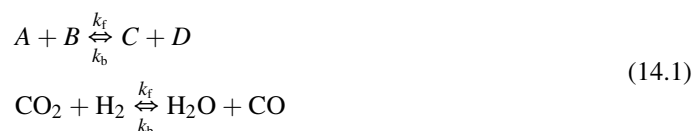
14.2 REACTION RATES

Reaction rates are governed by the movement and breakdown of the atoms or molecules in the gas mixture: reactions will occur if the participating 'particles' collide. The number of collisions occurring in a mixture will be closely related to the number densities (number per unit volume) of the 'particles'. The number density can be defined by the molar concentration, c , which is the amount of substance *per unit volume*. This is obviously a measure of the number of particles per unit volume since each amount of substance is proportional to the number of molecules, this is illustrated in Fig. 14.2. The molar concentration will be denoted by enclosing the reactant or product symbol in [].

**FIGURE 14.2**

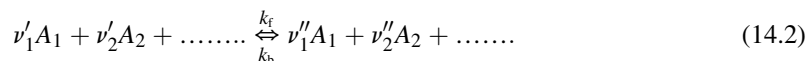
Diagrammatic representation of molar concentration. Molar concentration in (a) is approximately half that in (b).

Reactions occur when two, or more, reactants are capable of reacting. Many simple chemical reactions are second order, e.g.



where the first reaction is a general one and the second is an example based on the water gas reaction (chosen because the same number of reactants and products exist on both sides).

These reactions can be written as



where $A_1, A_2, \dots$ etc. are the elements or compounds involved in the reaction, and $\nu_1, \nu_2, \dots$ etc. are the respective stoichiometric coefficients. Equation (14.2) can be further generalised to



where q = total number of species being considered, ν' represents the stoichiometric coefficients of the reactants, and ν'' that of the products.

In this case q has been taken as the same on both sides of the equation because it is assumed that the same species *can* exist on both sides. If a species does not exist on one of the sides it is represented by a stoichiometric coefficient of zero ($\nu = 0$). e.g.



can be represented by



where

$$\begin{aligned}
 q &= 4 \\
 \nu_{ij} &= \text{stoichiometric coefficient of } i \text{ in reaction } j \\
 A_1 = \text{CO}_2 \quad \nu'_1 &= 1 \quad \nu''_1 = 0 \\
 A_2 = \text{H}_2 \quad \nu'_2 &= 1 \quad \nu''_2 = 0 \\
 A_3 = \text{H}_2\text{O} \quad \nu'_3 &= 0 \quad \nu''_3 = 1 \\
 A_4 = \text{CO} \quad \nu'_4 &= 0 \quad \nu''_4 = 1
 \end{aligned}$$

The law of mass action, which is derived from the kinetic theory of gases, states that the rate of formation, or depletion, of a species is proportional to the product of molar concentrations of the reactants, each raised to the power of its stoichiometric coefficient. Hence the rate of formation of species j , for an elementary reaction, is

$$R_j \propto [A_1]^{\nu_{1j}} [A_2]^{\nu_{2j}} \dots [A_n]^{\nu_{nj}}$$

or

$$R_j \propto \prod_{i=1}^n [A_i]^{\nu_{ij}} \quad \text{for } (j = 1, \dots, s). \quad (14.6)$$

and s = total number of simultaneous reactions.

Equation (14.6) may be written as

$$R_j = k_j \prod_{i=1}^n [A_i]^{\nu_{ij}} \quad \text{for } (j = 1, \dots, s), \quad (14.7)$$

where k_j is the *rate constant for the reaction*. In Eqns (14.1)–(14.5) the reaction was described as having a forward and backward direction, with rates k_f and k_b . The reaction shown in Eqn (14.7) can be described in this way as

$$R_{fj} = k_{fj} \prod_{i=1}^n [A_i]^{\nu'_{ij}} \quad \text{for } (j = 1, \dots, s), \quad (14.8)$$

and

$$R_{bj} = k_{bj} \prod_{i=1}^n [A_i]^{\nu''_{ij}} \quad \text{for } (j = 1, \dots, s). \quad (14.9)$$

The rate of change with time of species i is proportional to the change of the stoichiometric coefficients of A_i in the reaction equation (the system is effectively a first-order one attempting to achieve the equilibrium state). Thus, for the forward direction

$$\left. \frac{d[A_i]_j}{dt} \right|_f = (\nu'_{ij} - \nu''_{ij}) k_{fj} \prod_{i=1}^n [A_i]^{\nu'_{ij}} = \Delta \nu_{ij} k_{fj} \prod_{i=1}^n [A_i]^{\nu'_{ij}} \quad (14.10)$$

and, for the backward direction

$$\left. \frac{d[A_i]}{dt} \right|_b = (\nu''_{ij} - \nu'_{ij}) k_{bj} \prod_{i=1}^n [A_i]^{\nu''_{ij}} = -\Delta \nu_{ij} k_{bj} \prod_{i=1}^n [A_i]^{\nu''_{ij}}. \quad (14.11)$$

Hence the *net rate of formation of A_i* is

$$\left. \frac{d[A_i]}{dt} \right|_{net} = \Delta \nu_{ij} \left[k_{fj} \prod_{i=1}^n [A_i]^{\nu'_{ij}} - k_{bj} \prod_{i=1}^n [A_i]^{\nu''_{ij}} \right]. \quad (14.12)$$

Consider the following rate controlled reaction equation



the net rate of generation of species C is given by

$$\frac{d[C]}{dt} = [k_f [A]^{\nu_a} [B]^{\nu_b} - k_b [C]^{\nu_c} [D]^{\nu_d}]. \quad (14.14)$$

Using the notation $[A]/[A]_e = \alpha$, $[B]/[B]_e = \beta$, $[C]/[C]_e = \gamma$, and $[D]/[D]_e = \delta$, where the suffix e represents equilibrium concentrations, gives

$$d[C]/dt = k_f \alpha^{\nu_a} \beta^{\nu_b} [A]_e^{\nu_a} [B]_e^{\nu_b} - k_b \gamma^{\nu_c} \delta^{\nu_d} [C]_e^{\nu_c} [D]_e^{\nu_d}. \quad (14.15)$$

At equilibrium

$$k_f [A]_e^{\nu_a} [B]_e^{\nu_b} = k_b [C]_e^{\nu_c} [D]_e^{\nu_d} = R_j. \quad (14.16)$$

Therefore the net rate is

$$d[C]/dt = R_j [\alpha^{\nu_a} \beta^{\nu_b} - \gamma^{\nu_c} \delta^{\nu_d}]. \quad (14.17)$$

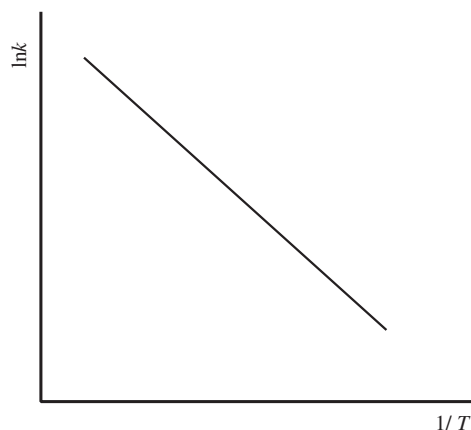
14.3 RATE CONSTANT FOR REACTION, k

The rate constant for the reaction, k , is related to the ability of atoms or ions to combine. In combustion engineering this will usually occur when two or more particles collide. Obviously the collision rate is a function of the number of particles per unit volume, and their velocity of movement: i.e. their concentration and temperature. Most chemical reactions take place between two or three constituents because the probability of more than three particles colliding simultaneously is too small. It has been found experimentally that most reactions obey a law like that shown in Fig. 14.3.

This means that the rate constant for the reaction can be defined by an equation of the form

$$k = A e^{-E/RT}. \quad (14.18)$$

This equation is called the *Arrhenius equation*. The factor A is called the pre-exponential factor, or the frequency factor, and is dependent on the rate at which collisions with the required molecular orientation occur. A sometimes contains a temperature term, indicating that the number of collisions is

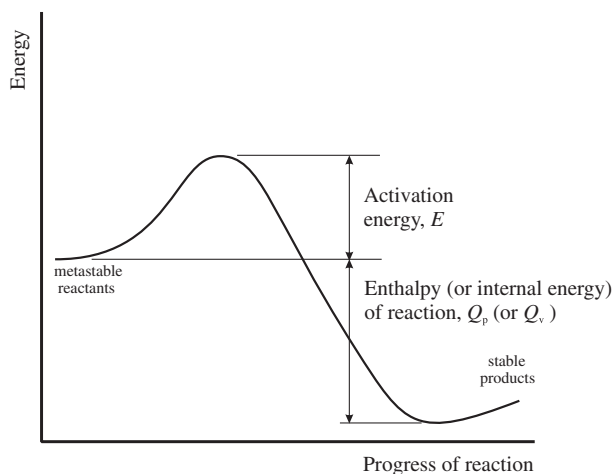
**FIGURE 14.3**

Relationship between reaction rate and temperature.

related to the temperature in those cases. The term E in the exponent is referred to as the *activation energy*. The values of A and E are dependent on the reactions being considered, and some values are introduced below. The significance of the activation energy, E , is shown in Fig. 14.4, where it can be seen to be the energy required to ionise a particular molecule and make it receptive to reacting. It appears in the exponential term because not all activated molecules will find conditions favourable for reaction.

14.4 CHEMICAL KINETICS OF NO

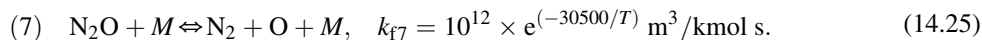
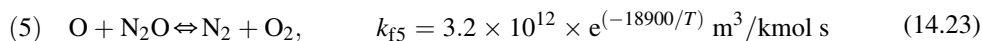
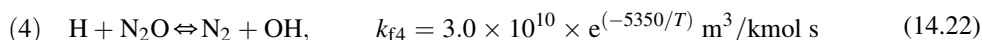
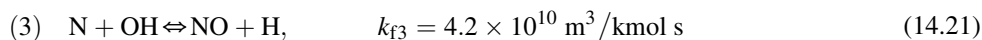
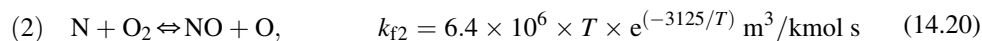
The chemical kinetics for the formation of NO are relatively well understood, and will be developed here. The chemical kinetics for other pollutants can be derived in a similar way if the necessary

**FIGURE 14.4**

Schematic interpretation of activation energy.

reaction rates are available, although it should be recognised that most other pollutants are produced by reactions between the oxygen in the air and a constituent of the fuel (e.g. carbon or sulfur). The formation of NO in combustion processes can occur from two sources: **thermal NO and prompt NO**. Thermal NO is formed by the combination of the oxygen and nitrogen in the air, and will be produced even if there is no nitrogen in the fuel itself. This section will restrict itself to considering thermal NO. Prompt NO is thought to be formed in the flame as a result of the combination of the *nitrogen in the fuel* with the oxygen in the air. The amount of nitrogen in most conventional hydrocarbon fuels is usually very low.

The governing equations for the mechanism of NO formation are (Lavoie et al. (1970))



In these equations the rate constants (k_{fi}) are all in $\text{m}^3/\text{kmol s}$. M is a third body which may be involved in the reactions, but is assumed to be unchanged by the reactions. These equations can be applied to the zone containing 'burned' products, which exists after the passage of the flame through the unburned mixture. It will be assumed that H and OH, and O and O_2 are in equilibrium with each other: these values can be calculated by the methods described in Chapter 12.

14.4.1 RATE EQUATIONS FOR NITRIC OXIDE

The rate of formation of nitric oxide can be derived in the following manner. Consider reaction j , let k_{fj} be the forward reaction rate, k_{bj} the backward rate and R_j the 'one way' equilibrium rate. Also let

$$[\text{NO}]/[\text{NO}]_e = \alpha, \quad [\text{N}]/[\text{N}]_e = \beta, \quad [\text{N}_2\text{O}]/[\text{N}_2\text{O}]_e = \gamma.$$

where suffix e denotes equilibrium values. Then the following expressions are obtained for the burned gas, or product, volume.

14.4.1.1 Expression for Nitric Oxide, NO

From Eqn (14.19) the net rate is

$$-k_{f1} [\text{N}] [\text{NO}] + k_{b1} [\text{N}_2] [\text{O}] = -\alpha\beta k_{f1} [\text{N}]_e [\text{NO}]_e + k_{b1} [\text{N}_2]_e [\text{O}]_e.$$

But

$$k_{f1}[\text{N}]_e[\text{NO}]_e = k_{b1}[\text{N}_2]_e[\text{O}]_e = R_1,$$

so the net rate for Eqn (14.19) becomes $-\alpha\beta R_1 + R_1$.

Using a similar procedure for Eqns (14.20), (14.21) and (14.24) involving NO gives the following expression, which allows for the change in volume over a time step,

$$\frac{1}{V} \frac{d}{dt}([\text{NO}]V) = -\alpha(\beta R_1 + R_2 + R_3 + 2\alpha R_6) + R_1 + \beta(R_2 + R_3) + 2\gamma R_6. \quad (14.26)$$

where V is the volume of the products zone.

14.4.1.2 Expression for Atomic Nitrogen, N

Equations (14.19)–(14.21), which all involve N, give

$$\frac{1}{V} \frac{d}{dt}([\text{N}]V) = -\beta(\alpha R_1 + R_2 + R_3) + R_1 + \alpha(R_2 + R_3). \quad (14.27)$$

14.4.1.3 Expression for Nitrous Oxide N_2O

Equations (14.22)–(14.25) all involve N_2O and can be combined to give

$$\frac{1}{V} \frac{d}{dt}([\text{N}_2\text{O}]V) = -\gamma(R_4 + R_5 + R_6 + R_7) + R_4 + R_5 + \alpha^2 R_6 + R_7. \quad (14.28)$$

A finite time is required for the reactions to reach their equilibrium values; this is called the *relaxation time*. It has been found (Lavoie et al. (1970)) that the relaxation times of reactions (14.27) and (14.28) are several orders of magnitude shorter than those of reaction (14.26), and hence it can be assumed that the $[\text{N}]$ and $[\text{N}_2\text{O}]$ values are at steady state, which means that the right-hand sides of Eqns (14.27) and (14.28) are zero. Then, from Eqn (14.27)

$$\beta = \frac{R_1 + \alpha(R_2 + R_3)}{(\alpha R_1 + R_2 + R_3)}, \quad (14.29)$$

and, from Eqn (14.28)

$$\gamma = \frac{R_4 + R_5 + \alpha^2 R_6 + R_7}{(R_4 + R_5 + R_6 + R_7)}. \quad (14.30)$$

These values can be substituted into Eqn (14.26) to give

$$\frac{1}{V} \frac{d}{dt}([\text{NO}]V) = 2(1 - \alpha^2) \left[\frac{R_1}{1 + \alpha[R_1/(R_2 + R_3)]} + \frac{R_6}{1 + [R_6/(R_4 + R_5 + R_7)]} \right] \quad (14.31)$$

This is the rate equation for NO that is solved in computer programs to evaluate the level of NO in the products of combustion. It should be noted that the variation in the *molar concentration* is a first-order differential equation in time and relates the rate of change of $[\text{NO}]$ to the instantaneous ratio of the actual concentration of NO to the equilibrium value (i.e. α). When the actual level of $[\text{NO}]$ is at the equilibrium level then $\alpha = 1$ and the rate of change of $[\text{NO}] = 0$.

14.4.2 INITIAL RATE OF FORMATION OF NO

Heywood et al. (1971) derived the initial rate of formation of NO in the following way. It can be shown that Eqn (14.31) is the dominant equation for the initial formation of NO. When the nitric oxide (NO) starts to form the value of $\alpha = 0$, and Eqn (14.31) can be written

$$\frac{1}{V} \frac{d}{dt} ([NO]V) = 2R_1 \quad (14.32)$$

$$R_1 = k_{f1}[O]_e[N_2]_e. \quad (14.33)$$

Heywood states that, using a three equation set for the formation of NO, the value of the rate constant for the reaction in the forward direction is

$$k_{f1} = 7.6 \times 10^{13} \times e^{(-38000/T)} \text{ cm}^3/\text{mol s} \quad (14.34)$$

It is necessary to note two factors about Eqn (14.34): the rate constant for the reaction is in $\text{cm}^3/\text{mol s}$, and the exponential term is significantly different from that in Eqn (14.19).

Hence,

$$\frac{1}{V} \frac{d}{dt} ([NO]V) = 2k_{f1}[O]_e[N_2]_e. \quad (14.35)$$

Heywood (1988) also shows that

$$[O]_e = \frac{K_{p(O)}[O_2]_e^{1/2}}{(\mathfrak{RT})^{1/2}}, \quad (14.36)$$

where

$$\begin{aligned} K_{p(O)} &= \text{equilibrium constant for the reaction } \frac{1}{2}O_2 \rightleftharpoons O \\ &= 3.6 \times 10^3 e^{(-31090/T)} \text{ atm}^{1/2} \end{aligned}$$

Substituting this value into Eqn (14.34) gives

$$\frac{d[NO]}{dt} = \frac{6 \times 10^{16}}{T^{1/2}} e^{(-69090/T)} [O_2]_e^{1/2} [N_2]_e \text{ cm}^3/\text{mol s} \quad (14.37)$$

The values of $[O_2]_e$ and $[N_2]_e$, which should be in mol/cm^3 , can be obtained from an equilibrium analysis of the mixture. The value of $[O]_e$ can be calculated from the perfect gas law, because

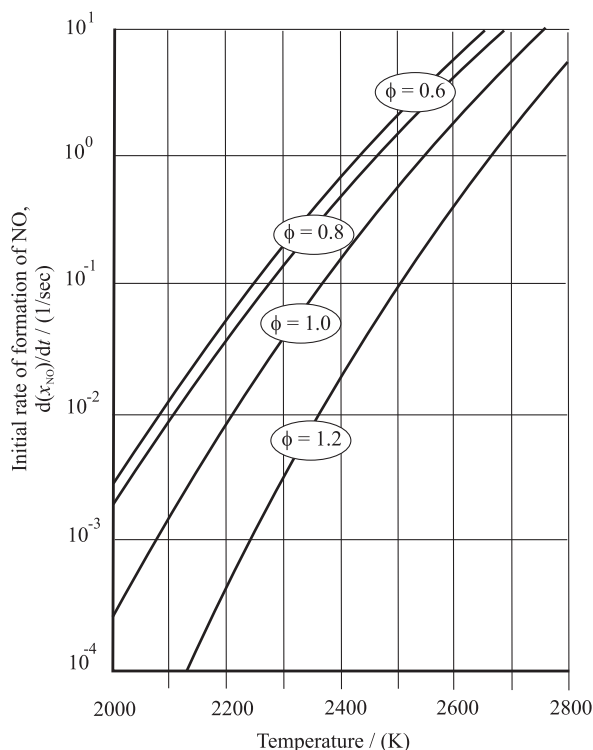
$$[O_2]_e = \frac{n_{[O_2]_e}}{V} = \frac{P_{[O_2]_e}}{\mathfrak{RT}} = \frac{x_{[O_2]_e}P}{\mathfrak{RT}}. \quad (14.38)$$

Likewise,

$$[N_2]_e = \frac{x_{[N_2]_e}P}{\mathfrak{RT}} \quad (14.39)$$

FIGURE 14.5

Initial rate of formation of nitric oxide for combustion of octane at a pressure of 15 bar (conditions as in Heywood (1988)).



Calculating the rate of change of NO with time gives the results shown in Fig. 14.5. The conditions used to evaluate Fig. 14.5 were pressure 15 bar; fuel octane, based on those in Heywood (1988). Using these conditions the equilibrium concentrations of all the reactants were calculated using the techniques described in Chapter 12. This gave the following mole fractions for the condition: $T = 2000$ K; $\phi = 0.6$.

$$x_{\text{O}} = 4.7725 \times 10^{-5}; \quad x_{\text{N}_2} = 7.5319 \times 10^{-1}; \quad x_{\text{O}_2} = 7.7957 \times 10^{-2}.$$

The rate kinetic values, which depict the rate of change of mole fraction of NO were then calculated in the following way. Equation (14.37) is based on cm^3 , mol and seconds rather than SI units of m^3 , kmol and seconds and this must be taken into account.

The mole concentration is defined as

$$[M] = \frac{x_M n}{V} = \frac{x_M}{v_m}, \quad \text{where } M \text{ is a general substance.} \quad (14.40)$$

$$v_m = \frac{\Re T}{p} = \frac{8.3143 \times 2000}{15 \times 10^5} \times 10^6 = 11086 \text{ cm}^3/\text{mol} \quad (14.41)$$

$$[\text{O}]_e = \frac{x_{\text{O}}}{11086} = \frac{4.7725 \times 10^{-5}}{11086} = 4.3051 \times 10^{-9} \text{ mol/cm}^3$$

$$[\text{N}_2]_e = \frac{x_{\text{N}_2}}{11086} = \frac{7.5319 \times 10^{-1}}{11086} = 6.7941 \times 10^{-5} \text{ mol/cm}^3$$

$$[\text{O}_2]_e = \frac{x_{\text{O}_2}}{11086} = \frac{7.7957 \times 10^{-2}}{11086} = 7.0320 \times 10^{-6} \text{ mol/cm}^3.$$

Using a combination of Eqns (14.34) and (14.35) gives

$$\begin{aligned} \frac{d[\text{NO}]}{dt} &= 2 \times 7.6 \times 10^{13} \times e^{(-38000/T)} [\text{O}]_e [\text{N}_2]_e \\ &= 15.2 \times 10^{13} \times e^{(-38000/2000)} \times 4.3051 \times 10^{-9} \times 6.7941 \times 10^{-5} \\ &= 2.491 \times 10^{-7} \text{ mol/cm}^3 \text{ s} \end{aligned} \quad (14.42)$$

A similar value can be obtained from Eqn (14.37), which gives

$$\begin{aligned} \frac{d[\text{NO}]}{dt} &= \frac{6 \times 10^{16}}{T^{1/2}} \times e^{(-69090/T)} [\text{O}_2]_e^{1/2} [\text{N}_2]_e \\ &= \frac{6 \times 10^{16}}{2000^{1/2}} \times e^{(-69090/2000)} \times (7.0320 \times 10^{-6})^{1/2} \times 6.7941 \times 10^{-5} \\ &= 2.4022 \times 10^{-7} \text{ mol/cm}^3 \text{ s}. \end{aligned} \quad (14.43)$$

These values can be converted from mole concentrations to more useful parameters and, in this case, they will be depicted as rate of formation of mole fraction. Rearranging Eqn (14.40) gives

$$x_M = [M]v_m, \text{ where } M \text{ is a general substance.} \quad (14.44)$$

Hence, the rate of production of NO in terms of mol fraction is given by

$$\frac{d(x_{\text{NO}})}{dt} = v_m \frac{d[\text{NO}]}{dt} \quad (14.45)$$

For this condition

$$\frac{d(x_{\text{NO}})}{dt} = 11086 \times 2.491 \times 10^{-7} = 2.762 \times 10^{-3} \text{ s}^{-1} \quad (14.46)$$

The curves on Fig. 14.5 were calculated in this manner. It can be seen that either Eqns (14.34) and (14.35), or Eqn (14.37) gives similar results. This indicates that the dissociation equation, Eqn (14.36) for oxygen is similar to that used in the program for calculating the values of mole fraction of atomic oxygen.

14.5 OTHER KINETICS-CONTROLLED POLLUTANTS

Carbon monoxide (CO) is formed in processes in which a hydrocarbon is burned in the presence of oxygen. If the mixture is rich (i.e. there is more fuel than oxygen available to oxidise it) then there is bound to be some carbon monoxide formed. However, even if the mixture is lean there will be some carbon monoxide due to the dissociation of the carbon dioxide; this was discussed in Chapters 12 and 13.

The amount of carbon monoxide reduces as the mixture gets leaner, until misfire occurs in the combustion device.

Sulfur dioxide (SO_2) is formed by oxidation of the sulfur in the fuel.

Carbon particulates are formed during diffusion combustion because the oxygen in the air is not able to reach all the carbon particles formed during the pyrolysis process while they are at a suitable condition to burn.

14.6 THE EFFECT OF POLLUTANTS FORMED THROUGH CHEMICAL KINETICS

14.6.1 PHOTOCHEMICAL SMOG

Photochemical smogs are formed by the action of sunlight on oxides of nitrogen, and the subsequent reactions with hydrocarbons. Photochemical smogs were first identified in Los Angeles in the mid-1940s, and brought about the stringent legislation introduced in California to control the emissions from automobiles. These smogs act as bronchial irritants and can also irritate the eyes.

Among the pollutants involved in photochemical smogs are ozone, nitrogen dioxide and peroxyacyl nitrate (PAN). The nitrogen dioxide, and other oxides of nitrogen, are primary pollutants produced by dissociation in combustion reactions, and both 'prompt' and 'thermal' NO_x can be involved in the reactions. Ozone and PAN are secondary pollutants produced by the action of sunlight on the primary pollutants and the atmosphere. Glassman (1986) describes in some detail the chemical chain that results in photochemical smog.

Oxides of nitrogen can be measured using non-dispersive infra-red equipment and the values are often quoted in parts per million (ppm), g/m^3 (at normal temperature and pressure), g/kWh or g/mile (if applied to a vehicle engine).

14.6.2 SULFUR DIOXIDE EMISSIONS

Sulfur emissions can only occur if there is sulfur in the fuel. The levels of sulfur in diesel fuel and petrol are being reduced at the refinery in the developed world, and the sulfur levels are often around 0.5% or lower. Sulfur dioxide (SO_x) emissions from vehicles are not a major problem. In the developing world, the levels of sulfur might be significantly higher and then the SO_x emissions from vehicles become a more serious problem. A further advantage of reducing the sulfur content of diesel fuels is that this reduces the synergy between the sulfur and the particulates, and reduces the quantity of particulates produced. The levels of sulfur dioxide produced in some power plant can be extremely high. Diesel engines running on 'heavy fuel', which has a high percentage of sulfur, will produce significant quantities of sulfur dioxide. Power stations running on heavy fuels or some coals will also produce large quantities of sulfur fumes, which smell noxious, cause corrosion and form acid rain. Many coal-burning power stations are now being fitted with *flue gas desulfurisation*, a process by which the sulfur dioxide reacts with limestone to form gypsum. These processes are suitable for stationary plant, but do consume copious amounts of limestone.

Sulfur in fuel has been a problem for a long time and caused high levels of acid rain in the UK up till recently. The move away from coal to natural gas for electricity generation, and the imposition of smokeless zones in urban areas have both reduced the problem to a more acceptable level. Sulfur can be removed from crude oil by catalytic hydrosulfurisation, but is often left in the residual oils which

are used for marine propulsion, power generation, etc. The use of orimulsion, a fuel obtained by water extraction of low-grade oils, also brings worries of high sulfur fuels.

Sulfur in the fuel tends to be oxidised into SO_2 during the combustion process. This can then form sulfurous (H_2SO_3) and sulfuric (H_2SO_4) acids, which have corrosive effects on exhaust stacks, chimneys, etc., before being released into the surrounding atmosphere to form acid rain. It is possible to use flue gas desulfurisation to reduce the levels of SO_x emitted to the atmosphere, but such systems are expensive to install and run. It has been stated that if all the SO_2 emitted from the UK power stations were converted to sulfuric acid the supply of this acid would exceed the UK demand.

14.6.3 PARTICULATE EMISSIONS

These are generated mainly by devices which rely on diffusion burning (see Chapter 15), in which a fuel rich zone can produce carbon particles prior to subsequent oxidation. Hence, particulate emissions tend to come from diesel engines, gas turbines and boiler plant – the particulates generated in gasoline direct injection engines are also becoming a cause for concern. The carbon formed during combustion can be an asset in a boiler because it increases the radiant heat transfer between the flame and the tubes of the boiler: however, it is necessary to ensure that the soot emissions from the stack are not excessive. The carbon formed in diesel engine and gas turbine combustion is not beneficial and it increases the heat transfer to the components, increasing the need to provide cooling. In the past, particulates were grouped under the broad term soot, which was measured by trapping dry soot on a filter paper to give a Bosch smoke number, assessed by the ‘reflectance’ of a filter paper on which the soot has been collected. The words particulates and soot were often used synonymously, but there is a difference in nature between these emissions. Stone (2010) refers to Eastwood (2008) and explains that particulates contain more than simply the dry soot, they often contain polycyclic aromatic hydrocarbons (PAH) that have condensed. The PAH compounds have a tendency to be carcinogenic. While old, or poorly maintained engines used to produce visible black smoke, modern engines produce particles much smaller than 100 nm: these are invisible because they are close to the wavelength of light. While such particles are very small they can be injurious to the lungs: while larger particles (>100 nm) get trapped in the nasal passages the smaller ones (≈ 10 nm) can be trapped deep in the lungs. The level of particulates is strongly affected by the amount of sulfur in the fuel, and increases with sulfur content. Particulates are measured by trapping the particles on glass-fibre filter papers placed in a dilution tunnel, and then weighing the quantity; they might be quoted in g/kWh.

14.6.4 GREENHOUSE EFFECT

The greenhouse effect is the name given to the tendency for the carbon dioxide (CO_2) in the atmosphere to permit the passage of visible (short wavelength) light, while absorbing the long wavelength infra-red transmission from objects on Earth. The effect of this is to cause the temperature of the Earth to increase. The evidence for global warming is not conclusive because the temperature of the Earth has never been constant, as shown by the Ice Ages of the past. There have been significant variations in temperature through the last few centuries, with warm summers at times and the freezing over of the Thames at others. It will take some time to prove conclusively whether global warming is occurring. What is indisputable is that mankind has released a large amount of carbon from its repository in hydrocarbons back into the atmosphere as CO_2 . The most convenient form of energy available to man

is that found as gas, oil or coal. These are all hydrocarbon fuels with the quantity of hydrogen decreasing as the fuel becomes heavier. The combustion of any of these fuels will produce carbon dioxide.

Obviously, the policy that should be adopted is for the amount of CO_2/kW , or CO_2/mile to be reduced. This can be achieved by using more efficient engines, or changing the fuel to, say, hydrogen. The most efficient power station, using conventional fuels, in terms of CO_2/kW is the combined cycle gas turbine plant running on methane. Such plant can achieve thermal efficiencies higher than 50% and claims of efficiencies as high as 60% have been made. Large marine diesel engines also achieve thermal efficiencies of greater than 50%, and other smaller diesel engines can achieve around 50% thermal efficiencies when operating at close to full-load. It is presaged that the inter-cooled regenerated gas turbine will also have efficiencies of this order.

The hydrogen-powered engine produces no carbon dioxide, but does form NO_x . However, the major problem with hydrogen is its production and storage, particularly for mobile applications. California has now introduced the requirement for the zero emissions vehicle (ZEV) which must produce no emissions. At present the only way to achieve this is by an electric vehicle. It has been said that a ZEV is an electric car running in California on electricity produced in Arizona! This is the major problem that engineers have to explain to politicians and legislators: the Second Law states that you cannot get something for nothing, or break-even. Many ideas simply move the source of pollution to somewhere else.

14.6.5 CLEAN-UP METHODS

The clean-up methods to be adopted depend upon the pollutant and the application. As stated above, the exhaust of a power station can be cleaned-up using desulfurisation plant to remove the sulfur compounds. It is also possible to remove the grit from the power station boilers by cyclone and electrostatic precipitators. These plants tend to be large and would be inappropriate for a vehicle, although investigations to adapt these principles to diesel engines are continuing.

All petrol-fuelled cars being sold in the USA, Japan and Europe are fitted with **catalytic converters** to clean up the gaseous emissions. This currently requires that the engine is operated at stoichiometric mixture strength so that there is sufficient oxygen to oxidise the unburned hydrocarbons (uHCs) while enabling the carbon monoxide (CO) and NO_x to be reduced. This means that the engine has to be operated under closed loop control of the air–fuel ratio over a significant operating range, and this is achieved by fitting a λ sensor (which senses the fuel–air equivalence ratio) in the exhaust system. The error signal from the sensor is fed back to the fuel injection system to change the mixture strength. The need to operate the engine at stoichiometric conditions at all times has a detrimental effect on the fuel consumption, and investigations into lean operation (reducing) catalysts are being undertaken. These include the use of exhaust gas recirculation and more complex combustion chambers to enable the engine to run smoothly at weak mixtures. This has two effects: first, the temperatures achieved in the cylinder are not as high as with stoichiometric combustion and, second, it is possible to achieve low powers without throttling the engine as much.

At present it is not possible to use catalytic converters on diesel engines because they always operate in the lean burn regime. This causes a problem because there is no mechanism for removing the NO_x produced in the diesel engine combustion process, and it has to be controlled in the cylinder

itself. Lean burn catalysts, based on zeolites, are currently under research and will have a major impact on engine operation – both spark-ignition and diesel.

Another pollutant from diesel engines is the particulates. These are a significant problem and attempts have been made to control them by traps. Cyclone traps are being investigated, as well as gauze-based devices. A major problem is that after a short time the trap becomes full and the carbon has to be removed. Attempts have been made to achieve this by burning the particulates, either by self-heating or external heating. At present this area is still being investigated.

Engine clean-up methods are discussed in more detail in Stone (2012).

14.6.6 OTHER METHODS OF PRODUCING POWER FROM HYDROCARBON FUELS

All of the devices discussed above, i.e. reciprocating engines, gas turbines, steam turbines, etc., produce power from hydrocarbon fuels by using the energy released from the combustion process to heat up a working fluid to be used in a 'heat engine'. Hence, all of these devices are limited by the Second Law efficiency of a heat engine, which is itself constrained by the maximum and minimum temperatures of the working cycle. It was shown in Chapters 2 and 4 that the maximum work obtainable from the combustion of a hydrocarbon fuel was equal to the change in Gibbs energy of the fuel as it was transformed from reactants to products: if there was some way of releasing all of this energy to produce power, then a Second Law efficiency of 100% would be achievable. A device which can perform this conversion is known as a **fuel cell**: this obeys the laws of thermodynamics but, because it is not a heat engine, it is not constrained by the Second Law efficiency of heat engines. Fuel cells are discussed in Chapter 21.

14.7 CONCLUDING REMARKS

This is the first time non-equilibrium thermodynamics has been introduced. It has been shown that, while most thermodynamics processes are extremely rapid, it is not always possible for them to reach equilibrium in the time available.

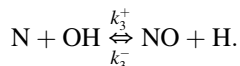
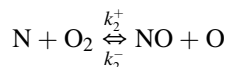
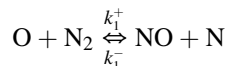
The effect of rate kinetics on the combustion reactions is that some of the reactions do not achieve equilibrium and this can be a major contributor to pollutants. The rate equations for nitric oxide have been developed.

Finally, the pollutants caused by combustion have been introduced, and their effects have been described.

14.8 PROBLEMS

- P14.1** A reaction in which the pre-exponential term is independent of temperature is found to be a 100 times faster at 200 °C than it is at 25 °C. Calculate the activation energy of the reaction. What will be the reaction rate at 1000 °C?
[30,840 kJ/kmol; 13,814]
- P14.2** A chemical reaction is found to be 15 times faster at 100 °C than at 25 °C. Measurements show that the pre-exponential term contains temperature to the power of 0.7. Calculate the activation energy of the reaction. What will be the reaction rate at 700 °C?
[31,433 kJ/kmol; 15,204]

P14.3 The rate of formation of nitric oxide (NO) is controlled by the three reversible chemical reactions



Use the steady state approximation for the nitrogen atom concentration and the assumption of partial equilibrium for the reactions governing the concentrations of O, O₂, H and OH show that

$$\beta = \frac{\delta R + \alpha}{\alpha R + 1}$$

where $\beta = [\text{N}]/[\text{N}]_e$, $\delta = [\text{N}_2]/[\text{N}_2]_e$, $\alpha = [\text{NO}]/[\text{NO}]_e$, $R = R_1/(R_2 + R_3)$, and R_j is the equilibrium reaction rate of reaction j , and $[]$ denotes the molar concentration, and $[]_e$ is the equilibrium molar concentration. Derive an expression for $d[\text{NO}]/dt$ in terms of R_1 , β , α and δ .

At a particular stage in the formation of nitric oxide the values of R and α are 0.26 and 0.1 respectively. Why is $\delta = 1$ likely to be a good approximation in this case? What is the error if the rate of formation of NO is evaluated from the larger approximation $d[\text{NO}]/dt = 2R_1$, rather than the equation derived in this question?

[3.64%]

P14.4 The rate of change of mole concentration of constituent A in a chemical reaction is expressed as

$$\frac{d[\text{A}]}{dt} = -k[\text{A}]^n.$$

While mole concentration is the dominant property in the reaction it is much more usual for engineers to deal in mole fractions of the constituents. Show that the rate of change of mole fraction of constituent A is given by

$$\frac{dx_A}{dt} \propto -kx_A^n \rho^{n-1}.$$

where ρ = density. Also show how the rate of change of mole fraction is affected by pressure. $[dx_A/dt \propto p^{n-1}]$

COMBUSTION AND FLAMES

15

15.1 INTRODUCTION

Combustion is the mechanism by which the chemical (bond) energy (see Chapter 11) in a ‘fuel’ can be converted into thermal energy, and possibly mechanical power. Most combustion processes require at least two components in the reactants – usually a *fuel* and an *oxidant*. The chemical bonds of these reactants are rearranged to produce other compounds referred to as *products*. The reaction takes place in a *flame*. There are three parameters which have a strong influence on combustion: *temperature*, *turbulence* and *time*. In designing combustion systems attention must be paid to optimising these parameters to ensure that the desired results are achieved. In reciprocating engines the time available for combustion is limited by the operating cycle of the engine, and it is often necessary to increase the turbulence to counterbalance this effect. In furnaces the time available for combustion can be increased by lengthening the path taken by the burning gases as they traverse the chamber.

There are two basically different types of flame: *premixed* and *diffusion*. An example of premixed flames occurs in conventional spark-ignition (petrol, natural gas, hydrogen) engines: see Chapter 16. Ignition is initiated by means of a spark, which ignites a small volume of the charge in the vicinity of the spark plug; this burning region then spreads through the remaining charge as a flame front. This type of combustion mechanism can be termed *flame traverses charge*, and once combustion has commenced it is very difficult to influence its progress. Diffusion flames occur in situations of heterogeneous mixing of the fuel and air, when fuel-rich and fuel-lean regions of mixture exist at various places in the combustion chamber. In this case the progress of combustion is controlled by the ability of the fuel and air to mix to form a combustible mixture – it is controlled by the *diffusion* of the fuel and air. An example of this type of combustion is met in the diesel engine, where the fuel is injected into the combustion chamber late in the compression stroke: see Chapter 16. The momentum of the fuel jet entrains air into itself, and at a suitable temperature and pressure part of the mixture spontaneously ignites. A number of ignition sites may exist in this type of engine, and the fuel–air mixture then burns as the local mixture strength approaches a stoichiometric value. This type of combustion is controlled by the mixing (or diffusion) processes of the fuel and air. Other examples of diffusion combustion are gas turbine combustion chambers, and boilers and furnaces.

These different combustion mechanisms have an effect on how the energy output of the combustion process can be controlled. In the homogeneous, premixed, combustion process the range of air–fuel ratios over which combustion will occur is limited by the flammability of the mixture. In early petrol engines the mixture strength varied little, and was close to stoichiometric at all operating conditions

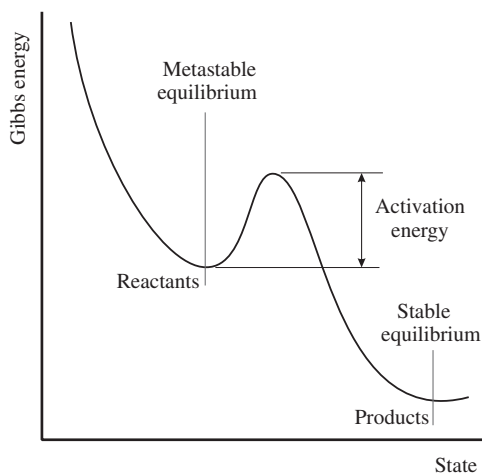
(the mixture was often enriched at high load to reduce combustion temperatures). In modern engines, attempts are made to run the engines with weaker mixtures (i.e. *lean-burn*). At present, most spark-ignition engines operate with a throttle to limit the air flow at low loads. This is known as *quantitative governing* of the engine power because the *quantity* of charge entering the engine is controlled, and this controls the power output. Throttling the engine reduces the pressure in the inlet manifold, and effectively the engine has to *pump* air from the inlet manifold to the exhaust system, giving a negative pumping work of up to 1 bar mean effective pressure (mep) (see Chapters 3 and 16). Nowadays many spark-ignition engines operate over part of their power range with lean mixtures, and some petrol engines operate with fuel injection directly into the cylinder but with ignition by a spark. The advantage of lean-burn engines is that the load control can be partly by making the mixture leaner, and partly by throttling. Engines are discussed in more detail in Chapter 16.

The power output of a diesel engine is controlled by changing the amount of fuel injected into the cylinder – the air quantity is not controlled. This means that the overall air–fuel ratio of the diesel engine changes with load, and the *quality* of the charge is controlled. This is referred to as *qualitative governing* and has the benefit of not requiring throttling of the intake charge. The diesel engine operates over a broad range of air–fuel ratios. However, the richest operating regime of a diesel engine is usually at an air–fuel ratio of greater than 20:1, whereas the petrol engine can achieve the stoichiometric ratio of about 15:1, or richer. This means that, even at the same engine speed, the diesel engine will only produce about 70% of the power output of the petrol engine. However, the lack of throttling, higher compression ratio and shorter combustion period mean that the diesel engine has a higher thermal efficiency than the petrol engine. (Note: the efficiency of engines should be compared on the basis of the specific fuel consumption (kg/kWh) rather than miles per gallon because the calorific values (kJ/kg) of diesel fuel and petrol are approximately the same, but the calorific value of diesel fuel in kJ/m³ is about 11% greater than that of petrol because the fuel density is about 11% greater. A diesel vehicle which achieves only 11% more miles/gallon than a petrol engine is not more efficient!) Gas turbine combustion chambers and boilers also control their output in a qualitative manner, by varying the air–fuel ratio: gas turbines are discussed in Chapter 17.

An important feature of a flame is its rate of progress through the mixture: referred to as the *flame speed*. Flame speed is easiest understood when related to a premixed laminar flame, but the concept of flame speed applies in all premixed combustion.

15.2 THERMODYNAMICS OF COMBUSTION

When fuel and air are mixed together they are in metastable equilibrium, as depicted schematically in Fig. 15.1. This means that the Gibbs energy of the reactants is not at the minimum, or equilibrium, value but is at a higher level. Fortunately it is still possible to apply the laws of thermodynamics to the metastable state, and hence the energies of reactants can be calculated in the usual way. Even though the reactants are not at the minimum Gibbs energy spontaneous change does not usually occur: it is necessary to provide a certain amount of energy to the mixture to initiate the combustion – basically to ‘ionise’ the fuel constituents. Once the fuel constituents (usually carbon and hydrogen) have been ‘ionised’ they will combine with the oxygen in the air to form compounds with a lower Gibbs energy than the reactants: these are called the *products* (usually carbon dioxide, water, etc.). In the case of the spark-ignition engine the ionisation energy is provided by the spark, which ignites a small kernel of the

**FIGURE 15.1**

Energy states associated with combustion.

charge from which the flame spreads. In the diesel engine, as the temperature of the charge is increased due to compression, part of the mixture produced in the cylinder cannot exist in the metastable state: it will spontaneously ignite. Such a mixture is termed a *hypergolic mixture*.

Some mixtures are unstable at room temperature, and their constituents spontaneously ignite. An example of such a mixture is hydrogen and fluorine. This concept of spontaneous ignition will be returned to later.

All of these thermodynamic processes take place somewhere in the combustion zone, and many of them occur in the flame. Before passing on to the detailed discussion of flames it is worthwhile introducing some definitions and concepts.

15.2.1 REACTION ORDER

The overall order of a reaction is defined as $n = \sum_{i=1}^q \nu_i$, summed over the q species in the reactants.

First-order reactions

These are reactions in which there is spontaneous disintegration of the reactants: these reactions do not usually occur, except in the presence of an 'inert' molecule.

Second-order reactions

These are the most common reactions because they have the highest likelihood of a successful collision between ions occurring.

Third-order reactions

These are less likely to occur than second-order ones but can be important in combustion. An example is when OH and H combine to produce an H₂O molecule. This H₂O molecule will tend to dissociate almost immediately unless it can pass on its excess energy – usually to a nitrogen molecule in the form of increased thermal energy.

15.2.2 PROCESSES OCCURRING IN COMBUSTION

The thermodynamics of combustion generally relate to the gas in isolation from its surroundings. However, the surroundings, and the interaction of the gas with the walls of a container, etc. can have a major effect on the combustion process. The mechanisms by which the combusting gas interacts with its container are

1. transport of gaseous reactant to the surface – diffusion;
2. adsorption of gas molecules on surface;
3. reaction of adsorbed molecules with the surface;
4. desorption of gas molecules from the surface;
5. transport of products from the surface back into the gas stream – diffusion.

These effects might occur in a simple container, say an engine cylinder, or in a catalytic converter. In the first case the interaction might stop the reaction, while in the second one it might enhance the reactions.

15.3 EXPLOSION LIMITS

The kinetics of reactions was introduced previously, and it was stated that reactions would, in general, only occur when the atoms or ions of two constituents collided. The reaction rates were derived from this approach, and the *Arrhenius equations* (see Section 14.3) were introduced. The tendency for a mixture to spontaneously explode is affected by the conditions in which it is stored. A mixture of hydrogen and oxygen at 1 bar, and 500 °C will remain in a metastable state, and will only explode if ignited. However, if the pressure of that mixture is reduced to around 10 mm Hg (about 0.01 bar) there will be a spontaneous explosion. Likewise, if the pressure was increased to about 2 bar there would also be an explosion. It is interesting to examine the mechanisms which make the mixture become hypergolic. The variation of explosion limits with state for the hydrogen–oxygen mixture is shown in Fig. 15.2.

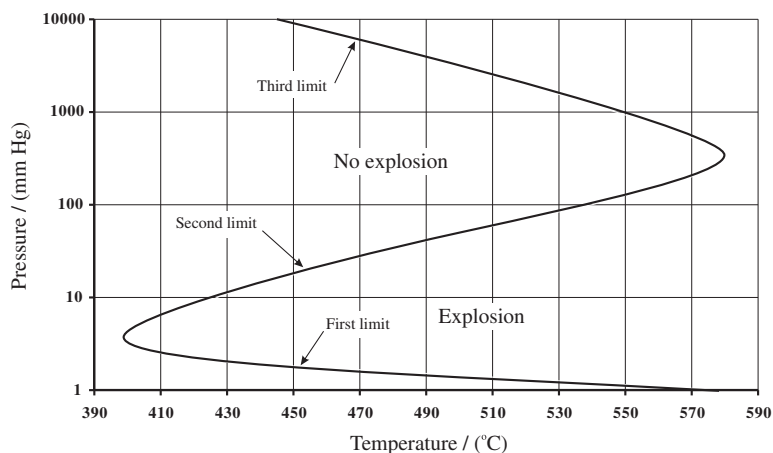
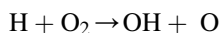


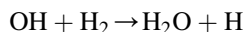
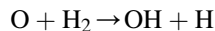
FIGURE 15.2

Explosion limits for a mixture of hydrogen and oxygen (from Lewis and von Elbe (1961)).

The kinetic processes involved in the $\text{H}_2\text{-O}_2$ reaction are



which leads to the further branching steps



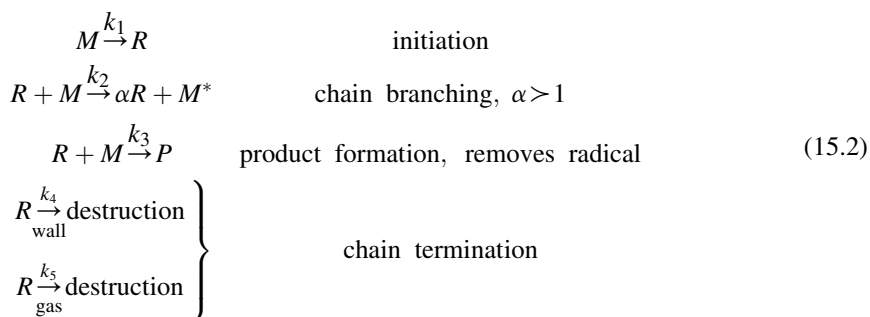
(15.1)

The first two of the three steps are called branching steps and produce two *radicals* (highly reactive ions) for each one consumed. The third step does not increase the number of radicals. Since all steps are necessary for the reaction to occur the multiplication factor (i.e. the number of radicals produced by the chain) is between 1 and 2. The first step is highly *endothermic* (it requires energy to be *supplied* to achieve the reaction), and will be slow at low temperatures. This means that an H atom can survive a lot of collisions without reacting, and can be destroyed at the wall of the container. Hence, $\text{H}_2\text{-O}_2$ mixtures can exist in the metastable state at room temperatures, and explosions will only occur at high temperatures, where the first step proceeds more rapidly.

15.3.1 THE EFFECT OF MULTIPLICATION FACTOR ON THE TENDENCY TO EXPLODE

The effect of the multiplication factor can be examined in the following way. Assume a straight chain reaction has 10^8 collisions/s, and there is 1 chain particle/ cm^3 , with 10^{19} molecules/ cm^3 . Then all the molecules will be consumed in 10^{11} s, which is approximately 30 years. However, if the multiplication factor is now 2 then $2^N = 10^{19}$, giving $N = 62$. This means that all the reactants molecules will be consumed in 62 generations of collisions, giving a total reaction time of 62×10^{-8} s, or 0.62 μs : a extremely fast reaction! If the multiplication factor is only 1.01 then the total reaction time is still only 10 ms. Hence, the speed of the reaction is very dependent on the multiplication factor of the reactions, but the overall multiplication factors do not have to be very high to achieve rapid combustion.

A general branched chain reaction may be written



where M is a molecule, R is a radical and P is a product. α is the multiplication factor. The value of α necessary to achieve an explosion can be evaluated. The rate of formation of the product, P , is given by

$$\frac{d[P]}{dt} = k_3[R][M]. \quad (15.3)$$

Table 15.1 Flammability and Explosion Limits (Mixtures Defined in % Volume) (at Ambient Temperature and Pressure) (Lewis and von Elbe (1961), data also in wiki (2014))

Mixture	Lean		Rich		Stoichiometric
	Flammability	Explosion	Flammability	Explosion	
H ₂ –air	4	18	74	59	29.8
CO–O ₂	16	38	94	90	66.7
CO–air	12.5		74		29.8
NH ₃ –O ₂	15	25	79	75	36.4
C ₃ H ₈ –O ₂	2	3	55	37	16.6
CH ₄ –air	5.3		15		9.51
C ₂ H ₆ –air	3.0		12.5		5.66
C ₃ H ₈ –air	2.2		9.5		4.03
C ₄ H ₁₀ –air	1.9		8.5		3.13

The steady state condition for the formation of radicals is

$$\frac{d[R]}{dt} = 0 = k_1[M] + k_2(\alpha - 1)[R][M] - k_3[R][M] - k_4[R] - k_5[R]. \quad (15.4)$$

Solving Eqn (15.4) for R and substituting into Eqn (15.3) gives

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [M]^2}{\{k_3 [M] + k_4 + k_5 - k_2(\alpha - 1)[M]\}}. \quad (15.5)$$

The rate of production of the product P becomes infinite when the denominator is zero, giving

$$\alpha_{\text{crit}} = 1 + \frac{k_3[M] + k_4 + k_5}{k_2[M]} = \left(1 + \frac{k_3}{k_2}\right) + \frac{k_4 + k_5}{k_2[M]}. \quad (15.6)$$

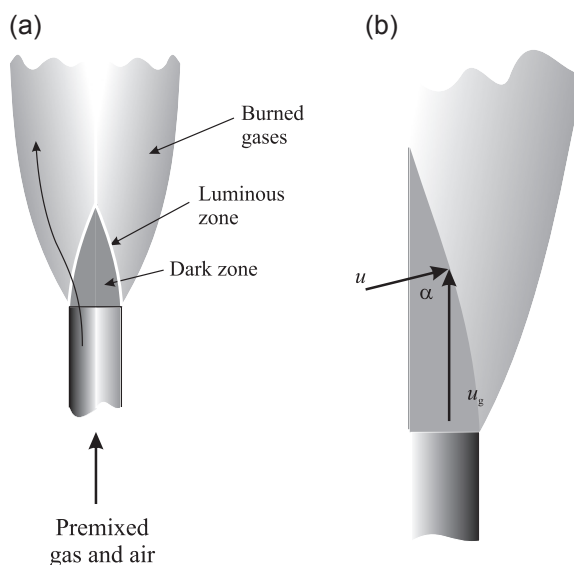
Thus, if $\alpha_{\text{react}} > \alpha_{\text{crit}}$ the reaction is explosive: if the $\alpha_{\text{react}} < \alpha_{\text{crit}}$ then the combustion is nonexplosive and progresses at a finite rate. A few explosion limits, together with flammability limits are listed in Table 15.1. This text will concentrate on nonexplosive mixtures from now on.

15.4 FLAMES

A flame is the usual mechanism by which combustion of hydrocarbons takes place in air. It is the region where the initial breakdown of the fuel molecules occurs. There are two different types of flame, as described above: premixed flames and diffusion flames. Premixed flames will be dealt with first because it is easier to understand their mechanism.

15.4.1 PREMIXED FLAMES

Premixed flames occur in any homogeneous mixture where the fuel and the oxidant are mixed prior to the reaction. Examples are the Bunsen burner flame and the flame in most spark-ignited engines. Premixed flames can progress either as *deflagration* or *detonation* processes. This text will consider

**FIGURE 15.3**

Schematic diagram of Bunsen burner flame (a) general arrangement (b) velocity vectors.

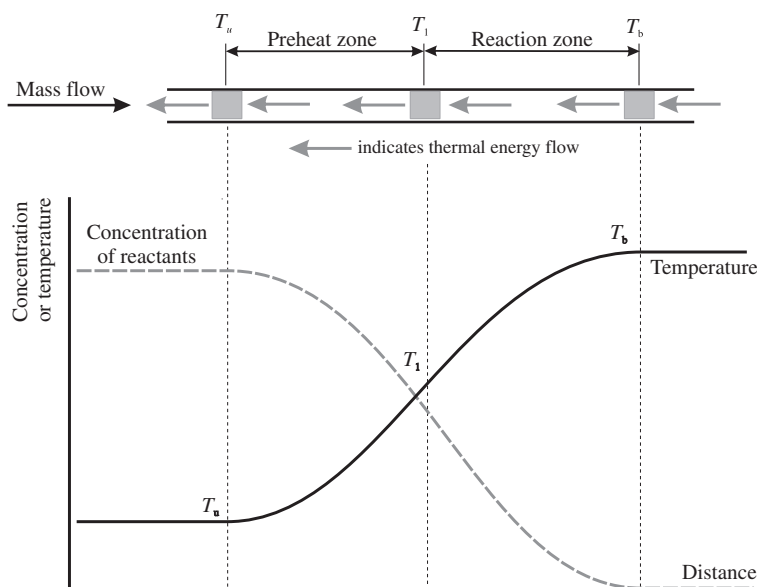
only deflagration processes, in which the flame progresses subsonically. Detonation processes do occur in some premixed, spark-ignited engines, when the 'end gas' explodes spontaneously making both an audible knock and causing damage to the combustion chamber components.

When considering laminar flame speed, it is useful to start with a qualitative analysis of a Bunsen burner flame, such as depicted in Fig. 15.3. If the flow velocity at the exit of the tube is low then the flow of mixture in the pipe will be laminar. The resulting flame speed will be the *laminar flame speed*. While most flames are not laminar, the laminar flame speed is a good indication of the velocity of combustion under other circumstances. It can be seen from Fig. 15.3(b) that the shape (or angle) of the inner luminous cone is defined by the ratio of the *laminar flame speed* (or *burning velocity*), u_l , to the flow velocity of the mixture. In fact, the laminar flame speed, $u_l = u_g \sin \alpha$. While this is a relatively simple procedure to perform it is not a very accurate method of measuring laminar flame speed because of the difficulty of achieving a straight-sided cone, and also defining the edge of the luminous region. Other methods are used to measure the laminar flame speed, including the rate of propagation of a flame along a horizontal tube and flat burners.

15.4.2 LAMINAR FLAME SPEED

There are a number of theories relating to laminar flame speed. These can be classified as

- Thermal theories;
- Diffusion theories;
- Comprehensive theories.

**FIGURE 15.4**

Schematic diagram of interactions in plane combustion flame.

The original theory for laminar flame speed was developed by Mallard and Le Chatelier (1883), based on a thermal model. This has been replaced by the Zel'dovitch and Frank-Kamenetsky (1938), and Zel'dovitch and Semenov (1940) model which includes both thermal and species diffusions across the flame. The details of these models will not be discussed but the results will simply be presented, for more information on this approach and other more recent ones refer to Kuo (1986).

A plane flame in a tube may be shown schematically as in Fig. 15.4. It can be seen that the thermal diffusion goes from right to left in this diagram, i.e. against the direction of flow. The flame also attempts to travel from right to left, but in this case the gas flow velocity is equal to the flame speed. If the gas had been stationary then the flame would have travelled to the left at the laminar flame speed.

Considering the physical phenomena occurring in the tube: heat flows, by conduction, from the burned products zone (b) towards the unburned reactants zone (u), while the gas flows from u to b. A mass element passing from left to right at first receives more heat by conduction from the downstream products than it loses by conduction to the reactants, and hence its temperature increases. At temperature T_1 the mass element now loses more heat to the upstream elements than it receives from the products, but its temperature continues to increase because of the exothermic reaction taking place within the element. At the end of the reaction, defined by T_b , the chemical reaction is complete and there is no further change in temperature.

The Zel'dovitch et al. (1938, 1940) analysis results in the following equation for laminar flame speed:

$$u_{\ell} = \left(\frac{2k}{c_p \rho_u c_u} \frac{Z' e^{-E/RT_b}}{(T_b - T_u)} \frac{RT_b^2}{E} \right)^{1/2} \quad (15.7)$$

In obtaining Eqn (15.7) the assumption had been made that the Lewis number,

$$Le = k/\rho c_p D = 1,$$

where k = thermal conductivity, ρ = density, c_p = specific heat at constant pressure and D = mass diffusivity.

Hence, Le is the ratio between thermal and mass diffusivities, and this obviously has a major effect on the transport of properties through the reaction zone. The assumption $Le = 1$ can be removed to give the following results for first- and second-order reactions.

For first-order reactions

$$u_\ell = \left\{ \frac{2k_b c_{p_b} Z'}{\rho_u \bar{c}_p^2} \frac{T_u}{T_b} \frac{n_R}{n_P} \frac{A}{B} \left(\frac{RT_b^2}{E} \right)^2 \frac{e^{-E/RT_b}}{(T_b - T_u)^2} \right\}^{1/2} \quad (15.8a)$$

and for second-order reactions

$$u_\ell = \left\{ \frac{2k_b c_{p_b}^2 Z' c_u}{\rho_u \bar{c}_p^3} \left(\frac{T_u}{T_b} \right)^2 \left(\frac{n_R}{n_P} \right)^2 \left(\frac{A}{B} \right)^2 \left(\frac{RT_b^2}{E} \right)^2 \frac{e^{-E/RT_b}}{(T_b - T_u)^3} \right\}^{1/2} \quad (15.8b)$$

where Z' is the pre-exponential term in the Arrhenius equation and c_u is the initial volumetric concentration of reactants.

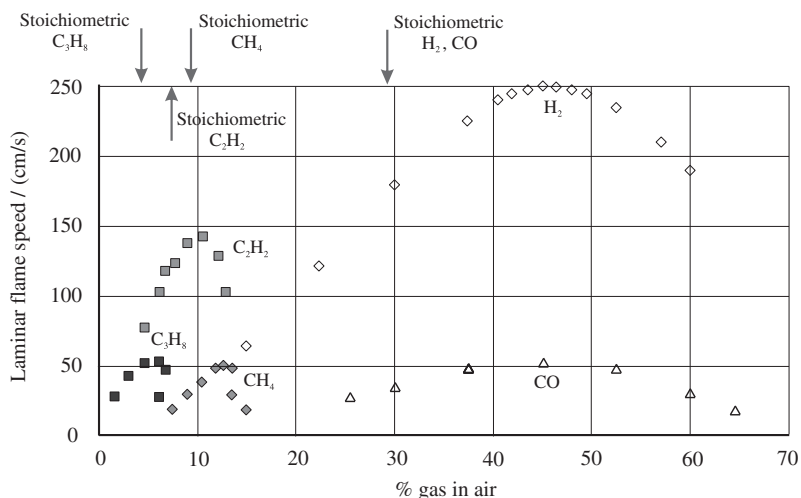
Equations (15.8a) and (15.8b) can be simplified to

$$u_\ell \approx \left\{ \frac{k c_{p_b}^2}{\rho_u \bar{c}_p^3} c_u Z e^{-E/RT_b} \right\}^{1/2} \approx \left\{ \frac{k}{\rho_u c_p} R \right\}^{1/2} \approx (\alpha R)^{1/2} \quad (15.9)$$

Hence the laminar flame speed is proportional to the square root of the product of thermal diffusivity, α , and the rate of reaction, R . Glassman (1986) shows that the flame speed can be written as

$$u_\ell = \left\{ \frac{k_b}{\rho_u c_p} \frac{(T_b - T_{ig})}{(T_{ig} - T_u)} \frac{m_{w_b}}{\rho_u} R \right\}^{1/2}. \quad (15.10)$$

which is essentially the same as Eqn (15.9), where $R = Z e^{-E/RT_b}$. Obviously the laminar flame speed is very dependent on the temperature of the products, T_b , which appears in the rate equation. This means that the laminar flame speed, u_ℓ , will be higher if the reactants temperature is high, because the products temperature will also be higher. It can also be shown that $u_\ell \propto p^{(n-2)/2}$, where n is the *order of the reaction*, and $n \approx 2$ for a reaction of hydrocarbon with oxygen. This means that the effect of pressure on u_ℓ is small. Figure 15.5 (from Lewis and von Elbe (1961)) shows the variation of u_ℓ with reactant and mixture strength for a number of fundamental 'fuels'. It can be seen that, in general, the maximum value of u_ℓ occurs at close to the stoichiometric ratio, except for hydrogen and carbon monoxide which have slightly more complex reaction kinetics. It is also apparent that the laminar flame speed is a function both of the reactant and the mixture strength. The effect of the reactant comes through its molecular weight, m_w . This appears in more than one term in Eqn (15.10) because density and thermal conductivity are both functions of m_w . The net effect is that $u_\ell \propto 1/m_w$. This explains the

**FIGURE 15.5**

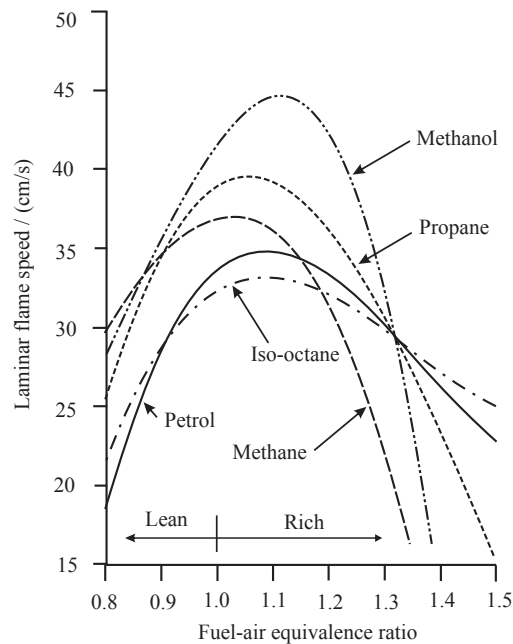
Variation of laminar flame speed with reactants and mixture strength. $p = 1$ bar; $T_u = 298$ K.

ranking order of flame speeds shown in Fig. 15.5, with the laminar flame speed for hydrogen being much higher than the others shown. While the molecular weight is a guide to the flame speed of a fuel other more complex matters, such as the reaction rates, included as Z' in these equations, also have a big influence on the results obtained. Figure 15.6, from Metgalchi and Keck (1980, 1982) shows a similar curve, but for fuels which are more typical of those used in spark-ignition engines.

It can be seen that the laminar flame speed is dependent on mixture strength, and this has major influence on the design of engines operating with lean mixtures. The other feature to notice is that the laminar flame speed would remain approximately constant in an engine operating over a speed range of probably 800–6000 rev/min. If the combustion process depended on laminar burning then the combustion period in terms of crankangle would change by a factor of more than 7:1. Consider an engine operating with methane (CH_4) at stoichiometric conditions: the laminar flame speed is about 50 cm/s (0.5 m/s). If the engine bore is 100 mm then the combustion period will be 0.1 s. At 800 rev/min this is equivalent to 480° crankangle – longer than the compression and expansion periods! Obviously the data in Figs 15.5 and 15.6 are not directly applicable to an engine: this is for two reasons.

First, the initial conditions of the reactants, at temperatures of 298 K or 300 K, are much cooler than in an operating engine. Kuehl (1962) derived an expression for the combustion of propane in air, which gave

$$u_{\ell} = \frac{0.78 \times 10^4}{\left(\frac{10^4}{T_b} + \frac{900}{T_u}\right)^{4.938}} P^{-0.09876} \quad (15.11)$$

**FIGURE 15.6**

Variation of laminar flame speed with mixture strength for typical fuels (based on 1 atm, 300 K).

where

p = pressure (bar)

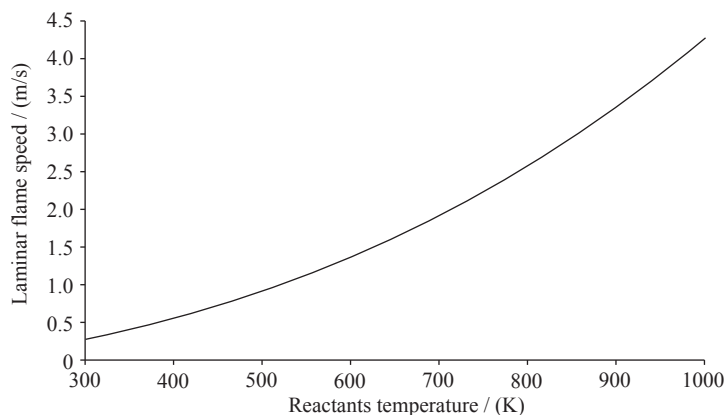
T = temperature (K)

u_{ℓ} = laminar flame speed (m/s).

It can be seen from Eqn (15.11) that the effect of pressure on flame speed is very small, as suggested above. Figure 15.7 shows how the laminar flame speed increases with reactants temperature: it has been assumed that the adiabatic temperature rise remains constant at 2000 K, which is approximately correct for a stoichiometric mixture. It can be seen that the speed increases rapidly, and reaches a value of around 4 m/s when the reactants temperature is 1000 K. This is an increase of about a factor of 8 on the previous value which would reduce the combustion duration to about 60° crankangle. This is still quite a long combustion duration, especially since it has been evaluated at only 800 rev/min: some other feature must operate on the combustion process to speed it up. This, second, parameter is *turbulence*, which enhances the laminar flame speed as described below.

15.4.3 IGNITION

Before continuing with the discussion of flames it is necessary to look at the initiation of the flame: this will be done by considering combustion in a spark-ignition engine (see Chapter 16). The ignition process is an extremely important one in the homogeneous charge engine because it has to be initiated

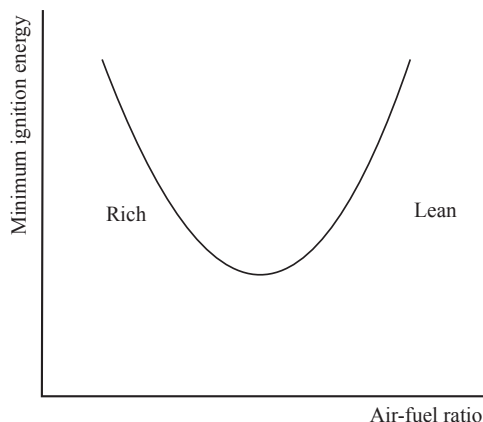
**FIGURE 15.7**

Variation of laminar flame speed with reactants temperature (predicted by Kuehl's equation, with $p = 1$ bar).

by an external source of energy – usually a spark plug. It can be shown that the minimum energy for ignition, based on supplying sufficient energy to the volume of mixture in the vicinity of the spark-gap

to cause a stable flame, is $Q_{p,\min} \propto \frac{k^3}{p^2 u_\ell^3}$. This means that the minimum energy is increased as the

inverse of the laminar flame speed, cubed. In other words, much more energy is required when u_ℓ is low. The typical level of energy required to ignite the mixture in a spark-ignition engine is around 30 mJ. As shown above, u_ℓ is dependent on the initial temperature of the reactants, and the equivalence ratio of the charge (because this affects the adiabatic temperature rise, and hence T_b). This means that the strongest spark is needed when the engine is cold, and also if the engine is running lean. This dependence also explains why it is attractive to develop *stratified charge engines*, with a rich mixture zone around the spark plug. The typical variation of minimum energy to ignite a mixture is shown in Fig. 15.8.

**FIGURE 15.8**

Minimum ignition energy against air–fuel ratio.

15.4.4 FLAME GROWTH

While the flame is small it is susceptible to local processes in the vicinity of the plug. Pischinger and Heywood (1988) show how the initial flame varies over a short period (300 μ s) after ignition. The growth of the flame is ‘laminar’ but the flame is affected by heat transfer to its immediate surroundings, the electrodes. While the flame is small the effects of flame curvature also influence its growth rate (Boulouchos et al. (1994)). As the flame grows it transforms from laminar to turbulent, and the actual trajectory of the flame is affected by both the local mean velocity and the turbulence intensity. Turbulence enhances the flame speed by wrinkling the reaction sheet. As the flame gets bigger than about 10 mm radius it becomes less affected by the mean flow. Pischinger and Heywood show that the growth of the flame is almost spherical once it has reached a critical size. It has to be recognised that the relationship between the flame radius and mass fraction burned is not a simple direct one because the density of the burned gas is about a quarter of that of the unburned mixture. This means that for a simple disc-shaped combustion chamber the mass fraction burned is less than 10% of the total mixture even when the flame is halfway across the chamber. The effect of combustion chamber shape modifies this relationship further, and it can be modelled by simple geometry to take some account of the combustion chamber geometry. The flame makes a transition from laminar to turbulent when it reaches about 5 mm in radius, and this takes between 5° and 10° crankangle at speeds of 1500–3000 rev/min.

The turbulent flame in spark-ignition engines can be characterised by the parameters given in Table 15.2.

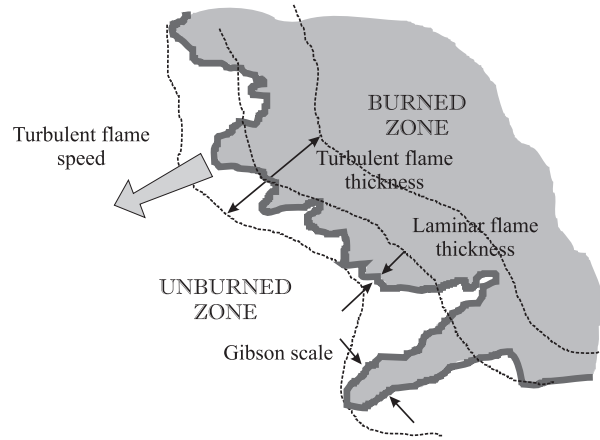
Schlieren photographs of the flame surface show ‘three-dimensional’ wrinkling of the form shown in Fig. 15.9. This wrinkling has a significant effect on the speed of the flame, which is enhanced by the turbulence. The turbulent Reynolds number associated with the flame is in the region 100–1000, while the Damkohler number (which relates the eddy turnover time to the residence time in the flame) is of the order of 100. This means that the laminar flame is wrinkled by the flame rather than having its thickness modified. The wrinkling also tends to ‘stretch’ the flame and this will tend to extinguish it.

Table 15.2 Typical Flame Parameters in Spark-Ignition Engines

Turbulence intensity, u'	2 m/s
Turbulent Reynolds number	300
Damkohler number	20
Karlovitz stretch factor, K	0.2
Integral scale	2 mm
Taylor microscale	0.7 mm
Kolmogorov scale	0.03 mm
Gibson scale	0.2 mm
Laminar flame thickness	0.02 mm
Laminar flame speed	0.5 m/s
Turbulence intensity/laminar flame speed	4
Turbulent flame speed/laminar flame speed	4
Mean flame radius of curvature	2 mm

FIGURE 15.9

Schematic diagram of turbulent flame in spark-ignition engine.



The parameters governing the extinction of the laminar flame are the Lewis and Karlovitz numbers, defined below.

Measurements have shown that the turbulence intensity at the time of combustion tends to be about half the mean piston speed. Since the turbulent burning velocity is related to the laminar flame speed by the turbulence intensity then the mass burning rate in the cylinder for the majority of the combustion period (say, from 10% to 90% of the in-cylinder charge) is almost independent of engine speed. Heywood quotes that the turbulent to laminar flame area is about 10 at 2000 rev/min. As the flame approaches the wall it is slowed down by heat transfer to the wall and also the smaller scales of turbulence existing close to the wall. There have been theories of flame quench at the wall but these are not very well understood in the context of engine combustion.

The flame in a spark-ignition engine propagates as a local laminar flame whose speed is enhanced by the effects of turbulence. The laminar flame speed is a function of a number of parameters, including the fuel, the equivalence ratio, temperature and pressure. The turbulent flame speed is a function of all of the parameters which affect the laminar flame speed plus the effect of turbulence in the cylinder. It was stated above that the flame is a wrinkled one, which basically means that the Kolmogorov scale of turbulence must be larger than the laminar flame thickness. This means that the laminar flame structure is maintained and that the turbulent flame is simply a distorted laminar one. If the distortion becomes too large it is possible for the flame to be extinguished. This tendency can be assessed by examining the Lewis and Karlovitz numbers. The Lewis number (Le) is the ratio of thermal to molecular diffusivity (defined in Eqn (15.12)), and was used to examine the basic flame propagation mechanisms.

$$Le = \alpha/D, \text{ where } \alpha = \text{thermal diffusivity, and } D = \text{mass diffusivity} \quad (15.12)$$

The Karlovitz number is the product of the turbulent strain rate and the transit time for flow through the laminar flame, τ_L , giving

$$K = \left(\frac{1}{F_L} \frac{dF_L}{dt} \right) \tau_L = \left(\frac{u'}{\ell_T} \right) \left(\frac{\delta_L}{S_L} \right) \quad (15.13)$$

where

F_L = area of laminar flame;
 u' = turbulence intensity;
 l_T = Taylor microscale;
 δ_L = laminar flame thickness;
 S_L = laminar flame speed.

Abdel-Gayed et al. (1987) and Bradley et al. (1992) investigated the way in which turbulence 'stretches' the flame and causes it to be extinguished. The results are summarised in Fig. 15.10, which is a graph of the ratio of turbulent to laminar flame speed, i.e. the flame speed factor defined in Section 15.4.5, Eqn (15.14) below, against the ratio of turbulence intensity to laminar flame speed. The abscissa is closely related to the Karlovitz number, K , which is a measure of the flame stretch. Also shown on Fig. 15.10 are lines of constant KLe , which is the product of Karlovitz and Lewis numbers, and lines of constant Re/Le^2 , which is the ratio of Reynolds number to the square of Lewis number. If the value of KLe is low (e.g. 0.0013) then the flame is a wrinkled laminar one, while if the value of KLe is high (e.g. 6) the flame is stretched sufficiently to quench it. This shows that the design of a combustion chamber must be a compromise between a high enough value of turbulence intensity to get a satisfactory flame speed, and one which does not cause extinction of the flame.

Abdel-Gayed et al. (1987) and Bradley et al. (1992) have shown that the higher the value of the product of Lewis and Karlovitz numbers (KLe) the more tendency is there for the flame to be extinguished by stretching. The Lewis number is about 1 for stoichiometric mixtures and remains about unity for a wide range of mixture strengths. Hence, the term KLe is dominated by the turbulence intensity (u') and the laminar flame speed (S_L). This means that lean mixtures, which have a relatively low laminar flame speed (see Fig. 15.6), will experience higher values of Karlovitz number than rich

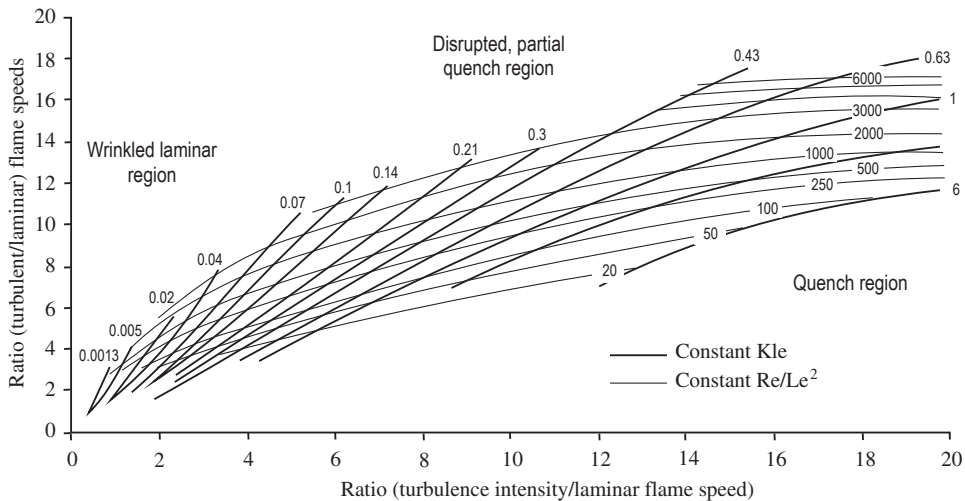


FIGURE 15.10

The effect of turbulence on the turbulent flame speed and tendency to quench for a premixed charge.

mixtures at the same turbulence intensity. Figure 15.10 shows that if the Karlovitz number is increased, by increasing the turbulence level in the combustion chamber, then the product KLe will also increase: this makes it more likely for the flame to be extinguished. Hence, there is a limit to how much the lower flame speed caused by a weak mixture can be compensated by increasing the turbulence level: at some point misfire will occur.

Flammability limits were introduced in Table 15.1, where they were listed with the explosion limits. The flammability limit of a mixture is defined as the mixture strength beyond which, lean or rich, it is not possible to sustain a flame. The flammability limit in practice is related to the situation in which the flame is found. If the flame is moving in a confined space it will be extinguished more easily because of the increase in the interaction of the molecules with the walls: this is known as *quenching*. It is also possible for the flame to be extinguished if the level of turbulence is too high, when the flame is *stretched* until it breaks. The lean flammability limit is approximately 50% of stoichiometric, while the rich limit is around three times stoichiometric fuel–air ratio.

It can be seen from Table 15.1 that the spread of flammability for hydrogen is much higher than the other fuels. This makes it an attractive fuel for homogeneous charge engines because it might be possible to control the load over a wide range of operation by qualitative governing rather than throttling. This would enable the hydrogen-powered engine to achieve brake thermal efficiencies similar to those of the diesel engine. The restricted range of flammability limits for hydrocarbon fuels limits the amount of power reduction that can be achieved by *lean-burn* running; it also restricts the ability of operating the engine lean to control NO_x . Honda quote one of their engines operating as lean as 24:1 air–fuel ratio, which enables both the engine power to be reduced and the emissions of NO_x to be controlled. Such lean-burn operation is achieved through careful design of the intake system and the combustion chamber. In practice, in a car engine the lean limit is set by the driveability of the vehicle and the tendency to misfire. A small percentage of misfires from the engine will make the unburned hydrocarbons (uHC) emissions unacceptable – these misfires might not be perceptible to the average driver.

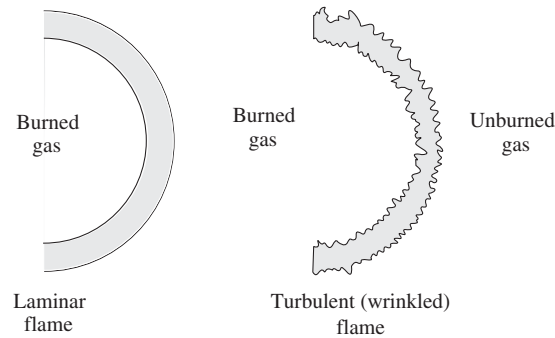
The rich and lean flammability limits come closer together as the quantity of inert gas added to a mixture is increased. Fortunately, the rich limit of flammability is more affected than the lean one, and basically the lean limit, which is usually the important one for engine operation, is not much changed.

15.4.5 TURBULENT FLAME SPEED

It was shown previously that the laminar flame speed is too low to enable engines to operate efficiently, particularly if they are required to work over a broad speed range. The laminar flame speed must be enhanced in some way, and turbulence in the flow can do this. A popular, relatively simple, model describing how turbulence increases the flame speed is the *wrinkled laminar flame model*, which is shown on a simplified diagram in Fig. 15.11.

The effect of turbulence on the flame, as introduced more comprehensively in Fig. 15.9, is threefold:

- The turbulent flow distorts the flame so that the surface area is increased;
- The turbulence may increase the transport of heat and active species and
- The turbulence may mix the burned and unburned gases more rapidly.

**FIGURE 15.11**

Comparison of laminar and turbulent flames.

The theory of turbulent flames was initiated by Damkohler (1940) who showed that the ratio of turbulent to laminar flame speeds, based on large scale eddies in the flow, is

$$\frac{u_t}{u_l} = \sqrt{\frac{\varepsilon}{\nu}}, \quad (15.14)$$

where

ε = eddy diffusivity

ν = kinematic viscosity of the unburned gas.

Experience shows that in spark-ignition engines the flame speed factor is a strong function of engine speed but not greatly affected by load. Experiments by Lancaster et al. (1976) have also shown that the level of turbulence intensity in an engine cylinder increases with engine speed, but is not quite proportional to it. This means that while turbulence increases the flame speed significantly the length of the burning period increases as engine speed is increased, which explains why the ignition timing has to be advanced.

15.4.6 ENGINE COMBUSTION MODELS

The main aims of an engine combustion model are to be able to predict:

- the rate of burning in the cylinder
- the power output of the engine
- the emissions of the process
- the heat transfer to the cylinder liner to evaluate the thermal stresses
- the exhaust gas conditions

The combustion model should also enable the emissions to be calculated prior to the catalyst, the flow in the exhaust system, and the energy for matching a turbocharger. In addition it might be able to predict the cyclic irregularity that might occur under certain conditions. An excellent summary of engine combustion models is given in Heywood (1994).

15.4.6.1 Flame speed models

The simplest flame speed model, which is used in many simulations, is based on a spherical flame front propagating from an initiation point. This gives the equation:

$$\frac{dm_b}{dt} = \rho_u F_f S_f \quad (15.15)$$

where dm_b/dt is the rate of production of products from the reactants, ρ_u is the density of the unburned reactants, F_f is the surface area of the flame and S_f is the flame speed. S_f may be either the laminar or turbulent flame speed. This model will result in a flame volume which is a portion of a sphere travelling out from the spark plug. This model is considered in more detail in the section on two-zone models in Chapter 16.

15.4.6.1.1 Laminar flame speed

Laminar flame speed can be measured in a number of ways by considering adiabatic combustion of an air–fuel mixture. Laminar flame speed has the form

$$u_\ell = u_{\ell,0} \left(\frac{T_u}{T_0} \right)^\alpha \left(\frac{p}{p_0} \right)^\beta \quad (15.16)$$

where $u_{\ell,0}$, α and β are constants for a particular fuel and air–fuel ratio. Metgalchi and Keck (1980, 1982) have shown the variation of u_ℓ with equivalence ratio and fuel for a number of common fuels, see Fig. 15.6. The variation of laminar flame speed with equivalence ratio has the general form

$$u_\ell(x_b) = u_{\ell,x_b=0} (1 - 2.06x_b^{0.77}) \quad (15.17)$$

where x_b is the mole fraction of burned gas diluting the charge. Hence, this can be used to estimate the effect of lean mixtures, and also exhaust gas recirculation.

15.4.6.1.2 Turbulent flame speed

There are a large number of models for relating turbulent flame speed to the laminar one. The simplest ones are simply the addition of an effect due to turbulence, or an enhancement (multiplying) of the effect due to turbulence. The former models have the form

$$\frac{u_t}{u_\ell} = 1 + c \left(\frac{u'}{u_\ell} \right) \quad (15.18)$$

whereas the latter are

$$\frac{u_t}{u_\ell} = c \left(\frac{u'}{u_\ell} \right). \quad (15.19)$$

In the first case if the enhancement due to turbulence is higher relative to the laminar flame speed then the intrinsic effects of the laminar flame speed can be swamped by the turbulence. This means that it is necessary to re-evaluate the enhancement at different equivalence ratios. The second approach does retain the intrinsic effects of the actual mixture.

Heikal et al. (1979) applied a similar approach to engine calculations, and defined the ratio of turbulent to laminar flame speed, often called the *flame speed factor*, as

$$f_f = \frac{u_t}{u_\ell} = \left[1 + \frac{b\nu}{\alpha P_r} \left(\frac{r(u_\ell + c\bar{V}_p^d)}{\nu} \right)^a \right]^{1/2} \quad (15.20)$$

where

α = molecular thermal diffusivity;
 P_r = Prandtl number;
 $\bar{V}_p$ = mean piston speed;
 a, b, c, d are all empirical constants.

A flame speed model by Brehod and Newman (1992) is of the type in Eqn (15.18) and gives the flame speed, u_t , as

$$\frac{u_t}{u_\ell} = 1 + C \left(\frac{\rho_u}{\rho_b} \right)^{1/2} \left(\frac{u'}{u_\ell} \right) \left(1 - e^{-r_f/r_c} \right) \quad (15.21)$$

where

r_f = instantaneous flame radius;
 r_c = a term of the order of the turbulence integral length scale, ℓ ;
 C = coefficient of the order of unity.

Such an equation contains a number of parameters which should be important in evaluating the flame speed in the engine, but it also has a number of degrees of freedom in matching the predictions to experiment. It is difficult to know how ‘universal’ the prediction is likely to be. One of the benefits of this model is that it accounts for the enhancement in flame speed that is likely to occur as the flame grows from a small kernel, when $r_f/r_c < 1$, to a developed flame, when $r_f/r_c > 1$. In the case of the small flame the exponential term $(1 - e^{-r_f/r_c})$ is approximately zero, resulting in the flame speed being almost equal to the laminar flame speed. When the flame radius is larger than the length scale the exponential term approaches unity, and Eqn (15.21) becomes similar to Eqn (15.18).

A very comprehensive model has been proposed by Herweg and Maly (1992), and this is given below:

$$\begin{aligned} \frac{u_t}{u_\ell} = & \underbrace{I_0 + I_0^{1/2}}_{\text{I: strain}} \underbrace{\left\{ \frac{[\bar{U}^2 + u'^2]^{1/2}}{[\bar{U}^2 + u'^2]^{1/2} + u_\ell} \right\}}_{\text{II: effective turbulence factor}} \underbrace{\left\{ 1 - \exp\left(-\frac{r_f}{\ell_I}\right) \right\}^{1/2}}_{\text{III: size dependent integral length scale}} \\ & \times \underbrace{\left\{ 1 - \exp\left(-\frac{t}{\tau_0}\right) \right\}^{1/2}}_{\text{IV: size dependent integral time scale}} \underbrace{\left(\frac{u'}{u_\ell} \right)^{5/6}}_{\text{V: fully developed turbulent combustion}} \end{aligned} \quad (15.22)$$

It is not proposed to discuss Eqn (15.22), but just to show how complex flame speed models can become. This equation includes a whole range of terms similar to those shown in Fig. 15.9, and this indicates that an incredibly detailed knowledge of the flow in the engine combustion chamber would be required before the equation could be used.

15.4.7 DIFFUSION FLAMES

The previous sections all related to premixed flames of the type found in Bunsen burners, or spark-ignition engines. The other major class of flames is called *diffusion flames*; in these flames the rates of reaction are not controlled by the laminar flame speed but by the rate at which the fuel and air can be brought together to form a combustible mixture. This type of combustion occurs in

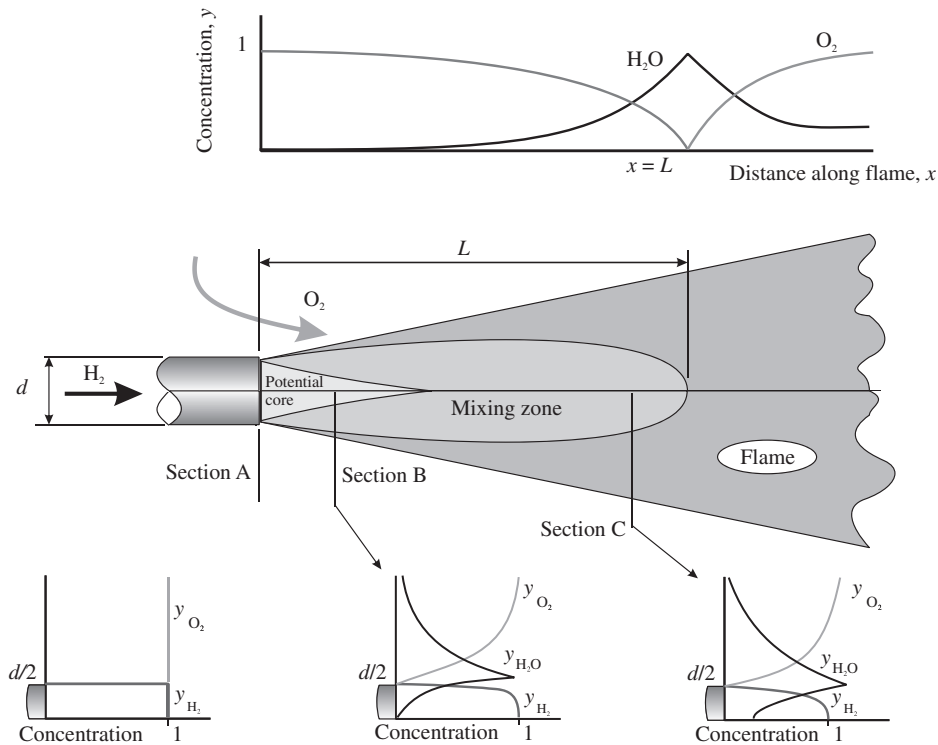
- Open flames, when mixing with secondary air enables combustion of a rich premixed core to continue to completion;
- Gas turbine combustion chambers, when the liquid fuel sprays are mixed with the air in the combustion chamber;
- Diesel engines, when the injected fuel has to mix with the air in the chamber before combustion can take place.

A typical arrangement of a diffusion flame might be that shown in Fig. 15.12. This is a simple example of a jet of hydrogen passing into an oxygen atmosphere. The principle is the same if the fuel is a more complex gaseous one passing into air, the major difference will be that the products of combustion will be more complicated. The three sections across the jet (at A, B and C) show the way in which the oxygen diffuses into the jet, usually by turbulent mixing brought about by the jet entraining the surrounding oxygen. At Section A the hydrogen and oxygen are completely separate, as indicated by the mass fraction curves. By Section B, some way from the end of the nozzle, the hydrogen has been mixed with the oxygen just outside the jet diameter due to turbulent entrainment. There has not yet been any mixing of hydrogen and oxygen in the potential core. Some combustion has also taken place by this section, as indicated by the mass fraction of water. Section C is located almost at the end of the mixing zone, after the end of the potential core and there is no pure hydrogen left in the jet. The edge of the mixing zone is now well within the diameter of the jet.

Considering the concentration of hydrogen and oxygen along the centreline of the jet, it can be seen that there is pure hydrogen right up to the end of the potential core. After that the hydrogen and oxygen on the centreline combine to form water, and it is not until the end of the mixing zone that the oxygen concentration starts to rise again, as the water and oxygen mix and dilute each other.

In this example it has been assumed that the oxygen and hydrogen burn as soon as they come intimately in contact. This presupposes that the chemical reaction rate is much faster than the diffusion rates: this is usually a reasonable assumption.

A similar, but more complex analysis may be made of the injection of diesel fuel into the cylinder of a diesel engine. In this case the entrainment of the fuel and air does not take place in the gaseous phase, but occurs because the droplets of fuel leaving the nozzle impart their momentum on the surrounding air by aerodynamic drag. Once the fuel and air are mixed it is possible for the droplets to evaporate to create a combustible mixture. The details of diesel combustion are beyond this text, but the principles are similar to the combustion of gaseous jets. Diesel engine combustion is discussed in

**FIGURE 15.12**

Combustion of a jet of hydrogen in an oxygen atmosphere.

more detail in Chapter 16. Gas turbine combustion chambers work in a similar way, with a spray of fuel entraining primary air to initiate the combustion, and subsequent entrainment of secondary air to complete the process: these are discussed briefly in Chapter 17.

15.5 CONCLUDING REMARKS

The physical phenomena which affect combustion have been introduced. It has been shown that premixed combustible mixtures exhibit a characteristic combustion velocity called the laminar flame speed. This is related to the mixture strength and temperature of the reactants, but is too slow for most engineering applications and must be enhanced by turbulence to achieve levels appropriate for power plant.

Diffusion flames which occur in heterogeneous mixtures have been described, and it has been shown that these rely on the mixing of the fuel and oxidant to achieve combustion of the mixture.

Chapters 16 and 17 explain how these basic phenomena are harnessed in engines, and show how flame speeds can be enhanced by combustion chamber design, and how entrainment of air can be brought about in heterogeneous combustion systems.

15.6 PROBLEMS

- P15.1** (a) What is meant by the terms
 (i) a global reaction;
 (ii) an elementary reaction;
 (iii) a reaction mechanism.
 (b) Describe the steps required to form a chain reaction and explain why chain reactions are important in combustion.
 (c) A reaction is found to be 25 times faster at 400 K than at 300 K. Measurements of the temperature exponent yielded a value of 0.7. Calculate the activation energy of the reaction. How much faster will the reaction be at 1000 K?
- P15.2** A combustible mixture of gas and air is contained in a well-insulated combustion bomb. It is ignited at a point and a thin flame propagates through the mixture completely burning the reactants. This mechanism produces multiple zones of products: prove that the temperature of an element of gas mixture which burned at pressure, p_b , has a temperature, $T(p, p_b)$ at a pressure, $p > p_b$

$$T(p, p_b) = \left[T_1 \left(\frac{p_b}{p_1} \right)^{\frac{\kappa-1}{\kappa}} + \frac{Q'_p}{c_p} \right] \left(\frac{p}{p_b} \right)^{\frac{\kappa-1}{\kappa}}$$

where

κ = ratio of specific heats,
 Q'_p = calorific value of fuel,
 and suffix 1 defines the conditions before ignition.

Calculate the final pressure, p_2 , in terms of p_1 , T_1 , Q'_p , c_v and κ . What is the difference between the final temperature and that of the first gas to burn if $T_1 = 300$ K, $\kappa = 1.3$ and $Q'_p/c_v = 1500$ K.

- P15.3** The structure of ethylene is $\text{H}_2\text{C} = \text{CH}_2$. Estimate the enthalpy of reaction when 1 kmol of ethylene is completely oxidised. Compare the value obtained with the tabulated value of -1323.2 MJ/kmol. Give reasons for the difference between the values.
 Neglecting dissociation, find the temperature reached after constant pressure combustion of ethylene with 50% excess air if the initial temperature of the reactants is 400 K. The specific heat at constant pressure of ethylene is approximately 1.71 kJ/kg K over the temperature range of the reactants.
 [1302.3 MJ/kmol; 2028 K]
- P15.4** Describe the construction of a boiler for burning pulverised coal. Explain how this design optimises the temperature, turbulence and time required for good combustion. What are the main emissions from this type of plant, and how can they be reduced.

RECIPROCATING INTERNAL COMBUSTION ENGINES

16

16.1 INTRODUCTION

The most common types of engine, or prime mover, met by many people are reciprocating internal combustion engines. The idealised operating cycles of these engines were considered in Chapter 3, and these were designated the Otto, diesel or dual combustion cycles. The use of these idealised heat engine cycles enabled some characteristics of the engines to be considered, but they fall short of defining the operating parameters of actual engines – partly because these engines are not ‘heat engines’. The assumptions made in Chapter 3 to define the ‘air-standard cycles’ were the following:

- the combustion process was replaced by a heat transfer process in which an amount of energy equivalent to the energy released by combustion was added to the air;
- the gas exchange process was replaced by a heat transfer process to a cold reservoir, so that the hot gases after expansion were returned to the state of the air after induction; and
- the compression and expansion processes were isentropic.

The first part of this chapter will extend the consideration of engine cycles in Chapter 3, and introduce some of the features that differentiate actual cycles from air-standard cycles.

It will then describe engine combustion systems in some detail, and will further discuss more realistic cycles, in which friction, and finite rates of combustion will be considered. Different combustion chamber shapes will be introduced, and the reasons for them will be discussed. It will be shown that each combustion chamber design is arrived at in an attempt to modify the intrinsic characteristics of the combustible mixture being used. The combustion rates can also be modified by changing the basic parameters of the engine cylinder, e.g. compression ratio, and also the operating conditions, e.g. air–fuel ratio. A more detailed review of engine combustion systems, including mixture preparation, and gas flow generation can be obtained from Stone (2012).

The processes of liquid atomisation, evaporation and ignition are of fundamental importance to the behaviour of all engine combustion systems: these processes are extremely dependent on the particular fuels being used. A significant effort has been expended by a range of manufacturers, particularly for the military, to make engines which are independent of the fuel – success has been limited. The early aspirations of Rudolf Diesel were to operate his engine on pulverised coal, and this approach was considered again in the 1980s, but wear was an overriding problem. Attempts have also been made to operate gas turbines on pulverised fuel, again with little success. So the majority of prime movers today operate on liquid or gaseous fuels containing a broad range of H–C ratios.

16.2 FURTHER CONSIDERATIONS OF BASIC ENGINE CYCLES

However, before getting involved in these details it is necessary to expand on some of the ideas introduced in Chapter 3.

In chapter 3, the compression ratio was defined as the ratio of volumes (V_1/V_2), see Fig. 16.1: this is normally called the nominal compression ratio of the engine. There are actually two compression ratios applicable to engines: the nominal compression ratio and the effective compression ratio. The nominal compression ratio is the volume of the cylinder at bottom dead centre (bdc) divided by the volume of the cylinder at top dead centre (tdc). The volume of the cylinder at tdc (V_2) is called the *clearance volume* (V_{cl}). The ‘size’ of an engine is defined by its swept volume, which is $V_1 - V_2$ for each cylinder; the capacity of an engine is its total swept volume, i.e. a 2-L engine with four cylinders has a swept volume of 500 cm³/cylinder. The compression ratio, r , can then be defined as

$$r = \frac{V_{tdc}}{V_{bdc}} = \frac{V_{cl} + V_s}{V_{cl}} = \frac{V_s}{V_{cl}} + 1 \quad (16.1)$$

However, the more important parameter from the point of view of the engine operation is the effective compression ratio. This is always less than the nominal value and is defined as the volume at inlet valve closure (ivc) divided by the clearance volume, i.e.

$$r_{eff} = \frac{V_{ivc}}{V_{cl}} \quad (16.2)$$

The position at which the inlet valve closes is dependent on the engine and its application. High speed, high performance engines will normally have the point of ivc well after bdc; this limits the effective compression ratio but improves airflow through the engine (see Winterbone and Pearson (1999)).

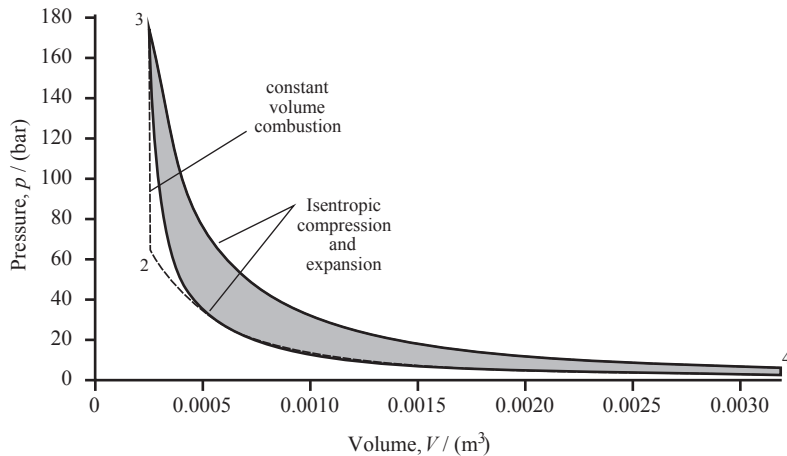


FIGURE 16.1

p - V diagrams for an ‘Otto’ cycle engine. A standard Otto cycle; an actual engine cycle.

Since the purpose of this book is to discuss thermodynamic principles rather than detailed engine design, having pointed out a practical aspect of engine operation, we will assume that ivc is at bdc; this makes the nominal and effective compression ratios equal.

It was shown that the thermal efficiency of an Otto cycle is defined by Eqn (3.16)

$$\eta_{\text{Otto}} = 1 - \frac{1}{r^{(\kappa-1)}}$$

where r is the compression ratio. It is apparent from this expression that higher values of compression ratio, r , result in higher thermal efficiencies. However, differentiating Eqn (3.16) with respect to r gives

$$\frac{d\eta_{\text{th}}}{dr} = \frac{(\kappa - 1)}{r^{\kappa}}, \quad (16.3)$$

which indicates that there are diminishing returns with increasing compression ratio, and by a compression ratio of 20:1 the increase of efficiency per unit increase in r is only 0.60%, or about 1% improvement in power output (based on an instantaneous efficiency of 60%).

It is also necessary to introduce another parameter that is commonly used to assess the load on a reciprocating engine: this is referred to as the mean effective pressure (mep), $\bar{p}$. If the mep is evaluated from the indicator diagram of an air-standard cycle (or any other p - V diagram) then it is called the *indicated mean effective pressure (imep)*. The mep is defined as the pressure, which if it operated over the whole swept volume, would produce the same work output as the actual cycle. Let the mep be denoted by $\bar{p}$, then

$$\bar{p}V_s = \oint p dV \quad (16.4)$$

Hence, for the Otto cycle, the imep is

$$\bar{p}_i = \frac{\oint p dV}{V_s} \quad (16.5)$$

The work output, $\oint p dV$, can be evaluated from the energy addition and the thermal efficiency. The energy addition is equivalent to the product of the lower calorific value of the fuel (Q'_v), which is the negative of the heat of reaction (Q_v), and the mass of fuel, which is normally defined in terms of the air-fuel ratio, ϵ . The quantity of energy added in the air-standard cycle is (Q'_v/ϵ), in kJ/kg of air. The mass of air trapped in the cylinder is given by

$$m = \frac{p_1 V_1}{RT_1} \quad (16.6)$$

which results in an energy addition of $\frac{Q'_v p_1 V_1}{\epsilon RT_1}$.

Hence the imep of an Otto cycle is

$$\bar{p}_i = \frac{p_1 V_1 Q'_v}{RT_1 \epsilon} \frac{\eta_{\text{th}}}{V_s} \quad (16.7)$$

But $V_s = V_1 \left(1 - \frac{1}{r}\right)$ and $\eta_{\text{th}} = 1 - \frac{1}{r^{\kappa-1}}$ giving

$$\bar{p}_i = \left(1 - \frac{1}{r^{\kappa-1}}\right) \frac{p_1 Q'_v}{RT_1 \varepsilon \left(1 - \frac{1}{r}\right)} \quad (16.8)$$

Equation (16.8) shows that the imep is directly proportional to the trapped pressure (p_1), if all other parameters remain constant. Hence the rating of an engine can be increased by pressurizing the inlet manifold (e.g. by turbocharging) at constant air–fuel ratio – in reality, the amount of fuel added has increased in proportion with the amount of air trapped in the cylinder.

Similar results can be evaluated for diesel and dual combustion cycles, and these will just be quoted here

1. Diesel cycle (see Fig. 3.14)

$$\eta_{th} = \frac{W}{Q_{23}} = 1 - \frac{1}{r^{\kappa-1}} \left(\frac{(\beta^{\kappa} - 1)}{\kappa(\beta - 1)} \right),$$

and

$$\bar{p}_i = \left\{ 1 - \frac{1}{r^{\kappa-1}} \left(\frac{\beta^{\kappa} - 1}{\kappa(\beta - 1)} \right) \right\} \frac{p_1 Q'_p}{RT_1 \varepsilon \left(1 - \frac{1}{r}\right)}, \quad (16.9)$$

where Q'_p is the negative of the enthalpy of reaction of the fuel, because the energy is added at constant pressure.

2. Dual combustion cycle (see Fig. 3.15)

$$\eta_{th} = 1 - \frac{1}{r^{\kappa-1}} \frac{(\alpha\beta^{\kappa} - 1)}{(\alpha\kappa(\beta - 1) + (\alpha - 1))},$$

and

$$\bar{p}_i = \left\{ 1 - \frac{1}{r^{\kappa-1}} \frac{(\alpha\beta^{\kappa} - 1)}{(\alpha\kappa(\beta - 1) + (\alpha - 1))} \right\} \frac{p_1 Q'_p}{RT_1 \varepsilon \left(1 - \frac{1}{r}\right)} \quad (16.10)$$

It has been assumed in deriving Eqn (16.10) that $Q'_v = Q'_p$; this is not unreasonable since the differences between these values are usually very small – see Chapter 10.

Example 16.2.1

Evaluate the cycle efficiency and imep of a petrol engine operating at an air–fuel ratio of 15:1 with a trapped pressure of 1 bar and trapped temperature of 100 °C. Consider compression ratios of 7 and 12:1 and evaluate the maximum cycle pressure.

Thermal efficiency of a constant volume cycle is given by:

$$\eta_{th} = 1 - \frac{1}{r^{\kappa-1}}$$

Thus the thermal efficiency at $r = 7$ is $\eta_{th} = 0.5408$, and at $r = 12$ is $\eta_{th} = 0.6299$.

For the air-standard cycle the thermal efficiency is only a function of compression ratio, r .

The imep can be evaluated from Eqn (16.8).

With $r = 7$,

$$\begin{aligned}\bar{p} &= \left\{ 1 - \frac{1}{r^{\kappa-1}} \right\} \frac{1 \times 10^5 \times 43000}{0.287 \times 373 \times 15 \times (1 - 1/r)} \times \frac{1}{10^5} \text{ bar} \\ &= \frac{0.5408 \times 1 \times 43000}{0.287 \times 373 \times 15 \times (1 - 1/7)} = 16.90 \text{ bar.}\end{aligned}$$

The maximum cycle pressure, p_3 , can be evaluated by calculating around the cycle from point 1.

Working around the cycle

$$p_2 = p_1(r)^{\kappa} = 1 \times (7)^{1.4} = 15.25 \text{ bar.}$$

This can be considered to be the point at which combustion (or, more accurately, energy transfer) commenced, initiated by a spark in this case.

$$T_2 = T_1(r)^{\kappa-1} = 373 \times 7^{0.4} = 812.36 \text{ K.}$$

The temperature at 3 can be evaluated from

$$T_3 = T_2 + \frac{q_{23}}{c_v}$$

The heat addition, q_{23} , per unit mass of air, is

$$q_{23} = \frac{Q'_v}{\varepsilon}$$

giving

$$\begin{aligned}T_3 &= T_2 + \frac{Q'_v}{\varepsilon c_v} = 812.36 + \frac{43000}{15 \times 0.715} \\ &= 4821.7 \text{ K.}\end{aligned}$$

(Note: this temperature is much higher than that achieved in an actual engine cycle, and would result in too high a thermal load on the structure).

It is now possible to evaluate the maximum pressure

$$p_3 = \frac{mRT_3}{V_3}$$

but

$$m = \frac{p_1 V_1}{RT_1}$$

and hence

$$\begin{aligned}p_3 &= \frac{p_1 V_1 RT_3}{RT_1 V_3} = \frac{p_1 V_1 T_3}{T_1 V_3} = p_1 r \frac{T_3}{T_1} \\ &= 1 \times 7 \times \frac{4821.7}{373} = 90.49 \text{ bar.}\end{aligned}$$

Considering the case of a compression ratio $r = 12$.

Then $\eta_{th} = 0.6299$ and

$$\bar{p}_i = \frac{0.6299 \times 1 \times 43000}{0.287 \times 373 \times 15 \times (1 - 1/12)} = 18.40 \text{ bar.}$$

The peak pressure is given by working around cycle

$$p_2 = p_1(r)^\kappa = 1 \times (12)^{1.4} = 32.42 \text{ bar}$$

$$T_2 = T_1(r)^{\kappa-1} = 1007.8 \text{ K.}$$

The peak temperature at 3, $T_3 = 1007.8 + 4009.32 = 5017.1 \text{ K}$ and the peak pressure, p_3 , is

$$p_3 = 1 \times 12 \times \frac{5017.1}{378} = 161.4 \text{ bar.}$$

This example shows that the increase of compression ratio from $r = 7$ to $r = 12$ gives an increase in the thermal efficiency from 54% to 63% but also results in a very large increase in the peak pressure (from 90 to 161 bar) while only achieving an increase in output (mep) from 16.9 to 18.4 bar. Hence an increase in compression ratio, while helping the efficiency, does bring problems in its wake. The higher compression ratio will result in higher pressures and temperatures, which will cause increased loadings, both mechanical and thermal on the engine structure, and significantly more dissociation further limiting the gains achieved from the higher compression ratio.

Example 16.2.2

Consider the effect on the imep of increasing the air–fuel ratio from 15 to 20:1. There is no effect on thermal efficiency, which is a function only of compression ratio. Consider compression ratio of $r = 7$ then

$$\bar{p}_i = 16.90 \times \frac{15}{20} = 12.7 \text{ bar.}$$

If compression ratio, $r = 12$

$$\bar{p}_i = 18.40 \times \frac{15}{20} = 13.8 \text{ bar.}$$

Hence the imep is inversely related to the air–fuel ratio in an air-standard Otto cycle, as would be expected because the amount of fuel burned has been reduced.

16.2.1 REALISTIC ENGINE CYCLES

In a real engine cycle, the rate at which fuel is burned, equivalent to the rate at which energy is added to the cycle, usually referred to as the rate of heat release, cannot achieve the constant volume or constant pressure combustion required by the Otto or diesel cycles – see Fig. 16.1. This means that the actual p – V diagram will be rounded as shown in Fig. 16.2. Considering only the Otto cycle, this can be considered to consist of an infinite number of infinitesimal cycles, as shown. Each of these cycles approximates to an Otto cycle and has an efficiency of (Eqn (3.16))

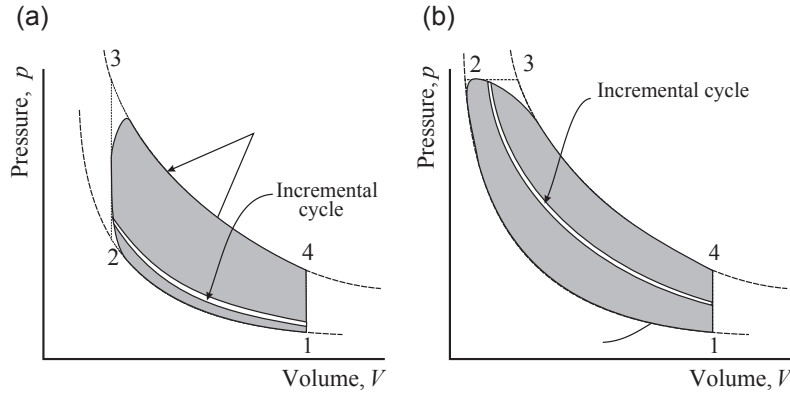


FIGURE 16.2

p - V diagrams comparing realistic cycles with air-standard cycles (a) Otto cycle; (b) diesel cycle.

$$\eta_{th} = 1 - \frac{1}{r_e^{\kappa-1}}$$

but now r_e is not the nominal compression ratio but is an effective compression ratio, or more accurately the expansion ratio, for that incremental cycle.

The incremental cycle can be considered to be brought about by addition of δq units of energy and hence the work output of the whole engine cycle is

$$W = \sum \delta q \left(1 - \frac{1}{r_e^{\kappa-1}} \right) \quad (16.11)$$

whilst the energy addition is

$$Q = \sum \delta q \quad (16.12)$$

So the efficiency is

$$\eta_{th} = \frac{\sum \delta q \left(1 - \frac{1}{r_e^{\kappa-1}} \right)}{\sum \delta q} \quad (16.13)$$

which results in η_{th} being less than the maximum value of $\left(1 - \frac{1}{r^{\kappa-1}} \right)$ and depending on the ‘roundness’ of the diagram. It is possible to take this into account using a diagram factor (η_d) such that the actual efficiency (and work output) can be related to the ideal cycle by

$$\eta = \eta_d \eta_{th} = \eta_d \left(1 - \frac{1}{r^{\kappa-1}} \right) \quad (16.14)$$

η_d is usually about 0.7.

16.3 SPARK-IGNITION ENGINES

In spark-ignition engines, the fuel and air are usually premixed prior to admission to the engine cylinder. This used to be done in a carburettor, but now fuel is usually injected either into the inlet port, manifold or even the cylinder by means of a fuel injection system. The first two of these systems prepare the charge prior to it entering the cylinder, although it is probable that the fuel enters the cylinder with a large proportion in the liquid phase. Under fully warmed-up conditions, this fuel will have evaporated by the time of ignition. At start-up this will not be the case, and enrichment, beyond stoichiometric, is done to ensure that the light fractions of the fuel give a combustible mixture; the remaining liquid fuel causes high levels of unburned hydrocarbons (uHCs). It was stated in Chapter 15 that a high level of *turbulent* gas motion in the cylinder will increase the flame speed, and this can be achieved by various mechanisms. In older engines, discussion of which is worthwhile because it is easy to see the underlying rationale for the chamber shape, the shape of the piston and cylinder head produced a *squish* motion as the piston approached tdc and this enhanced the turbulence in the region of the spark plug, and increased the flame speed (see Fig. 16.3).

Other designs were proposed, including the May 'Fireball' combustion chamber (Fig. 16.4(a) and (b)) which produces a high level of turbulence by 'squeezing' the gas into a small combustion chamber under either the intake or exhaust valve. While this system produces high turbulence it occurs too late to achieve its aims. A May chamber was fitted to a Jaguar engine (Google, 2014) and produced better fuel economy by enabling leaner mixtures to be used. More modern engines attempt to increase the turbulence levels around the spark plug by the break-up of *barrel swirl* or *tumble*. The gas entering the engine has a combination of swirl (vortex motion in a horizontal plane) and barrel swirl (vortex motion in the vertical plane) (see Fig. 16.4(c) and (d)). Swirl momentum is preserved during compression, but is not very useful for spark-ignition engine combustion. Barrel swirl cannot be preserved as ordered motion because the shape of the vortex is destroyed as the aspect ratio of the combustion chamber

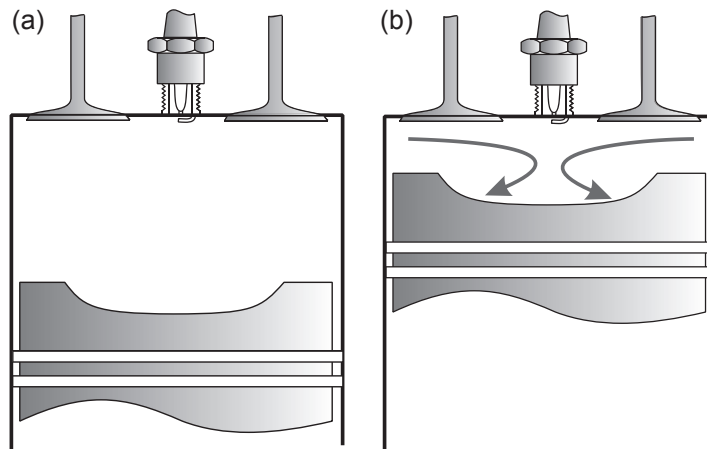
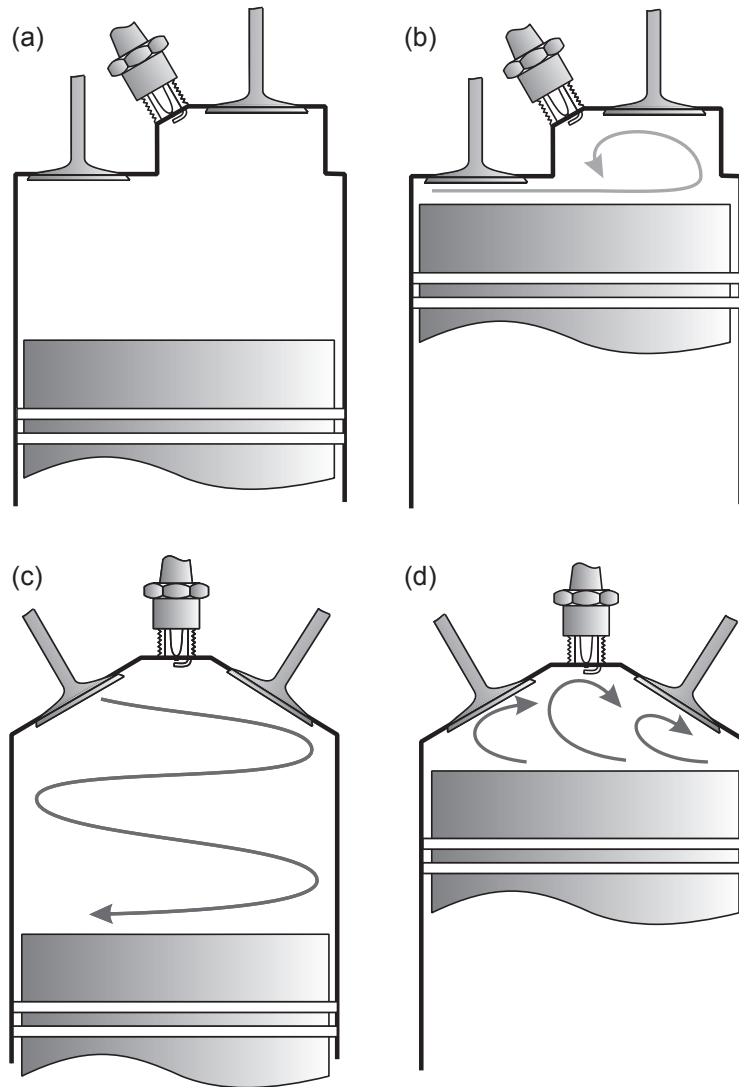


FIGURE 16.3

Squish flow in 'bath tub' combustion chamber (a) piston at mid-stroke (b) piston approaching top dead centre (tdc) and squishing gas from top land region.

**FIGURE 16.4**

High activity cylinder heads for spark-ignition engines (a) May 'Fireball' combustion chamber – note combustion chamber under valve (b) May combustion chamber with piston near top dead centre (tdc) – note squishing of charge into compact chamber (c) modern pent-roof (4-valve) head – note barrel swirl set up in cylinder (d) pent-roof chamber with piston near tdc – note high activity of gas around plug.

changes: barrel swirl is broken down into smaller scale motion which enhances the flame speed. In more modern engines, and with the introduction of manifold or in-cylinder fuel injection, and computer-based control systems, it is possible to operate engines over a wide range of air–fuel ratios. Horie and Nishizawa (1992) describe the operating regions of the Honda VTEC engine, which can run with very low mixture strengths (down to $\lambda = 0.67$) in certain regions of its operation. This engine is discussed in Stone (2012), where he shows a section of the combustion chamber, and the engine's operating regions – the latter are shown in Fig. P16.15. It is noticeable that the engine, which has a four-valve head, runs with only one inlet valve opening at low speed, and the two valves only operate at higher speeds, where they are necessary to achieve the gas flow through the engine. The effect of using only one valve at low speed is to produce a 'tumble', or barrel-swirl vortex in the cylinder (see Fig. 16.4(c) and (d)). This is broken down into general turbulence as the piston approaches tdc, which enhances the flame speed factor, f_f , enabling the weak mixtures to be burnt.

Further features which must be borne in mind with spark-ignition engine combustion chambers are:

1. reducing zones where combustion can be quenched (see top land region in Fig. 16.3);
2. limiting zones which might trap the end gases and cause *detonation*;
3. reducing crevice volumes where uHCs might be trapped, e.g. around top ring groove.

Recently a significant advance in engine combustion systems has been the gasoline direct injection (GDI) engine in which the air–fuel ratio can be varied over the operating range of the engine: this degree of control gives improved fuel consumption and lower emissions. In an ideal GDI engine, it would be possible to achieve qualitative control of the engine power output, doing away with the need for the throttle valve. This would minimise the engine pumping loss, and the efficiency of the engine could approach that of the diesel engine. The first commercial GDI engine was produced by Mitsubishi in 1996 (Kume et al. (1996)): most of the major manufacturers have direct injection (di) versions in their product line now. Besides being able to introduce lean-burn operation at low speed and load, di allows stoichiometric operation during mid-range, and rich operation at high load (to reduce thermal load on the engine). A further benefit of di is that the liquid fuel lowers the temperature in the cylinder, and this increases the volumetric efficiency and enables the engine to have a higher compression ratio. These engines are described in Stone (2012).

16.4 DIESEL (COMPRESSION IGNITION) ENGINES

The design of diesel engine combustion chambers is different from that of spark-ignition engines because of the nature of the diesel process. Fuel, in liquid form, is injected into the diesel engine cylinder through a high-pressure injector. The difference between conventional diesel injection and that in the GDI engine is that in the former the injection occurs very close to tdc, whereas in the GDI injection is earlier. This fuel enters the engine as a jet, or jets, which has to entrain air to enable evaporation of the fuel and subsequent mixing to a point where hypergolic (see Chapter 15) combustion occurs. The mixing and combustion processes are similar to that shown in Fig. 15.11 for a gaseous jet. The droplet size of the fuel varies but is of the order of 20 μm ; the size depends on the hole size of the injection nozzle and the fuel injection pressure, which might be 0.20 mm and 700 bar, respectively, in a small high-speed di diesel engine. The prime considerations in the design of a combustion chamber for a diesel engine are to obtain efficient mixing and preparation of the fuel and air in the time available in the cycle.

The majority of small diesel engines originally designed for passenger cars used the *indirect injection (idi)* process. In these engines, see Fig. 16.5(b), the fuel was injected not directly into the main combustion chamber but into a small swirl chamber (e.g. Ricardo Comet V) connected to the main chamber by a throat. This approach was adopted because it was possible to achieve good mixing of the fuel and air in the pre-chamber due to the high swirl velocities that could be generated there as air was forced into the pre-chamber by the piston travelling towards tdc. This approach had a further advantage that relatively simple fuel injection equipment could be used, with a single-hole nozzle and low-pressure injection pump. Combustion of the rich mixture commenced in the pre-chamber, and the burning gases entered the main chamber, which contained pure air, and generated high turbulence which ensured good mixing of the burning plume and the ‘secondary’ air. Such combustion systems are very tolerant of fuel quality, need relatively simple fuel injection equipment, and can be run at relatively low air–fuel ratios before producing black smoke. Their disadvantage is that their fuel economy is about 10%, or more, worse than their di counterparts.

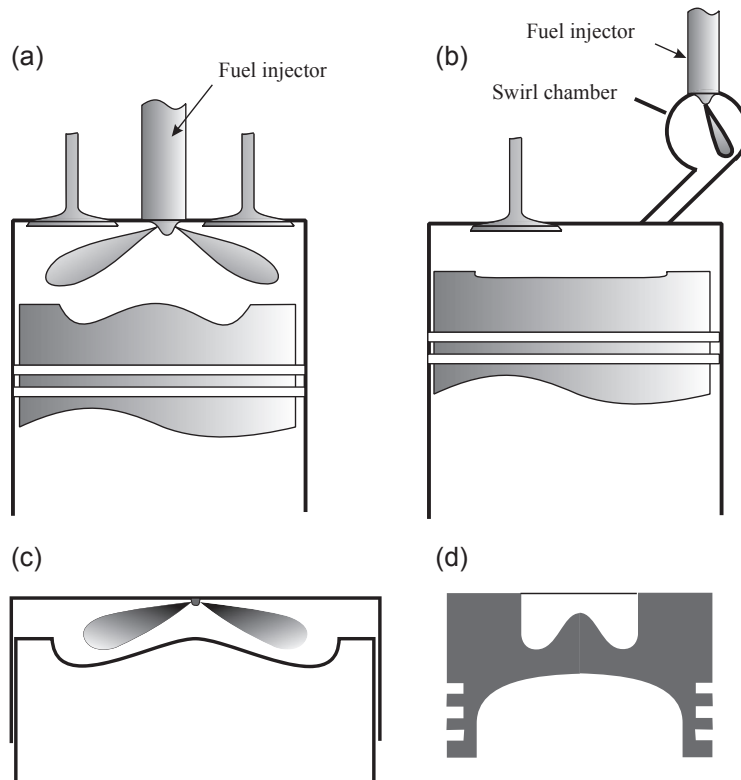


FIGURE 16.5

Some combustion chamber arrangements for diesel engines (a) basic schematic of direct injection (di) diesel engine (b) basic schematic of indirect injection diesel engine (c) combustion chamber arrangement of low- or medium-speed diesel engine (d) combustion chamber arrangement of high-speed di diesel engine.

Direct injection diesel engines (shown schematically in Fig. 16.5(a), and in more detail in Fig. 16.5(c) and (d)) used to dominate the larger size range. However, the introduction of higher injection pressures, and in particular common-rail injection, has resulted in most small vehicular diesel engines (say 400 cm³/cylinder) being di. Nearly all truck diesel engines are di, as are those for rail and marine applications. The bottom limit of size for di diesel engines is reducing all the time and four cylinder engines as small as 1.6 L are available for van and car applications. The largest di diesel engines, with bores as large as 1000 mm, have *quiescent* combustion chambers, in which there is no organised air motion. The mixing of the fuel and air is achieved by the multiple fuel jets entraining air into themselves and bringing about the necessary mixing. More than six holes might be used in the fuel injector nozzle to give good utilisation of the air in the chamber. The relatively low engine speed of large engines allows sufficient time for combustion to occur. As the engine bore size reduces so the engine rotational speed increases, and the time available for combustion becomes shorter. Also the appropriate size of injector hole reduces, until it reaches the limit that can be achieved by production techniques (around 0.18 mm diameter) The increased engine speed, and reduced time for mixing, requires that the rate of mixing of the fuel and air is enhanced above that which can be achieved using a quiescent combustion chamber. The mixing rate can be increased by imparting air motion to the charge, and this is done in the form of *swirl* in the diesel engine. The fuel jets injected into a swirling flow have the peripheral fuel stripped off to form combustible mixture, which is where ignition is initiated. Figure 16.6 shows the ignition points located by high-speed photography in a high-speed di engine: Stone (2012, Plate 2) shows the photographs taken by Zambare (1998) and Winterbone et al. (1997) describe how these were obtained.

Figure 16.6 also shows that the fuel jets impact upon the wall of the piston bowl. This also plays an important contribution in the mixing of the fuel and air, and is necessary at present because high enough mixing rates cannot be achieved in the centre of the bowl itself.

The design of combustion systems for diesel engines must aim at ‘optimising’ the overall combustion process. This takes place in two distinct modes: premixed and diffusion combustion. The

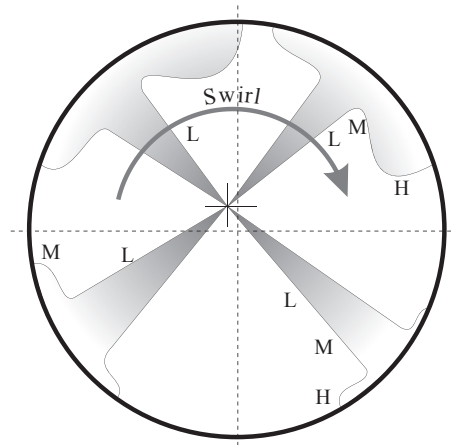


FIGURE 16.6

Sprays and combustion initiation points in a small high-speed direct injection diesel engine H = high swirl; M = medium swirl; L = low swirl.

first fuel that is injected into the cylinder is not ready to ignite until it has evaporated and produced the necessary conditions for hypergolic combustion. This takes a finite time, referred to as the *ignition delay period*, during which the fuel is prepared but not yet ignited. At the end of this period, there is rapid combustion of the premixed fuel and air, which gives rise to a high rate of heat release and produces high temperatures in the combustion chamber. This period has a major effect on the amount of NO_x produced in the engine. Typical equations for the ignition delay period are:

$$t_{ig} = \frac{0.446 e^{(4650/T_{ig})}}{p_{ig}^{1.19}} \text{ ms} \quad (16.15a)$$

Or one developed by Hardenberg and Hase (1979)

$$t_{ig} = (0.36 + 0.22\bar{V}_p) e^{\left[E_A \left(\frac{1}{RT} - \frac{1}{17190} \right) \left(\frac{21.2}{p-12.4} \right)^{0.63} \right]} \text{ }^\circ\text{crank angle} \quad (16.15b)$$

where

$\bar{V}_p$ = mean piston speed (m/s)

p = pressure (bar)

T = temperature (K)

E_A = activation energy = 618,840/(CN + 25)

CN = cetane number

Both Eqns (16.15a) and (16.15b) have a similar form, and are related to the Arrhenius equation introduced in Section 14.3 to define the rate equations. Equation (16.15b) is a more recent formulation than Eqn (16.15a), and has a more complex structure. Both equations are the result of experimental tests on engines with a range of fuels, and cannot be extended far beyond the regime under which they were evaluated, but they do give a basic structure for ignition delay. It should be noted that Eqn (16.15b) contains a term for the CN of the fuel. The value of E_A reduces as the CN increases and this means that the ignition delay is inversely related to CN. A mechanical method for limiting the overall ignition delay is to use two-stage or split injection. In this type of system, a small quantity of pilot fuel is injected into the cylinder some time prior to the main injection process. The pilot charge is prepared and ready to ignite before the main charge enters the chamber, and in this way, the premixed combustion is limited to the pilot charge.

After the premixed period is over the main combustion period commences, and this is dominated by diffusion burning, controlled by the mixing of the fuel and air. Whitehouse and Way (1970) attempted to model both periods by the two equations given below.

Reaction rate

$$R = \frac{K}{N} \frac{p_{O_2}}{\sqrt{T}} e^{\left(\frac{-E_A}{T} \right)} \int_{\alpha_{inj}}^{\alpha} (P - R) d\alpha \quad (16.16a)$$

and, preparation rate

$$P = K' m_i^{(1-x)} m_u^x (p_{O_2})^z \quad (16.16b)$$

where

- p_{O_2} = partial pressure of oxygen
- P = rate of preparation of fuel by mixing
- R = rate of reaction
- m_i = mass of fuel injected
- m_u = mass of fuel unburned

These equations result in instantaneous 'heat release' (the energy added by combustion) patterns of the form shown in Fig. 16.7. One of the diagrams has a short ignition delay (higher CN, or operating temperature), and it can be seen that the instantaneous rate of heat release does not reach such a high level as for the long delay (lower CN, or cold conditions). This is because the time for the physical and chemical processes to enable the fuel to reach a hypergolic state is less, and consequently less fuel is available for spontaneous ignition. The long delay results in a large amount of fuel burning spontaneously, with high temperature rises, high rates of pressure rise ($dp/d\alpha$) and a high level of noise generation. The initial period is governed by the rate of reaction, R . After the premixed phase has taken place the temperatures inside the combustion chamber are high and the rate of reaction is much faster than the rate of preparation, P . At this stage, the combustion process is governed by Eqn (16.16b), which models a diffusion process. During this process, the rate of combustion is controlled by the rate at which the fuel and air mix, and in this phase the hydrocarbon fuel in the centre of the jet is burning in insufficient oxygen. The fuel pyrolyses and forms the precursors of the carbon particles produced in the exhaust system. It is important to mix the burning fuel with the air at the appropriate rate to ensure that the carbon produced during the combustion process is consumed before the exhaust valve opens.

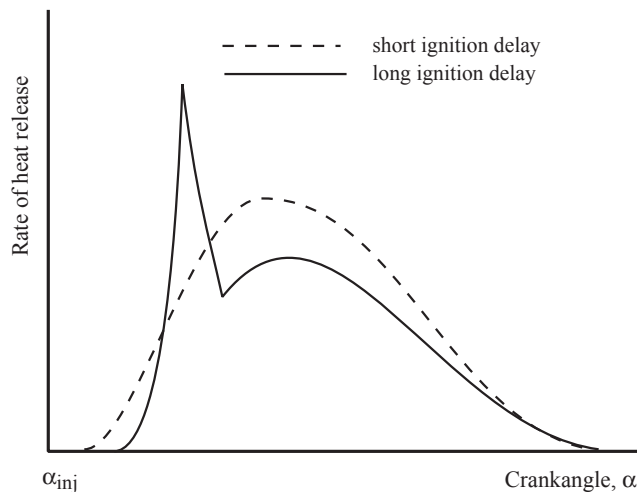


FIGURE 16.7

Effect of ignition delay on rate of heat release diagram.

16.5 FRICTION IN RECIPROCATING ENGINES

The basic equation defining the variation of thermal efficiency of an engine operating on the Otto cycle was derived in Chapter 3, and is from Eqn 3.16

$$\eta_{th} = 1 - \frac{1}{r^{(\kappa-1)}}$$

This thermal efficiency is the *indicated* thermal efficiency. The more important parameter for the engine user is *brake* thermal efficiency, because this relates the energy input in the fuel to the power output at the crankshaft. The brake thermal efficiency is defined as

$$\eta_b = \eta_{th}\eta_m \quad (16.17)$$

where η_m is the mechanical efficiency. The mechanical efficiency accounts for all the losses between the fuel input and the power output, and includes friction, effects of heat loss, and ‘pumping work’, when the gas is flowing through the valves.

$$\eta_m = \frac{\text{brake work}}{\text{indicated work}} = \frac{\text{bmep}}{\text{imep}} = \frac{\bar{p}_b}{\bar{p}_i} \quad (16.18)$$

The value of mechanical efficiency changes over the operating range of the engine. If the engine is idling then the mechanical efficiency is zero because the brake output is zero. The efficiency is maximum at a high power output. A typical value of *maximum* mechanical efficiency for a reciprocating engine is between 80% and 90%: it is very dependent on the rating (bmep) of the engine.

While mechanical efficiency appears to be a useful measure of losses in reciprocating engines, it is better to evaluate these losses using the friction mean effective pressure (fmep). Equation (16.5) relates imep to work output by

$$\bar{p}_i = \frac{\oint p dV}{V_s}$$

where $\bar{p}_i$ is the imep.

The area of the large rectangle in Fig. 16.8 is equal to that of the p - V diagram, because $\bar{p}_i V_s$ has the same area as 1-2-3-4-1.

Also shown on Fig. 16.8 are the brake mean effective pressure (bmep), $\bar{p}_b$, and the fmep, $\bar{p}_f$. These can be related to the imep by

$$\bar{p}_i = \bar{p}_b + \bar{p}_f. \quad (16.19)$$

While imep can be evaluated directly from the p - V , or indicator diagram, fmep and bmep usually have to be evaluated from the output of the engine on a dynamometer. It is relatively easy to evaluate the bmep of an engine using the following equation for power output, P , in kW

$$P = \frac{\bar{p}_b V_s n_{cyl} n_{cyc}}{1000} = \frac{\bar{p}_b L A n_{cyl} n_{cyc}}{1000} = \frac{\bar{p}_b L A n_{cyl} N_{cyc}}{60 \times 1000} \text{ kW}, \quad (16.20)$$

where

L = stroke (m)

A = bore area (m^2)

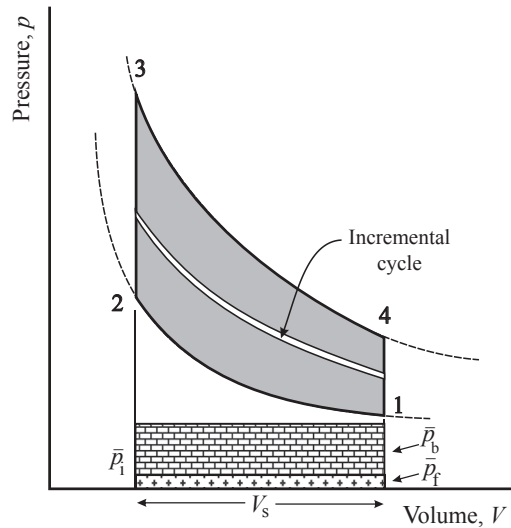


FIGURE 16.8

Otto cycle with friction.

 n_{cyl} = number of cylinders
$$n_{\text{cyc}} = \text{number of cycles/s}$$
$$N_{\text{cyc}} = \text{number of cycles/min}$$

Now, friction mep can be obtained by simple subtraction of the bmep from the imep. However, imep which is evaluated by integrating to obtain the area of the p - V diagram presents some difficulties in measurement accuracy because the imep values are extremely sensitive to:

- crank angle error;
- thermal shock on the pressure transducer.

Also care should be taken when considering f_{mep} since it is difficult to separate frictional effects from pumping work (and even auxiliaries). The pumping work of an engine is that required to draw the gas through the engine. The pumping work of a naturally aspirated engine is almost always negative, i.e. air has to be pumped from the inlet to the exhaust system. In a petrol engine, pumping work is used to control the engine speed by throttling the intake. This is one of the reasons why a petrol engine is less efficient than a diesel engine, especially at part load. In turbocharged engines, especially diesel engines, it is possible for the pumping work to be positive: this is because the pressure in the intake manifold can be larger than that in the exhaust.

Even taking these provisos into consideration, a better measure of the power loss due to friction is the frictional torque or fmep. This tends to be related to engine speed but not closely related to the engine load. Hence a correlation for fmep for four-stroke engines is of the form suggested by Chen and Flynn (1965),

$$\bar{p}_f = C_1 + C_2 \frac{N}{1000} + C_3 \hat{p} \quad (16.21)$$

where $\hat{p}$ is the maximum cylinder pressure and N = engine speed (rev/min). Other models for fmep are discussed in Stone (2012).

The Chen and Flynn equation is a relatively simple expression containing speed and load terms. The coefficients are evaluated from experimental results, and the terms based on engine speed are normally more significant than those for maximum pressure. Hence, at constant engine speed, the fmep is almost a constant, and not dependent on the engine power output (bmep or imep).

16.5.1 THE EFFECT OF FRICTION ON OPTIMUM COMPRESSION RATIO

If an Otto engine is free to work without a peak pressure ($\hat{p}$) limitation then the maximum efficiency is achieved with high compression ratios (r) (see Chapter 3, Eqn (3.16)), i.e.

$$\eta_{th} = 1 - \frac{1}{r^{(\kappa-1)}}$$

However, high compression ratios can result in very high peak pressures, and these might cause detonation of the gas at the end of combustion (called the end gas) as well as high mechanical stresses. If the Otto cycle is limited in peak pressure then the situation changes and *the compression ratio for maximum efficiency will occur when the full pressure rise is achieved by compression: however, the work output will be zero*, as discussed in Chapter 6. If friction is included the situation changes yet again and a compression ratio resulting in the maximum brake thermal efficiency can be evaluated.

Consider that the fmep is constant (at a particular speed), then the compression ratio for maximum thermal efficiency, with a fixed peak pressure, can be evaluated.

For an Otto cycle, shown in Fig. 16.8

$$p_2 = p_1 r^\kappa \quad (16.22)$$

$$p_3 = p_2 \frac{T_3}{T_2} \quad (16.23)$$

Hence energy addition/unit mass

$$q_{23} = c_v (T_3 - T_2) \quad (16.24)$$

Now

$$T_2 = T_1 r^{\kappa-1} \quad \text{and} \quad T_3 = \frac{p_3}{p_2} T_2 = \frac{\hat{p}}{p_1 r^\kappa} T_2 = \frac{\alpha}{r^\kappa} T_2,$$

where $\alpha = \frac{\hat{p}}{p_1}$

$$\text{giving} \quad q_{23} = c_v T_1 r^{\kappa-1} \left\{ \frac{\alpha}{r^\kappa} - 1 \right\} \quad (16.25)$$

By definition, indicated work/unit mass

$$w_i = \eta_{th} q_{23} = \left(1 - \frac{1}{r^{\kappa-1}} \right) c_v T_1 r^{\kappa-1} \left\{ \frac{\alpha}{r^\kappa} - 1 \right\} \quad (16.26)$$

The imep, $\bar{p}_i$ is

$$\begin{aligned}\bar{p}_i &= \int \frac{pdV}{V_s} = \frac{w_i}{V_1 \left(1 - \frac{1}{r}\right)} \\ &= \frac{(r^{\kappa-1} - 1) \left\{ \frac{\alpha}{r^{\kappa}} - 1 \right\}}{(\kappa - 1) \left(1 - \frac{1}{r}\right)} p_1.\end{aligned}\quad (16.27)$$

The imep given in Eqn (16.27) is exactly the same as in Eqn (16.8), except that the term $\frac{p_1 Q'_v}{RT_1 \varepsilon (1 - 1/r)}$ has been subsumed into the ‘shape’ of the diagram, e.g. the temperature rise.

The bmep is $\bar{p}_b = \bar{p}_i - \bar{p}_f$. Let $\bar{p}_f$ be a constant, for example -1 bar.

Then

$$\bar{p}_b = \frac{(r^{\kappa-1} - 1) \left(\frac{\alpha}{r^{\kappa}} - 1 \right)}{(\kappa - 1) \left(1 - \frac{1}{r}\right)} p_1 - \bar{p}_f \quad (16.28)$$

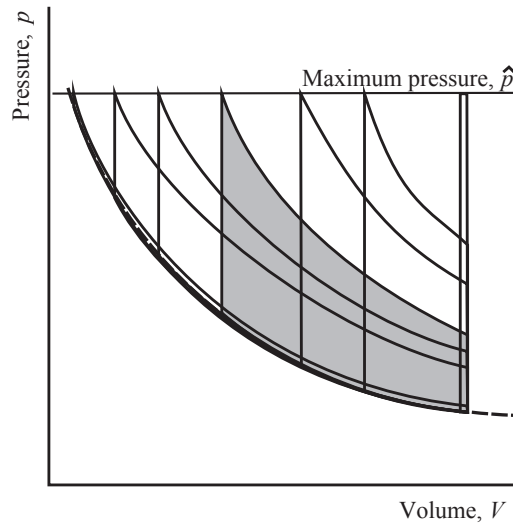
The brake thermal efficiency $\eta_b = w_b/q_{23}$ and $w_b = \bar{p}_b V_s$.

Thus

$$\eta_b = \frac{\bar{p}_b V_s}{c_v T_1 r^{\kappa-1} \left\{ \frac{\alpha}{r^{\kappa}} - 1 \right\}} \quad (16.29)$$

$$\begin{aligned}&= \left\{ \frac{\bar{p}_i}{p_1} - \frac{\bar{p}_f}{p_1} \right\} \frac{(\kappa - 1)}{r^{\kappa-1}} \frac{\left\{ 1 - \frac{1}{r} \right\}}{\left\{ \frac{\alpha}{r^{\kappa}} - 1 \right\}} \\ &= \eta_{th} - \frac{\bar{p}_f}{p_1} \frac{(\kappa - 1)}{r^{\kappa-1}} \frac{\left(1 - \frac{1}{r} \right)}{\left(\frac{\alpha}{r^{\kappa}} - 1 \right)}\end{aligned}\quad (16.30)$$

Figure 16.8 shows imep, bmep and fmeep on a p - V diagram. The fmeep is subtracted from the imep to give the bmep. Figure 16.9 shows that, within a given peak pressure, the ideal work output (neglecting frictional and other losses) of the cycle varies from zero through a maximum value and back to zero again as the compression ratio varies between 1 and $\hat{\alpha} = (\hat{p}/p_1)^{1/\kappa}$. If the peak pressure of an Otto cycle is limited, then it can be seen that there is a compression ratio that maximises the work output of the cycle. This is depicted in Fig. 16.9, which shows a range of cycles with compression ratios from 1 (which is equivalent to heat addition at constant volume) to the maximum value (where an infinitesimal amount of heat can be transferred because the maximum pressure is reached during compression). If these cycles are drawn on a T - s diagram, the one at maximum compression ratio is equivalent to a Carnot cycle, producing no *power output* but achieving an efficiency of $1 - T_C/T_H$.

**FIGURE 16.9**

Comparison of Otto cycles with same peak pressure.

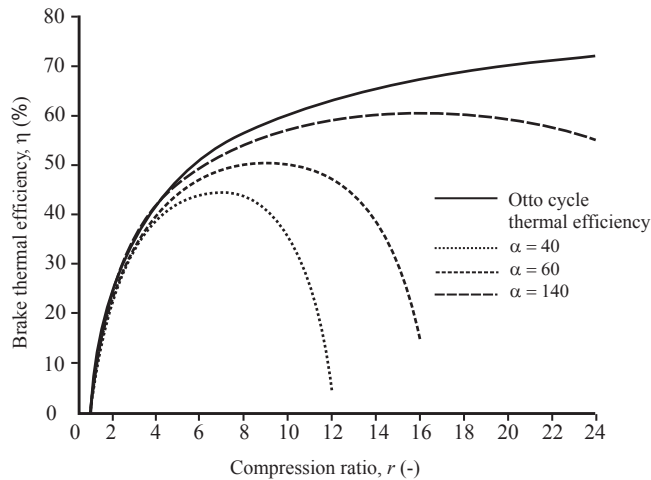
When $\alpha = \hat{\alpha}$ the cycle achieves an efficiency equal to that of a Carnot cycle between the same temperature limits – but produces zero work output. When $\alpha = 1.0$, the situation is equivalent to a constant volume combustion bomb – a temperature rise is achieved but no work is extracted. In between these extremes, there will be a cycle which gives the maximum work output.

Similarly, the efficiency of the cycle is now not a monotonic function of the compression ratio. If the fmep remains constant while the imep is varying then this will cause the efficiency to peak at single value of compression ratio. Figure 16.10 shows the variation of brake thermal efficiency (η_b) as compression ratio varies, calculated using Eqn (16.30). This diagram has been constructed using three values of maximum pressure and an fmep of 1 bar.

Three features are apparent from this diagram.

1. The Otto cycle efficiency increases monotonically with compression ratio. This is because the peak pressure (and peak temperature) increases also.
2. The higher the value of $\hat{p}/p_1$, the higher the maximum efficiency obtained. This reaches a value of about 61% with $\alpha = 140$ at a compression ratio of 16:1. If the peak pressure ratio is reduced, the maximum efficiency and the compression ratio at which it is achieved are significantly reduced, until at $\hat{p}/p_1 = 40$, the optimum compression ratio reduces to around 7:1 with the peak efficiency going down to 44%.
3. If the fmep is increased to 2 bar the maximum efficiency and optimum compression ratio at $\hat{p}/p_1 = 60$ are reduced from 50% to 43% and 9:1 to 7:1 respectively. Developing a graph similar to Fig. 16.10 is set as a problem in P16.9.

From these results, it can be deduced that engines should be designed to achieve the highest practicable peak pressure ratio ($\alpha = \hat{p}/p_1$) and also the lowest practicable fmep ($\bar{p}_f/p_1$). The $\hat{p}/p_1$ value of 40 would result in peak pressure of 40 bar for a naturally aspirated engine, and this is relatively low

**FIGURE 16.10**

Variation of brake thermal efficiency with compression ratio. Maximum pressures = 40, 60, 140 bar: $f_{mep} = 1$ bar.

by modern standards. Petrol engines will normally be operating in the range of 60 bar peak pressure whereas diesel engines will achieve values up to 140 bar (this applies to medium speed engines producing around 1000–3000 kW). At these peak pressures, the optimum compression ratio will be in the range 12:1 to 18:1. The effect of friction on the efficiency is less in this case because $\bar{p}_b$ is greater.

16.6 SIMULATION OF COMBUSTION IN SPARK-IGNITION ENGINES

Combustion processes were described in detail in Chapter 15, and the way in which these basic principles apply in engines was discussed above. A simplified model of combustion in spark-ignition engines, based on the paper by Benson et al. (1975), which includes constant pressure in the inlet and exhaust manifolds, will be used here to investigate various parameters affecting engine ‘cycles’. The resulting computer program, entitled SPIE (SPark Ignition Engine), is available in executable form for the reader to use to perform his/her own investigations, and has been used to develop some problems at the end of this chapter. This program can be accessed by visiting <http://booksite.elsevier.com/9780444633736/>. While this section is based on the simulation of a spark-ignition (petrol) engine cycle many of the conclusions would be similar for a compression ignition (diesel) engine. In the spark-ignition engine combustion can be considered to be based on the propagation of a flame through a premixed medium of fuel and air. The mixture can be formed by fuel injection equipment mounted in the inlet manifold upstream of the inlet valve. In some engines currently under development injection directly into the cylinder is used to introduce stratified combustion to allow the engine to operate at lower overall air–fuel ratios. There are difficulties in achieving good combustion under all operating conditions. A brief description of diesel engine combustion was given in Section 16.4, when it is stated that the initial combustion is the spontaneous ‘explosion’ of the initially premixed fuel and air, followed by the diffusion burning of the later fuel as it is injected into the cylinder. The examples discussed in Section 16.3 could be expanded to consider the flow of gases into and out of the cylinder, but

in these examples this aspect of the engine ‘cycles’ has been omitted. Those interested in the gas exchange processes of internal combustion engines should refer to Winterbone and Pearson (1999).

Ignition is achieved in a spark-ignition engine by means of a spark plug, which adds about 30 mJ to the charge in the vicinity of the spark gap. Once a reasonable sized flame kernel has been created the flame will propagate through the charge. The speed of propagation is a function of the laminar flame speed of the mixture and the level of turbulence in the combustion chamber. If the mean flow in the chamber is negligible then the flame will attempt to traverse the charge in a hemispherical mode. The latter is affected by the shape of the combustion chamber. A simple model of such a situation is depicted in Fig. 16.11(a) and (b) for a disc chamber with a central spark plug. The hemispherical mode of growth of the burned zone would mean that combustion would advance at an ever increasing rate as the flame radius increased. However, this situation is affected by the geometry of the combustion chamber, and in particular the piston. When the flame contacts the piston surface the rate of energy release is decreased because the enflamed region does not grow as rapidly.

In many modern engines, the cylinder head is not flat, and often the design is like that in Fig. 16.11(c) and (d), referred to as a pent-roof chamber. The shape of the cylinder head has an effect on the flow in the chamber and it is possible to develop high levels of turbulence, which will enhance the flame speed (see Section 15.4). In addition, the shape of the chamber will affect the volume of the flame during its initial travel, simply because its volume will be reduced by the cylinder geometry. The flame travel is depicted in Fig. 16.11(c) and (d), and the rate of entrainment of charge can be compared to Fig. 16.11(a) and (b) – however, the reduction in volume is compensated by the increased turbulence of the mixture, which increases the flame factor f_t (discussed below, and in Chapter 15).

A computer program has been used to simulate combustion in spark-ignition engines. The combustion process is based on a two-zone combustion model, in which a flame traverses the charge, and has *burned* and *unburned zones*, in which the properties are calculated using equilibrium thermodynamics (see Chapter 13) – hence it will not calculate the levels of pollutants. The unburned zone contains the reactants (fuel and air), and no reactions occur between the constituents. The burned zone contains the products of combustion and dissociation.

The basic parameters of the simulated engine are listed in Table 16.1.

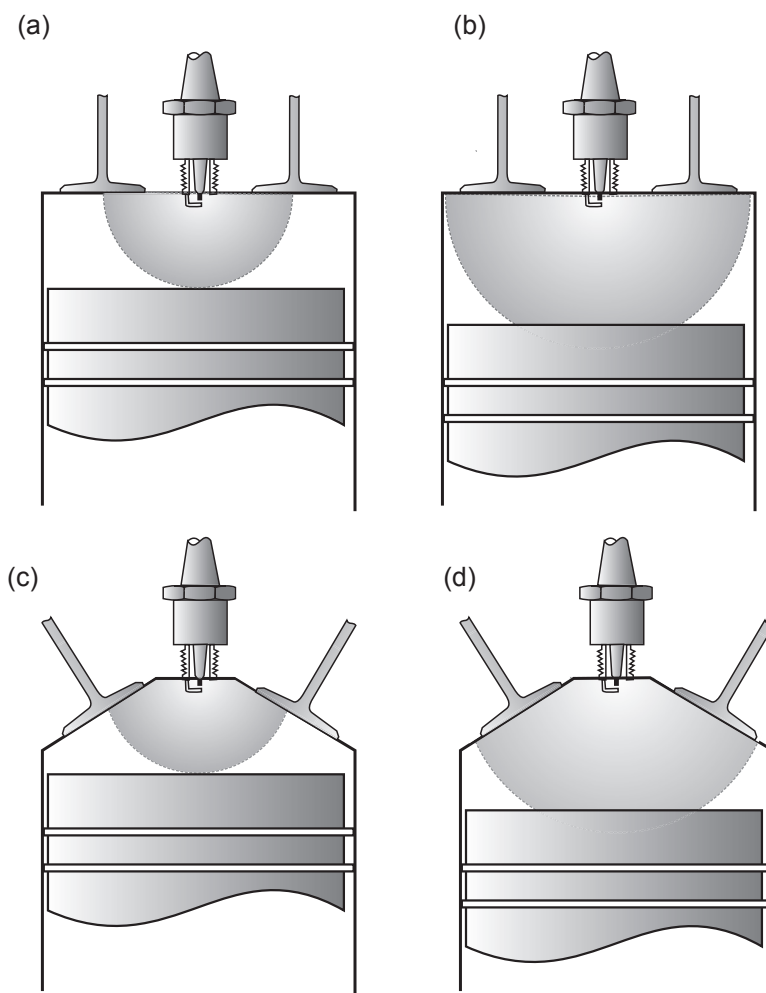
The program has been used to investigate the effect of the following engine parameters on the pressure, temperature and flame radius inside the cylinder of the engine considered:

- compression ratio
- engine speed
- air–fuel ratio
- ignition timing
- flame speed factor
- exhaust gas recirculation (egr).

These effects are shown as the basic parameters plotted against crankangle, related to the angle after tdc firing (atdc).

16.6.1 EFFECT OF COMPRESSION RATIO ON ENGINE COMBUSTION

The compression ratio, in this case for a realistic engine it is the effective one, has two effects on combustion. The first, and obvious effect, is on the thermodynamic cycle. The pressure and temperature at the end of compression will be affected by the compression ratio, with a higher compression

**FIGURE 16.11**

Schematic diagram of flame propagation in a spark-ignition engine with central spark plug and flat cylinder head and piston crown (the so-called *disc chamber*) (a) hemispherical flame has not reached piston (b) flame has reached piston and is truncated (c) and (d) similar flame size in pent-roof chamber.

ratio increasing both these parameters. Compression ratio will also have a significant effect on the geometry of the combustion chamber, and a higher compression ratio will often result in a combustion chamber of narrower aspect ratio. This means that the flame will contact the piston earlier (see Fig. 16.11(b)), and this will tend to reduce the rate of heat release. The compression ratio of the base engine was both increased and decreased as shown in Table 16.2.

The effect of compression ratio on the engine cycle is shown in Figs 16.12 and 16.13. It can be seen that a higher compression ratio gives a higher peak pressure, but has little effect on the release

Table 16.1 Specification of Engine Used for This Exercise

Engine swept volume	1.6 L Engine
Nominal compression ratio	9.60
Engine speed	3500.0 rev/min (58.333 rev/sec)
Molar fraction of residuals	0.050
Mixture strength (equivalence ratio)	1.000
Ignition angle	692.0 Delay = 1.0
Flame speed factor(actual/laminar flame speed)	4.000

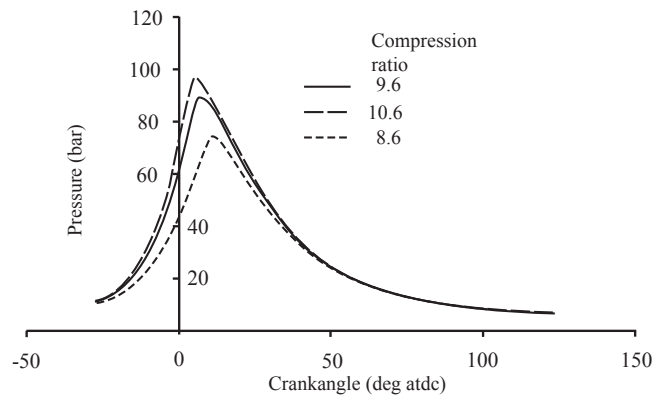
*Data in **bold** have been changed during parameter study.*

Table 16.2 Compression Ratios

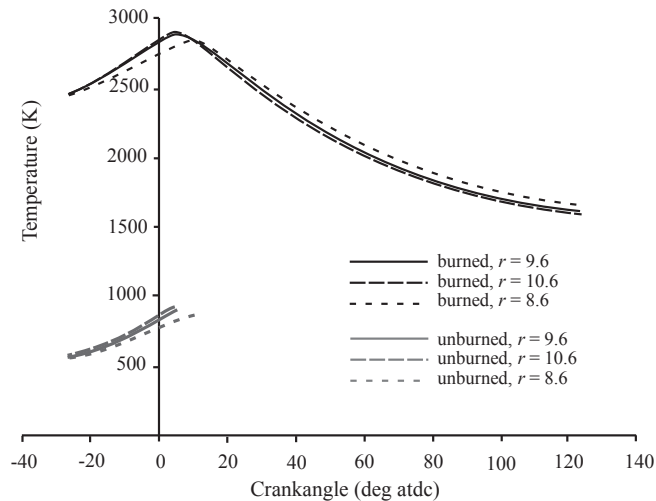
Lower compression ratio	8.6
Baseline compression ratio	9.6
Higher compression ratio	10.6

pressure. Also the higher compression ratio slightly increases the maximum temperature achieved in the burned and unburned zones, but actually reduces the release temperature (at exhaust valve opening (evo)).

This is because the peak temperature of the burned zone is reached earlier, and then the effective expansion ratio is bigger. The higher temperature and pressure at the end of the compression stroke also have an effect on the speed of the flame during the combustion. Hence, from these observations it can be

**FIGURE 16.12**

Variation of pressure with compression ratio.

**FIGURE 16.13**

Variation of gas temperatures with compression ratio.

deduced that a higher compression ratio increases the efficiency of the cycle, as would be expected from the Otto cycle analysis; increases the emissions of NO_x , because of the higher combustion temperature; and increases the mechanical loading on the engine structure. Also, the conditions of the gas at the end of the combustion process (the *end gas*, which is trapped around the periphery of the combustion chamber) will have a greater tendency to spontaneously ignite (*detonate*) at higher compression ratios because both the pressure and temperature are higher at the crucial time.

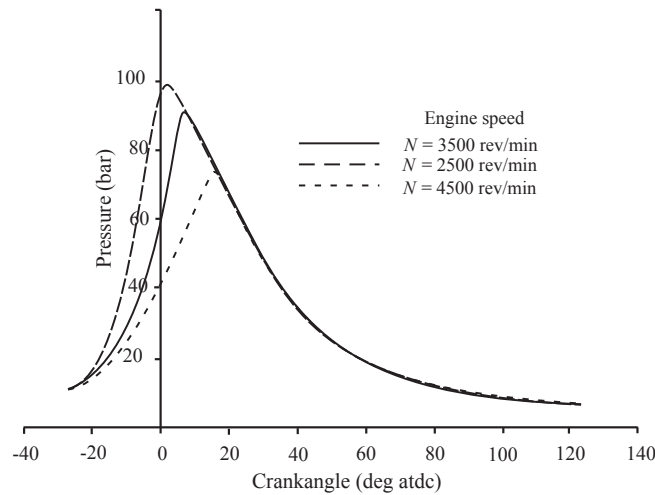
16.6.2 EFFECT OF ENGINE SPEED ON COMBUSTION

Three values of engine speed have been considered, as shown in Table 16.3. The only parameter changed in this case was the engine speed, and this means that the ignition timing is not the optimum for all the speeds.

It can readily be seen, from Fig. 16.14, that the spark timing is over-advanced for the lower speed of 2500 rev/min, because the peak pressure occurs at tdc. However, the ignition timing would have to be advanced for the engine speed of 4500 rev/min to improve the efficiency of the cycle. The effect of not having the optimum timing is that the peak temperature is highest at 2500 rev/min, and this will produce excessive NO_x and give a tendency to detonation. The reason for this change in pressure and

Table 16.3 Engine Speeds

Lower engine speed (rev/min)	2500
Baseline engine speed (rev/min)	3500
Higher engine speed (rev/min)	4500

**FIGURE 16.14**

The effect of engine speed on the pressure–crank angle diagram.

temperature diagrams is how the flame speed varies, in terms of crank angle, with engine speed. The actual variation of flame speed with time will be quite small, but the effect of increasing the engine speed is to spread the heat release period over a longer crank angle interval, and hence further down the expansion stroke. This will reduce the efficiency of the engine cycle at high speeds because the effective expansion ratio of the gas is reduced. In this example, the flame speed factor, f_f , was maintained constant although in a real engine this might change as the speed varies. It has been shown that the turbulence levels in an engine do increase with speed, but less than proportionally, which means that f_f will decrease slightly as engine speed increases. Because the combustion period, in terms of crank angle, changes with engine speed the ignition timing of spark-ignition engines is related to engine speed, either by a mechanical (fly-weight) system or by the electronic engine management system. The timing is *advanced* (moved farther before tdc (bt dc)) as the engine speed increases.

16.6.3 THE EFFECT OF AIR–FUEL RATIO ON ENGINE COMBUSTION

The power output of a spark-ignition engine is basically controlled by the *quantity* of charge taken into the engine cylinder. This is achieved by opening and closing a throttle valve in the intake system, or by directly changing the trapped air–fuel ratio if the engine is a GDI one. The effect of the throttle valve is to produce a depression in the intake manifold, and reduce the density of the charge trapped in the cylinder at inlet valve closure (ivc). The power output of a diesel engine (and a GDI one, to some extent) is controlled by changing the amount of fuel delivered to the engine cylinder while maintaining the quantity of air trapped in the cylinder essentially constant: it is controlled by changing the *quality* of the charge in the engine cylinder. A major advantage of the diesel engine when operating at low load is that the pumping work required to pass air through the engine is not increased, whereas the spark-ignition engine has to ‘pump’ air from a low pressure in the inlet manifold to atmospheric pressure in the exhaust.

Table 16.4 Equivalence Ratios		
Equivalence ratio 1	$\lambda = 0.6$ (<i>lean</i>)	Air–fuel ratio, $\epsilon = 25.20$
Equivalence ratio 2	$\lambda = 0.7$ (<i>lean</i>)	Air–fuel ratio, $\epsilon = 21.60$
Equivalence ratio 3	$\lambda = 0.8$ (<i>lean</i>)	Air–fuel ratio, $\epsilon = 18.90$
Equivalence ratio 4	$\lambda = 0.9$ (<i>lean</i>)	Air–fuel ratio, $\epsilon = 16.80$
Baseline equivalence ratio	$\lambda = 1.0$ (stoichiometric)	Air–fuel ratio, $\epsilon = 15.12$
Equivalence ratio 5	$\lambda = 1.1$ (<i>rich</i>)	Air–fuel ratio, $\epsilon = 13.75$
Equivalence ratio 6	$\lambda = 1.2$ (<i>rich</i>)	Air–fuel ratio, $\epsilon = 12.60$
Equivalence ratio 7	$\lambda = 1.3$ (<i>rich</i>)	Air–fuel ratio, $\epsilon = 11.63$

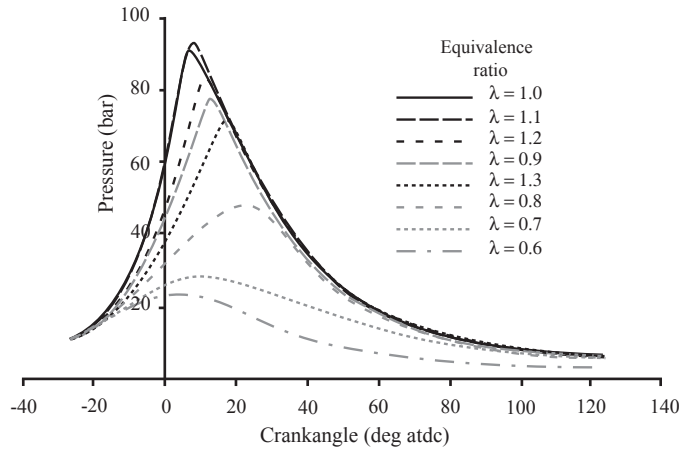
It is possible that future, lean-burn spark-ignition engines (GDI) will employ a combination of quantitative and qualitative governing. Advantages of operating spark-ignition engine in the lean-burn mode are:

- lower pumping losses at low load, giving improved low-load fuel economy;
- lower NO_x emissions.

The effect of air–fuel ratio on flame speed was discussed in Chapter 15. Its influence on engine performance, defined by the equivalence ratio ($\lambda = \epsilon_{\text{stoic}}/\epsilon$), has been investigated over the range shown in Table 16.4. The range of equivalence ratios goes from $0.6 < \lambda < 1.3$, where 0.6 is a weak mixture with an air–fuel ratio of 25.2, and 1.3 is a rich mixture with an air–fuel ratio of 11.63. The weakest mixture is just about being achieved in modern vehicles, but requires a high level of air motion in the cylinder to achieve complete combustion and to avoid the possibility of misfire.

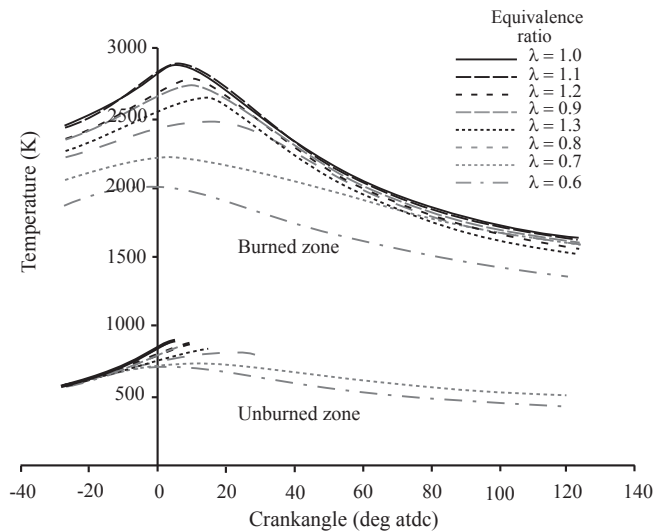
It can be seen from Fig. 16.15 that equivalence ratio has a large effect on the pressure–crank angle diagram for the engine cycles. The baseline data achieved a peak pressure of 91.76 bar whilst the slightly richer cycle, with $\lambda = 1.1$, achieved 93.73 bar, and can be seen to produce more work output. This aligns with experimental experience, where the maximum power output of a spark-ignition engine occurs slightly to the rich side of stoichiometric. Examination of Fig. 16.16 shows that the maximum temperature reached with this cycle is almost the same as the stoichiometric one. As the mixture is made richer the maximum pressure achieved in the cycle decreases, and the combustion period increases. Both these effects are detrimental to the fuel economy of the engine, in addition to the inability of the air to fully oxidise all the fuel in the charge.

When the mixture is made weaker the peak pressure achieved in the cycle reduces, and so does the area of the p – V diagram. Hence, the weaker cycles are producing less power. This means that the power output of the engine can be controlled by the air–fuel ratio rather than using the throttle. There are other advantages in this approach, because the peak cycle temperature is reduced significantly at high air–fuel ratios, and this will have a beneficial effect on the emissions of NO_x . Hence, a spark-ignition engine operating in the lean-burn regime looks an attractive proposition for meeting emissions legislation at low load. There is, however, a problem with running engines in the lean region, and this is the significant reduction in flame speed that occurs. The flame speed is highest at around stoichiometric mixture strength (see Figs 15.5 and 15.6), but does not change much within a small band of λ on either side. However, by the time λ has reduced to 0.8 the flame speed will have gone down considerably, and when λ is 0.7 and less the flame does not travel quickly enough to burn all the

**FIGURE 16.15**

Effect of equivalence ratio on pressure–crank angle diagram.

charge in the cylinder and there is still some unburned charge in the cylinder at evo. This effect can be overcome by increasing the turbulence in the cylinder by various means, including the use of variable valve porting and timing at part-load. The flame radius continues to increase as the flame follows the piston down the cylinder. This is also indicated on Fig. 16.16, where it can be seen that the unburned charge, as evidenced by the temperature associated with it, still exists at evo.

**FIGURE 16.16**

Effect of equivalence ratio on temperature–crank angle diagrams.

Table 16.5 Ignition Timings	
Advanced ignition timing	687
Baseline ignition timing (°ca)	692
Retarded ignition timing 1	697
Retarded ignition timing 2	702

16.6.4 EFFECT OF IGNITION TIMING ON ENGINE COMBUSTION

The ignition timing used in the standard case was 692° crank angle, which is 28 °btdc. It was decided to investigate the effect of both advancing (i.e. taking the spark initiation farther btdc) and retarding the timing, (i.e. taking the spark initiation closer to tdc). Three cases were examined, as shown in Table 16.5; 687° means the timing was advanced by 5° and 695° and 702° means that the ignition was retarded in two 5° steps. The effect of these timings on pressure can be seen in Fig. 16.15, where advancing increases the peak pressure achieved in the cylinder, while retarding reduces the peak pressure. It can also be seen that advancing the timing increases the peak temperature (see Fig. 16.18) achieved during combustion, but tends to decrease the release temperature, while retarding reduces the peak temperature but increases the release temperature. This shows how retarding the ignition timing can have a beneficial effect on the emissions of NO_x, while reducing the tendency for the engine to knock. However, retarding does increase the release temperature, which might be detrimental to the life of the exhaust valve, but could be helpful in achieving earlier catalyst light-off. It is obvious from Fig. 16.17 that retarding the ignition has reduced the power output of the cycle, and hence the cycle efficiency.

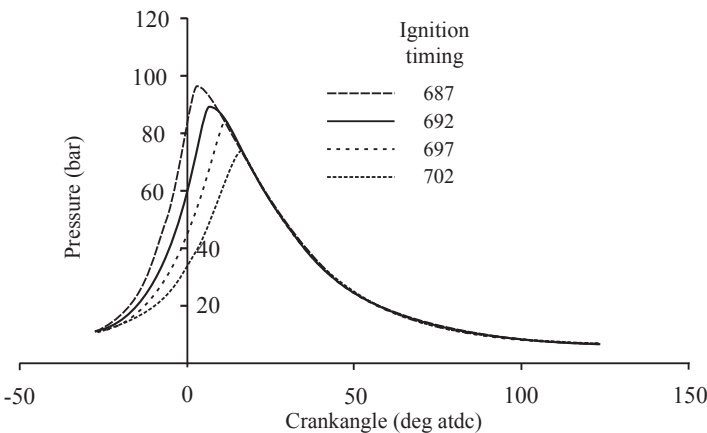
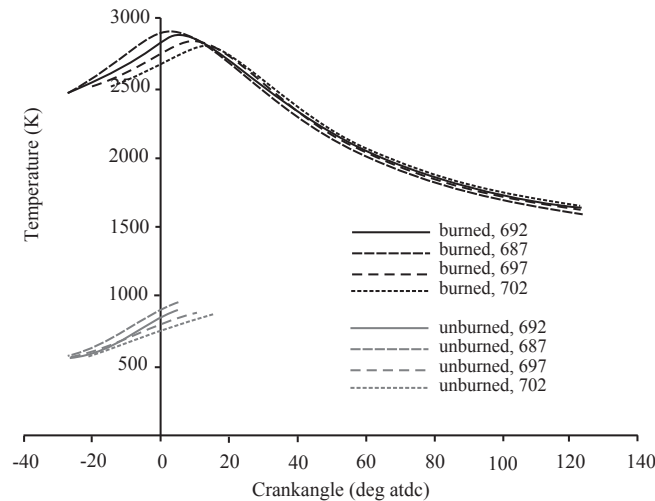


FIGURE 16.17
Effect of ignition timing on pressure–crank angle diagram.

**FIGURE 16.18**

Effect of ignition timing on temperature–crank angle diagrams.

16.6.5 EFFECT OF FLAME SPEED FACTOR ON ENGINE COMBUSTION

The flame speed factor used for the base set of data was $f_f = 4.00$. This means that the turbulent flame speed (see Section 15.4.3) is given by:

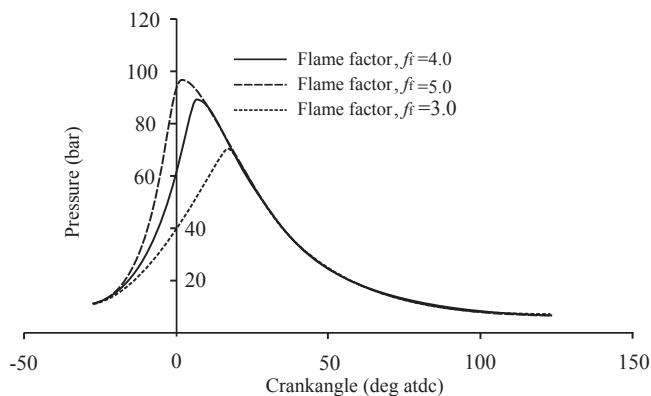
$$u_t = f_f u_{\ell}. \quad (16.31)$$

This value of $f_f = 4.00$ was obtained by comparing the measured and predicted pressure–crank angle diagrams for this engine when running on a test bed. The flame speed factor was both increased and decreased as shown in Table 16.6.

The results obtained are shown in Fig. 16.19. This shows that if f_f is increased to 5.00 then the combustion is more rapid, and the peak pressure moves closer to tdc, while its magnitude increases significantly. This has a small effect on the variation of temperature in the combustion chamber, although slightly higher peak temperatures are achieved in the burned zone, which will increase the emissions of NO_x . The time for the combustion to reach the full radius of the chamber reduces from about 32° to 27° crank angle. A slower burning velocity, as achieved with the smaller flame speed factor of 3.00, lengthens the burning period to about 47° . The slower burning velocity also reduces the peak pressure, and moves it later in the cycle. More importantly, slower burning makes the conditions in the end gas (the unburned gases) more susceptible to detonation (*knock*), because both the temperature and pressure of the end gas is increased. Some of the major recent improvements in engine

Table 16.6 Flame Speed Factors

Lower flame speed factor	3.00
Baseline flame speed factor	4.00
Higher flame speed factor	5.00

**FIGURE 16.19**

The variation of cylinder pressure with flame speed factor, f_t .

combustion have come about by the increase in the value of f_t through the use of cylinder head and valve arrangements which enhance the turbulence in the cylinder during combustion. Such an improvement in the value of f_t is particularly necessary to achieve good combustion with lean mixtures and high levels of egr (see section 16.6.6).

16.6.6 EFFECT OF RESIDUALS FRACTION (OR EGR) ON ENGINE COMBUSTION

The residuals, the products of combustion from a previous cycle, which exist inside an engine cylinder when the inlet valve closes can come from the following sources:

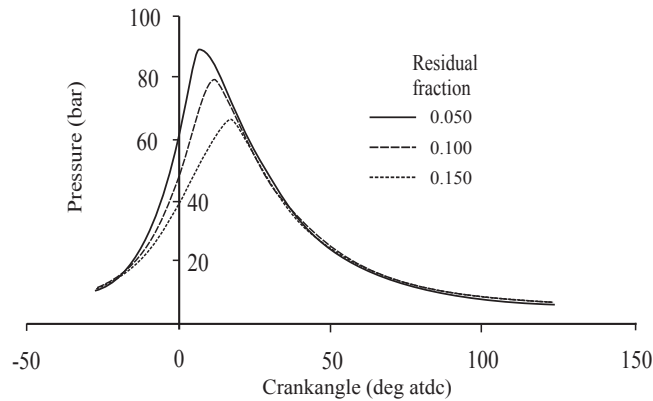
- incomplete scavenge of the engine cylinder during the gas exchange process;
- back flow through the exhaust valve at the end of the gas exchange process; and
- exhaust gas recirculated from the exhaust manifold to the inlet with the express purpose of controlling emissions.

In the first two cases, the exhaust gases will be hot because they will not have undergone any form of cooling or heat transfer. In the last case the gases could be cold, having passed through a heat exchanger on their way from the exhaust pipe to the inlet manifold.

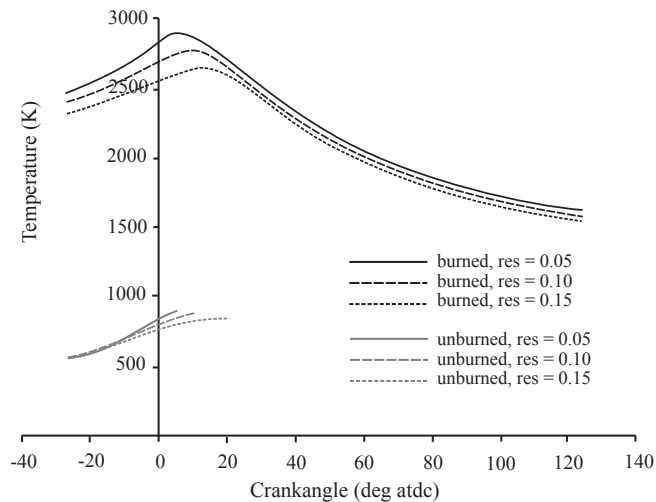
The effect of egr is to change the composition of the charge before combustion. The exhaust gases primarily consist of CO_2 , H_2O , and N_2 , and this mixture contains a significant quantity of triatomic gases. These have a higher value of c_p and a lower value of κ , which means that the index of compression is reduced and the temperature at the end of compression is also decreased. This has the overall effect of reducing the temperatures achieved during combustion, and has a significant effect on the production of NO_x . The effect of increasing the cold residual fraction in the cylinder at ivc is shown in [Figs 16.20 and 16.21](#). The residual fraction was increased from 5% (0.05) to 15% (0.15) for the cases shown. [Figure 16.20](#) shows how the increase in residual fraction reduces the pressures achieved in the cylinder, and the impact this will have on power output. It can be seen from [Fig. 16.21](#) that the egr has reduced the peak temperature by about 250 K (from 2885.8 to 2643.7 K), and has resulted in a significant reduction in the period the temperature is above 2000 K – an important factor in the production of NO_x .

These effects have come about for two reasons:

- the addition of exhaust gas to the charge has changed the gas properties, as discussed above;
- the egr has effectively added more inert gas to the charge, and reduced the amount of fuel that can be burned to maintain the stoichiometric air–fuel ratio (based on the *oxygen* in the charge).

**FIGURE 16.20**

The effect of residuals (exhaust gas recirculation (egr)) on cylinder pressure.

**FIGURE 16.21**

The effect of residuals (exhaust gas recirculation (egr)) on burned and unburned gas temperatures.

16.7 CONCLUDING REMARKS

Having spent the initial chapters of this book developing thermodynamic theory the reader has at last been introduced to actual 'hardware'. Brief descriptions of engine combustion chambers have been given, and analysed to examine the basic principles that have affected their design. It has been demonstrated that the thermodynamic engineer has to try to manipulate the real world to achieve the aim of high efficiency along with reduced emissions.

This chapter has brought together the theoretical developments in Chapters 3 and 15. It shows how actual cycles differ from the heat engine cycles and even air-standard cycles that form the basis of much fundamental thermodynamic analysis. While pointing the engineer in the right direction these underestimate the influence of the extraneous influences. An excellent demonstration of this is that an engine

operating on an Otto cycle, as many engines approach in real life, can achieve the Carnot efficiency if an infinitesimal amount of fuel is burned, and the engine produces zero power output. This agrees with the concept developed in Chapter 6, when endoreversible engines were examined to find their efficiency at maximum power. This idea was taken further, and it was shown that friction can have a dramatic effect on the brake thermal efficiency of a reciprocating engine, and the compression ratio at which it occurs.

Finally, an engine simulation was 'exercised' to see the effect of changing various parameters in isolation: something that is practically impossible in the real world. This enabled the effects of compression ratio, engine speed, air–fuel ratio, ignition timing, flame speed and egr to be investigated. The results give an insight into the effect of these parameters on cylinder pressures and temperatures. They show that combustion is not an instantaneous process but one that can become quite protracted under certain circumstances, e.g. high engine speeds with slow flame speeds, or the wrong ignition timing; and the broad effect of operating at extreme air–fuel ratios.

16.8 PROBLEMS

- P16.1** (a) One of the main problems encountered in the design of a diesel engine combustion system is the mixing of the air and fuel sufficiently rapidly to ensure complete combustion. Explain, using diagrams, how these problems are catered for in the design of
- (i) large automotive diesel engines;
 - (ii) the smallest automotive diesel engines.

Give two relative advantages of each type of combustion system.

(b) Compare and contrast the combustion systems of diesel and spark-ignition engines in the forms they are applied to passenger cars.

- P16.2** A method of reducing (improving) engine fuel consumption and reducing the emissions of NO_x in a spark-ignition engine is to run it lean, i.e. with a weak mixture. Discuss the problems encountered when running engines with weak mixtures, and explain how these can be overcome by design of the engine combustion chamber.
- P16.3** Calculate the ignition delay period (in deg ca) in a diesel engine using Eqns (16.15a) and (16.15b) using the conditions at the beginning of fuel injection that exist after compression in the engine with the following initial parameters.

Compare the results to those calculated by the equation proposed by Watson (1979):

$$t_{\text{ig}} = \frac{3.52e^{(2100/T_{\text{ig}})}}{p_{\text{ig}}^{1.022}}$$

Conditions at ivc: $p = 1.3$ bar; $T = 310$ K; compression index, $n_c = 1.35$. Assume $\text{CN} = 50$.

- (a) Effective compression ratio, $r = 10:1$; engine speed, $N = 2000$ rev/min.
- (b) Effective compression ratio, $r = 15:1$; engine speed, $N = 2000$ and 4000 rev/min.

Comment on these results – do they seem reasonable?

[(a) 78.7; 27.8; 5.61; (b) 16.92; 10.63; 2.57; 33.84; 21.27; 4.59]

P16.4 This question is based on Fig. 16.9. An engine operating on an Otto cycle has a maximum peak pressure of 60 bar. If the pressure and temperature at the beginning of the cycle are 1.0 bar and 300 K respectively, evaluate the compression ratio that results in the maximum work output from the cycle. What is the thermal efficiency of that cycle? What effect does the peak pressure have on the result?
[2:1; 24.2%]

P16.5 Compare the air-standard cycle thermal efficiencies of an Otto cycle obtained by calculating the state points around the cycle with the value obtained from Eqn (3.16) for an 'engine' operating with a compression ratio, r , of 15:1, and an air-fuel ratio, $\epsilon = 28:1$. The trapped conditions are 1.0 bar and 27 °C. Assume $Q_p' = 44000$ kJ/kg, the specific heat capacity at constant volume, c_v , is 0.721 kJ/kg K, and $\kappa = 1.4$. The trapped conditions are 1 bar and 27 °C.
[66.1%; 65.62%]

P16.6 Compare the air-standard cycle thermal efficiencies of a diesel cycle obtained by calculating the state points around the cycle with the value obtained from Eqn (3.20) for an 'engine' operating with a compression ratio, r , of 15:1, and an air-fuel ratio, $\epsilon = 28:1$. The trapped conditions are 1.0 bar and 27 °C. Assume $Q_p' = 44000$ kJ/kg, the specific heat capacity at constant volume, c_v , is 0.721 kJ/kg K, and $\kappa = 1.4$. The trapped conditions are 1 bar and 27 °C.
[56.8%; 55.4%]

It has been suggested in Fig. 16.2 that it is possible to evaluate the thermal efficiency of a diesel cycle by considering it to be an infinite number of incremental Otto cycles. Examine the truth of this statement by dividing the diesel cycle into 10 incremental Otto cycles.

[56.7%]

P16.7 Recalculate the Otto cycle in P16.5 using EQUIL2 to evaluate the conditions around the cycle. Do these calculations both with and without considering dissociation. How has the use of more accurate data, and a better evaluation of the combustion process affected the results? Is the effect of dissociation appreciable? Explain your reasoning.
[47.98%]

P16.8 Recalculate the diesel cycle in P16.6 using EQUIL2 to evaluate the conditions around the cycle. Do these calculations both with and without considering dissociation. How has the use of more accurate data, and a better evaluation of the combustion process affected the results? Is the effect of dissociation appreciable? Explain your reasoning.
[46.8%]

P16.9 It was shown that the brake thermal efficiency of an engine with friction peaked at relatively low compression ratios (see Fig. 16.10). Recalculate this diagram with fmep, $\bar{p}_f = 2$ bar. Comment on the effect of higher friction values.
[5.5, 37.1%; 7, 43.4%; 13, 54.9%]

The following problems are based on using the simulation program SPIE. This program can be accessed by visiting <http://booksite.elsevier.com/9780444633736/>. The basic engine data for the program is available in a file (basic.data), and this is based on the data used to calculate Figs 16.12 to 16.21 – however, certain minor changes internal to the data mean that the results obtained by you will not exactly replicate those diagrams. The trends and general conclusions will, obviously, be the same.

- P16.10** Use SPIE to evaluate the optimum equivalence ratio (λ) for the engine defined in basic.data, with the following operating conditions:
 $N = 4000$ rev/min; Compression ratio = 10.0:1; $\alpha_{ig} = 695^\circ$ (25 °btdc); flame speed factor, $f_f = 5.0$; and residual fraction = 0.050.
 How did you define this optimum value? Did you use maximum power, or maximum efficiency?
- P16.11** Use SPIE to evaluate the optimum values for the data in P16.10, but with a lower compression ratio of 8:1.
 Comment on how the results have changed.
- P16.12** Discuss the results of P16.10 and P16.11. Consider the pressure–crank angle diagrams, the temperature diagrams, the power outputs and the thermal efficiencies in your discussion.
- P16.13** Vary the flame speed factor over the following range: $3.0 < f_f < 7.0$. Discuss the effects. Describe which types of combustion chamber will produce the low values of f_f , and which will produce the high ones.
- P16.14** Investigate the effect of varying the ‘spark timing’ over the range $685^\circ < \alpha_{ig} < 710^\circ$. Describe the influence of the spark timing on the engine performance. What is the limitation to having very early ignition? Basic engine data: $N = 4000$ rev/min; Compression ratio = 9.0:1; flame speed factor, $f_f = 5.0$; and residual fraction = 0.050.
- P16.15** The Honda VTEC engine can operate at values of $\lambda = 0.67$ ($\epsilon = 22:1$ for petrol/gasoline) over certain parts of its operating range – see Fig. P16.15, based on Horie and Nishizawa (1992). Using SPIE, and limiting the fuel to octane, investigate what has to be done to achieve viable cycles at these very weak mixtures (Note that the Honda engine reduces the area of the inlet valve at low load, but this will not be done in this question. This will have a

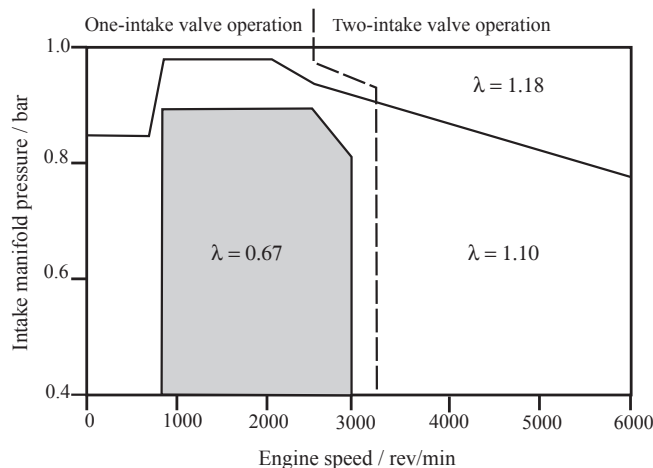


FIGURE P16.15

Based on operating region of Honda VTEC engine Horie and Nishinaga (1992).

minor effect on the principles being illustrated). Assume compression ratio = 9.0:1; $\alpha_{ig} = 695^\circ$ (25 °btdc); flame speed factor variable; and residual fraction = 0.050.

{Hint: to achieve the low intake manifold pressures stated, it is necessary to modify basic.data in the following way.

Block 200 1.100 800.00 1.34 1.013 290.00

becomes 200 1.100 800.00 1.34 p_{in} T_{in}

Block 550 1.100 320.0 becomes 550 $p_{trapped}$ $T_{trapped}$.

Use $p_{trapped} = 1.1p_{in}$, and $T_{trapped} = T_{in} + 40$ }

P16.16 Why is the Honda VTEC engine operated at $\lambda = 1.18$ at high load. Use the basic engine data for P16.15 for your calculations.

GAS TURBINES

17

Gas turbines have a number of distinct characteristics which make them attractive for certain applications:

- low weight;
- low basic volume;
- low vibration level;
- low noise output;
- good multi-fuel capability;
- rapid start-up and load changes.

However, at present they have a major drawback to general use which is poor fuel consumption (relative to the diesel engine), particularly at part-load conditions.

This has resulted in gas turbines finding application in certain well-defined areas, viz.:

- aircraft;
- high-performance ships;
- off-peak power generation – although hardly used;
- oil rigs.

All these applications have a common factor of high power/weight (power density) or power/bulk ratio. Another application is the *combined cycle gas turbine (CCGT)* for power generation. In this cycle a gas turbine is used as the first stage of a two stage power generator, with a steam turbine being used as the next – bottoming – stage. This type of plant has a number of advantages over the more traditional steam turbine, and these include the following:

- lower first cost;
- faster construction time;
- less SO_x production because of natural gas fuel;
- faster warm-up time when coming on load;
- higher thermal efficiency;
- better part-load efficiency.

It is also presaged that the next generation of intercooled regenerated (ICR) gas turbines will compete in terms of fuel consumption with low-speed diesel engines in marine propulsion. The current minimum size of this plant does not bring them into the diesel engine power envelope at present.

There are two types of gas turbine – open cycle and closed cycle. By far the greatest proportion of gas turbines built is the open cycle type. The closed cycle gas turbine requires a cooler (cf. the condenser of a steam turbine) to enable the working fluid to circulate through the system – and this allows exotic fluids, e.g. mercury, to be considered, as done in a nuclear cycle.

17.1 THE GAS TURBINE CYCLE

The gas turbine is similar to the internal combustion engine inasmuch as it is not usually a ‘heat engine’. The exception to this is the closed cycle gas turbine shown in Fig. 17.1(a). In this device the working fluid, air or a similar ‘perfect gas’, circulates through the components and undergoes a thermodynamic cycle. Much of the analysis of gas turbine cycles is based on the closed cycle, but the basic conclusions can be applied to the open cycle engine.

The gas turbine cycle is referred to as the *Joule* or *Brayton* cycle, and this was discussed briefly in Section 3.2.5: the basic cycle is shown in Fig. 17.2 (which is exactly the same as Fig 3.17). The closed cycle gas turbine consists of a compressor, turbine, heater and cooler. Hence energy is added to the working fluid in the heater (analogous to the boiler of a steam turbine). A major difference between the energy addition and rejection processes of the gas turbine and steam turbine is that in the former the processes are at almost constant pressure but varying temperature (because the gas does not change phase) whereas in the latter the temperature range is quite small because there is a phase change to contain the energy. This has an effect on the cycle efficiency and the work ratio. The work done in the cycle is depicted by the areas of the p - V and T - s diagrams in the case of reversible processes.

The most common type of gas turbine is the open cycle one in which the air is used to burn the fuel. The air does not undergo a cycle and there are mass transfers across the engine boundaries hence the device is not a heat engine. A schematic diagram is shown in Fig. 17.1(b). This engine produces a net power output via the shaft connecting the compressor and turbine: the exhaust gas is at approximately atmospheric pressure. The ‘cycle’ for this engine is the same as for the closed cycle one, except the working fluid is not cooled from 4 to 1, and is shown in Fig. 17.2(a) and (b). Another variant of the open cycle gas turbine is that used in aircraft, when often the requirement is to produce a jet of

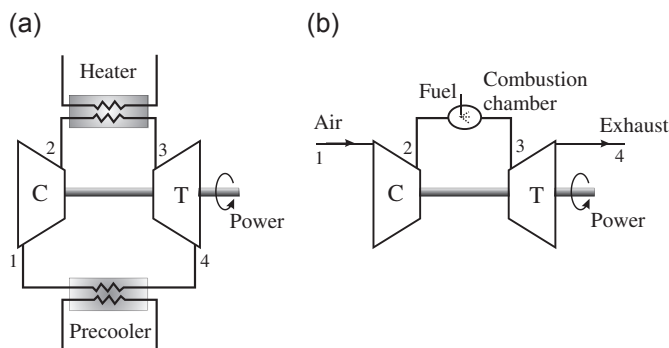
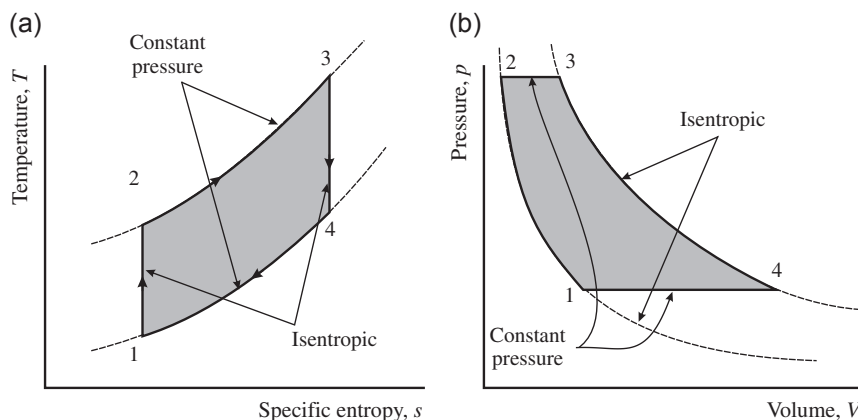


FIGURE 17.1

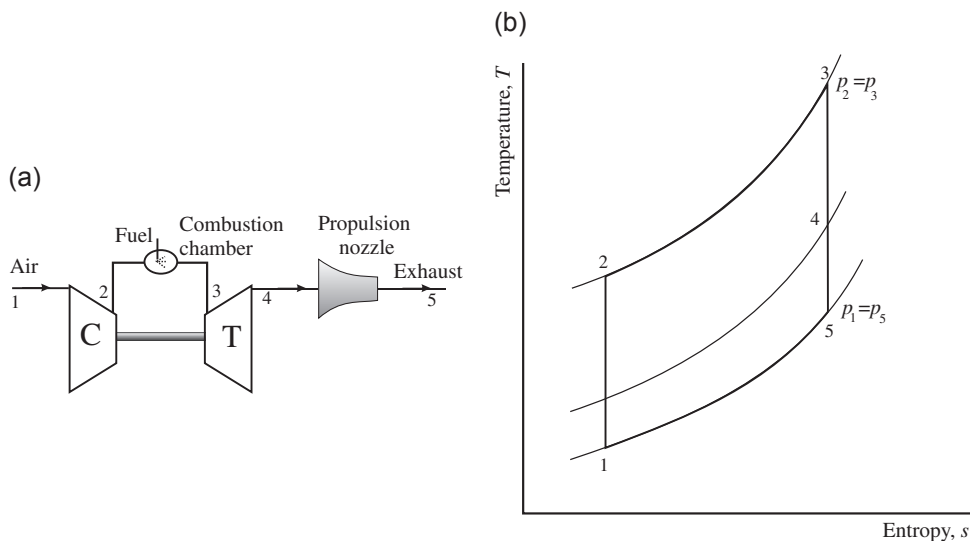
(a) Closed cycle gas turbine. (b) Open cycle gas turbine.

**FIGURE 17.2**

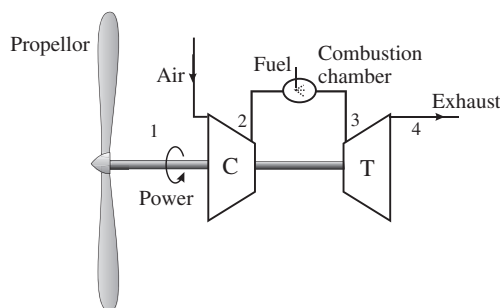
Property diagrams for gas turbine cycle. (a) Temperature–entropy ($T-s$) diagram. (b) Pressure–volume ($p-V$) diagram.

hot exhaust gas but no shaft power. This engine is depicted in Fig. 17.3(a) and the cycle is shown in Fig. 17.3(b).

In the basic jet engine there is a power balance between the compressor and turbine and no shaft work is delivered. The output of a jet engine is the net thrust provided by the engine, which is a result of the momentum change of the air across the engine and, in the case of sonic exhaust, the pressure

**FIGURE 17.3**

Jet gas turbine. (a) Schematic of engine. (b) Temperature–entropy ($T-s$) diagram for cycle.

**FIGURE 17.4**

Turboprop aircraft gas turbine.

difference across the engine. These engines are discussed in [Section 17.3](#). In certain variants, e.g. the turboprop and the fan engines, some shaft work is also taken out of the main shaft to drive the propeller or fan. This modifies the design of the components and the power balances. A schematic of a turboprop gas turbine is shown in [Fig. 17.4](#).

Gas turbines are being increasingly used for power generation, when they are used in combination with steam turbines to make a CCGT power plant. A schematic diagram of such a plant is shown in [Fig. 17.5\(a\)](#). This has been much simplified, and usually more than one gas turbine is coupled to the steam turbine. The thermal efficiency of such plant is higher than that of the gas turbine or steam turbine operating on its own. This is because the temperature range of the combined cycle is bigger than the range of either of the individual components, as can be seen in [Fig. 17.5\(b\)](#) which shows the cycles for a CCGT. A further advantage of this type of plant is that the load control can be achieved by changing the number of gas turbines coupled to the steam turbine. For example, if there are four gas turbines the power output might be controlled down to 75% load by reducing the output of all the gas turbines. At between 75% and 50% load perhaps only three turbines will be run, and so on. This means that the gas turbines are always working close to full load – their most efficient operating regime. The power output of the steam turbine reduces as the load level goes down.

17.2 SIMPLE GAS TURBINE CYCLE ANALYSIS

The simple gas turbine cycle can be examined quite easily by going around the cycle; consider [Fig. 17.2\(a\) and \(b\)](#) for the closed cycle gas turbine, and assuming unit mass of fluid:

Compressor work, w_{12}

$$w_{12} = -(h_2 - h_1) = -c_p(T_2 - T_1) \quad (17.1)$$

Turbine work, w_{34}

$$w_{34} = -(h_4 - h_3) = c_p(T_3 - T_4) \quad (17.2)$$

The heat supplied (at constant pressure), q_{23} is

$$q_{23} = c_p(T_3 - T_2) \quad (17.3)$$

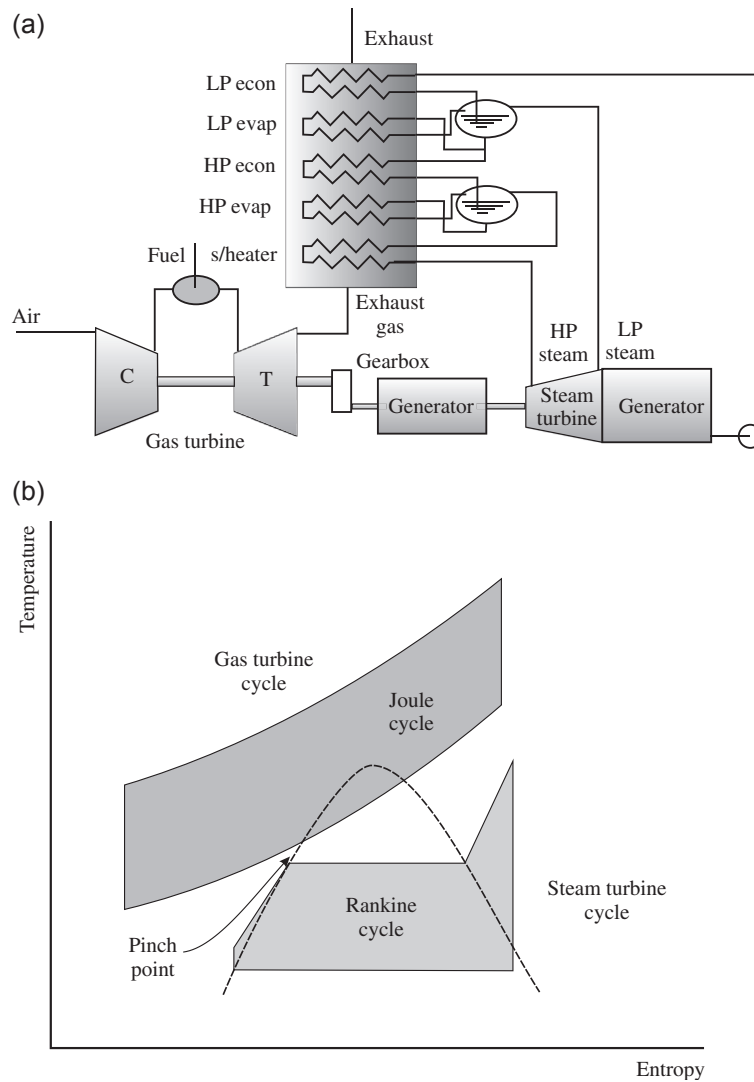


FIGURE 17.5

(a) Schematic of combined cycle gas turbine power plant. (b) Joule and Rankine cycles of combined cycle gas turbine power plant. LP, low pressure; HP, high pressure.

Thus the cycle efficiency,

$$\eta = \frac{w_{\text{net}}}{q_{23}} = \frac{w_{34} + w_{12}}{q_{23}} = \frac{(T_3 - T_4) - (T_2 - T_1)}{(T_3 - T_2)} \quad (17.4)$$

Assuming that the processes 1–2 and 3–4 in Fig. 17.2 are isentropic then the temperatures can be related to the pressure ratios. Let

$$r_p = \frac{p_2}{p_1} = \frac{p_3}{p_4} \quad (17.5)$$

Then, for isentropic processes,

$$T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{\kappa-1}{\kappa}} = T_1 r_p^{\frac{\kappa-1}{\kappa}} \quad (17.6)$$

and

$$T_4 = T_3 \left(\frac{p_4}{p_3} \right)^{\frac{\kappa-1}{\kappa}} = \frac{T_3}{r_p^{\frac{\kappa-1}{\kappa}}} \quad (17.7)$$

Substituting in Eqn (17.4) gives

$$\eta = 1 - \frac{1}{r_p^{\frac{\kappa-1}{\kappa}}} \quad (17.8)$$

The work ratio of the cycle, which defines the *sensitivity of the engine to irreversibilities*, is

$$r_w = \frac{w_{\text{net}}}{w_{34}} = \frac{w_{34} + w_{12}}{w_{34}} = \frac{(T_3 - T_4) - (T_2 - T_1)}{T_3 - T_4} \quad (17.9)$$

which can be written as

$$r_w = 1 - \frac{T_2}{T_3} = 1 - \frac{T_1}{T_3} r_p^{\frac{\kappa-1}{\kappa}}. \quad (17.10)$$

Equation (17.8) shows that the efficiency of a gas turbine is dependent on the ratio of maximum and minimum pressures, whereas in the reciprocating engine it is dependent on the ratio of maximum and minimum volumes. Equation (17.10) shows that the work ratio, which is a measure of the sensitivity of the engine to irreversibilities, is a function of both the pressure ratio and the temperature ratio. To get maximum values of efficiency and work ratio it is necessary to operate the turbine at the highest values of r_p and T_3 and the minimum value of T_1 . Normally T_1 is limited by atmospheric conditions, say around 300 K at sea level. T_3 will be limited by the metallurgical properties of the blade materials: attempts to increase T_3 are brought about by film cooling of the blades of the turbine or coating them with ceramic materials.

Note that it is possible to define the maximum pressure ratio that can be used by relating this to the temperature ratio. In this case

$$\hat{r}_p = \left(\frac{T_3}{T_1} \right)^{\frac{\kappa}{\kappa-1}} \quad (17.11)$$

and then

$$\hat{\eta} = 1 - \frac{T_1}{T_3} \quad (17.12)$$

so that the efficiency of this cycle is the Carnot efficiency. However, if $\hat{r}_p$ is used this also implies that the full temperature rise occurs through compression without any fuel addition and hence the cycle is of infinitesimal width and produces no work.

Figure 17.6 shows the effect of changing the compressor pressure ratio on the T - s diagram, and hence the work achieved from the cycle. The area of a typical cycle, with pressures of p_1 and p_2 , is quite significant and the temperature rise is split between the isentropic temperature rise in the compressor and that caused by burning fuel in the combustion chamber. In the low-pressure ratio cycle (p_2'') the compressor pressure ratio is negligible and the small distance between the isobars results in a small work output and consequently low efficiency. This 'cycle' is essentially that of a combustion chamber alone. If the pressure ratio is such that the compression process achieves the maximum temperature limit (p_2) then the capacity to do work is negligible but, as stated above, the efficiency is the Carnot efficiency. The diagram in the last case approaches the typical rectangle of the Carnot cycle.

It is apparent from Fig. 17.6 that there must be a cycle which derives the maximum net work for the process, i.e. maximises the area of the T - s diagram. This can be evaluated from the equation for net work.

$$w_{\text{net}} = c_p T_3 \left\{ 1 - \frac{1}{r_p^{(\kappa-1)/\kappa}} \right\} - c_p T_1 \left\{ r_p^{(\kappa-1)/\kappa} - 1 \right\} \quad (17.13)$$

If $\sigma_r = r_p^{(\kappa-1)/\kappa}$, where σ_r is the isentropic temperature ratio, then

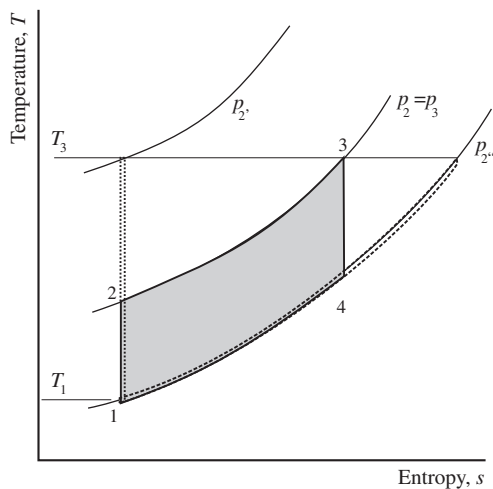


FIGURE 17.6

Effect of pressure ratio on the gas turbine cycle.

$$w_{\text{net}} = c_p T_3 \left\{ 1 - \frac{1}{\sigma_r} \right\} - c_p T_1 \{ \sigma_r - 1 \}. \quad (17.14)$$

The maximum net work is obtained when $\partial w_{\text{net}} / \partial \sigma_r = 0$, hence

$$\frac{\partial w_{\text{net}}}{\partial \sigma_r} = c_p T_3 \frac{1}{\sigma_r^2} - c_p T_1 = 0, \quad (17.15)$$

giving

$$\sigma_r^2 = \frac{T_3}{T_1} \quad \text{or} \quad \sigma_r = \left(\frac{T_3}{T_1} \right)^{1/2} = \sqrt{\gamma}, \quad (17.16)$$

where γ is the ratio of the maximum to minimum temperature. Now the isentropic ratio, $\sigma_r = T_2/T_1 = T_3/T_4$. Thus, for maximum net work $\frac{T_2}{T_1} \frac{T_3}{T_4} = \gamma$, but by definition, $\gamma = T_3/T_1$ and hence $T_2 = T_4$.

This means that in the cycle which produces the maximum net work the temperature of the gas leaving the compressor (T_2) is equal to the temperature of the gas leaving the turbine (T_4). An effect of this is that a heat exchanger cannot be used in this cycle (see Section 17.2.2).

17.2.1 EFFECT OF TEMPERATURES FOR DELIVERING AND REJECTING ENERGY

In the previous section it was shown that the cycle efficiency can approach the Carnot efficiency: this occurs when an infinitesimal quantity of energy is added at ‘constant temperature’. If the working fluid is considered to be a perfect gas (i.e. constant specific heats) then the energy levels in the cycle are linearly related to the temperature of the gas. This enables the following analysis to be performed. A typical gas turbine cycle is shown in Fig. 17.7. It is assumed that the maximum temperature of the cycle is limited to T_b because of metallurgical considerations (e.g. turbine blade temperatures). The inlet temperature is T_a . Energy is added (in the combustion chamber) between 1 and 2 and the *mean temperature of energy addition* is $\bar{T}_B$. For an ideal cycle, with a perfect gas as the working fluid, the *mean temperature of energy rejection* is $\bar{T}_A$, which can be evaluated from T_1 and T_4 .

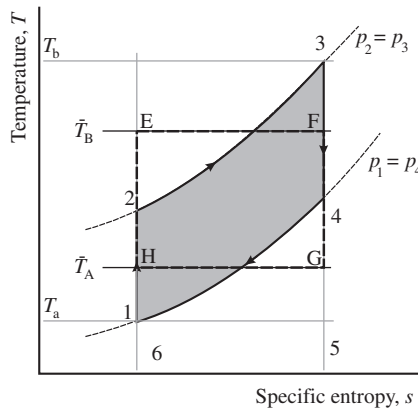


FIGURE 17.7

Mean temperature of energy addition and rejection in gas turbine.

In Fig. 17.7, it is possible to evaluate the mean temperature of energy transfer. If the gas were an ideal one then its enthalpy would be

$$h = \int_0^T c_p dT = \int_0^S T ds, \quad \text{along an isobar.} \quad (17.17)$$

This would result in mean temperatures of energy addition and rejection of

$$\bar{T}_B = \frac{\int_2^3 T ds}{s_3 - s_2}, \quad (17.18)$$

and

$$\bar{T}_A = \frac{\int_1^4 T ds}{s_4 - s_1}. \quad (17.19)$$

This means that, in Fig. 17.7, the areas 23562 and EF56E (which represent the energy addition) are equal, as are the areas for energy rejection – 14561 and HG56H. Similarly, the areas representing work (12341 and EFGHE) are equal. The efficiency of the Joule cycle is given by

$$\eta_{\text{Joule}} = \left(1 - \frac{Q_A}{Q_B}\right) = \left[1 - \frac{\bar{T}_A(s_5 - s_6)}{\bar{T}_B(s_5 - s_6)}\right] = 1 - \frac{\bar{T}_A}{\bar{T}_B}. \quad (17.20)$$

This is the same efficiency as a Carnot cycle operating between the temperatures of $\bar{T}_A$ and $\bar{T}_B$. The reason the Joule cycle does not achieve the efficiency of the Carnot cycle operating between T_a and T_b is because the temperature of isobaric heat reception and rejection varies as the heat transfer occurs, and a certain amount of potential for work is lost in the irreversible heat transfer processes between the hot and cold reservoirs and the working fluid. The only time that $\bar{T}_A$ can equal T_a and $\bar{T}_B$ can equal T_b is for the trivial case when the whole temperature rise occurs in the compressor – and no work is produced, as discussed above. The poor use of available energy has been discussed in Chapter 4.

Thus, the way to improve the efficiency of operation of the cycle is to increase the *mean* temperature of energy addition and reduce the *mean* temperature of energy rejection. There are a number of ways of achieving this and these will be discussed below.

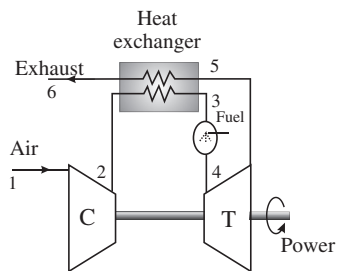
17.2.2 GAS TURBINE WITH HEAT EXCHANGER

One method of improving the efficiency of gas turbines is to fit a heat exchanger between the exhaust gas and that entering the combustion chamber. A schematic of such an engine is shown in Fig. 17.8. The effect of the heat exchanger is apparent from Fig. 17.9 which shows the cycle with heat exchange.

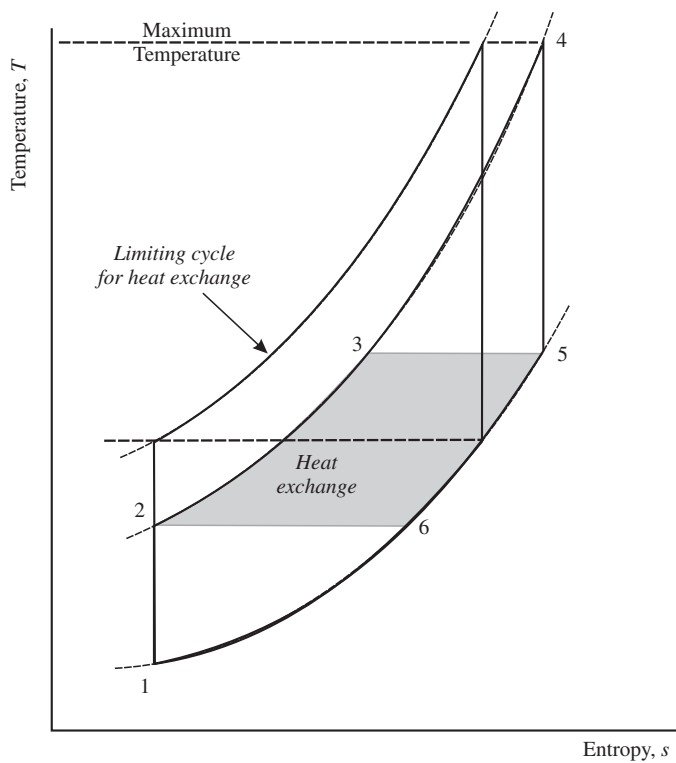
The heat exchange is depicted by the shaded area and, in this case the heat exchanger is 100% effective. The heat exchanger effectiveness is defined as (Fig. 17.9)

$$\epsilon = \frac{T_3 - T_2}{T_5 - T_2} \quad (17.21)$$

i.e. it is the actual rise in temperature achieved compared to the maximum rise that could be achieved. In this case $T_3 = T_5$ and $T_2 = T_6$.

**FIGURE 17.8**

Gas turbine and heat exchanger.

**FIGURE 17.9**

Gas turbine cycle with heat exchange.

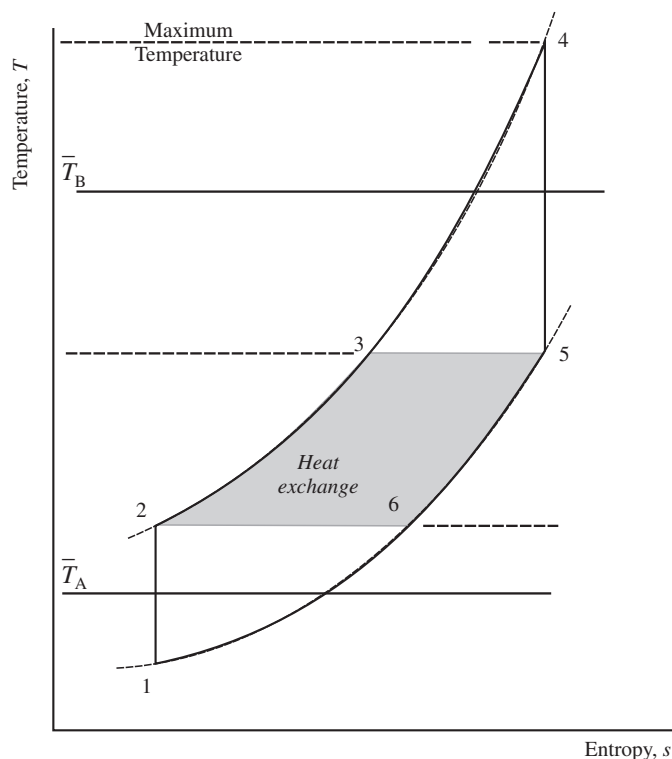


FIGURE 17.10

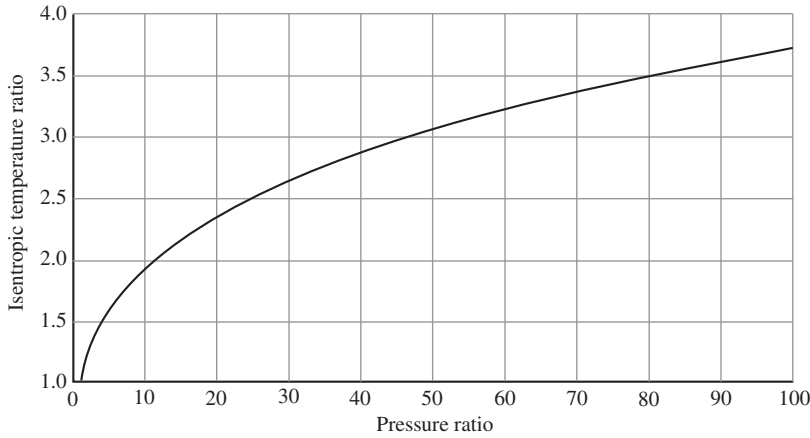
Mean temperatures of energy addition and rejection for gas turbine with heat exchanger.

The effect of the heat exchanger is obviously to reduce the amount of energy required from the fuel for the same maximum temperature, while the actual work output of the gas turbine (1-2-4-5-1) remains constant. However, another way to consider this is to look at the mean temperatures of energy addition and rejection (see Fig. 17.10). The values depicted by $\bar{T}_B$ and $\bar{T}_A$ for the heat exchange cycle can be compared with those for the non-heat exchange one: these are shown by dotted lines. Hence, heat exchange raises the mean temperature of energy addition and lowers the mean temperature of energy rejection.

Figure 17.9 also shows how heat exchange is more effective with low-pressure ratio gas turbines than high ones. As the pressure ratio increases for the same maximum temperature the difference between T_5 and T_2 diminishes until, at some limiting pressure ratio they become equal. Obviously it is not possible to use a heat exchanger for this cycle. A convenient way of analysing gas turbines is to plot parameters against the *isentropic temperature ratio* defined as

$$\sigma_r = r_p^{(\kappa-1)/\kappa} \quad (17.22)$$

where r_p is the compressor pressure ratio. This relationship is shown in Fig. 17.11.

**FIGURE 17.11**

Relationship between pressure ratio (r_p) and isentropic temperature ratio (σ_r).

As stated before, this approach relates the pressure ratio and temperature ratio graphs through a ‘logarithmic’ transformation. Then, compressor work

$$w_C = \frac{c_p T_1}{\eta_C} (\sigma_r - 1); \quad (17.23)$$

the energy addition

$$q_{23} = c_p \left[T_3 - T_1 \left\{ 1 + \frac{1}{\eta_C} (\sigma_r - 1) \right\} \right]; \quad (17.24)$$

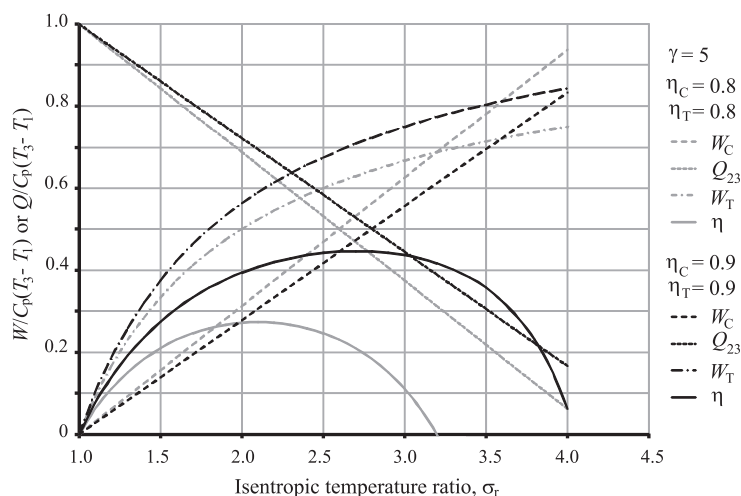
and the turbine work

$$w_T = c_p \eta_T T_3 \left[1 - \frac{1}{\sigma_r} \right] \quad (17.25)$$

It is possible to introduce $\gamma = T_3/T_1$ and then

$$q_{23} = c_p T_1 \left[\gamma - \left\{ 1 + \frac{1}{\eta_C} (\sigma_r - 1) \right\} \right]. \quad (17.26)$$

The relationships derived in Eqs (17.23)–(17.26), and the values of efficiency (η) and net work (w_{net}) are shown in Fig. 17.12. This shows that it is possible to get high efficiencies with high values of the ratio between the maximum and minimum temperatures of the cycle, γ . A value of $\gamma = 5$ is equivalent to $T_{\text{max}} = 1500$ K if the inlet temperature is 300 K: of course, for an aircraft engine, at altitude the value of T_1 will be significantly lower, giving a concomitant reduction in T_{max} . Similarly, as shown in Fig. 17.12, the overall efficiency of the turbine is very dependent on the individual efficiencies of the turbine and the compressor. With component efficiencies of 90% the engine can achieve an efficiency of about 44% at an isentropic temperature ratio, σ_r , of around 2.7 (equivalent to a pressure

**FIGURE 17.12**

Gas turbine performance as a function of isentropic temperature ratio, $\gamma = 5$. $T_3/T_1 = 5$; $\eta_C = 0.8$ and 0.9 ; $\eta_T = 0.8$ and 0.9 .

ratio of 32:1). If the component efficiencies are reduced to 80% then the overall efficiency drops to about 28%, at $\sigma_r = 2.2$ (equivalent to $p_r = 16:1$). Similar calculations can be performed with $\gamma = 4$, when the overall efficiency drops dramatically; e.g. with $\gamma = 4$, $\eta_C = \eta_T = 0.8$, the overall efficiency drops to just over 20% at a pressure ratio of about 8:1.

The previous discussions show that it is important to operate gas turbines at as high a temperature ratio as the blade alloys can sustain, and the component efficiencies must be well above 80%. While optimum conditions can be attained for full-load operation, giving an acceptable efficiency, the values given above (which could simulate part-load conditions, including reductions in both the turbine and compressor efficiencies at off-design conditions) show that the gas turbine performance drops dramatically as the power output is reduced. Using a similar approach to that used when calculating Fig. 17.12 it can be shown that the maximum net work (the shaft output of the turbine) would drop from 28 to 19 units for the change in conditions discussed above. Hence, at a part-load condition of about 70%, the gas turbine overall efficiency is only about 20%: a similar load level for a large diesel engine would result in a much smaller reduction in efficiency. The Achilles' heel of gas turbines used for producing shaft power is their poor part-load efficiency.

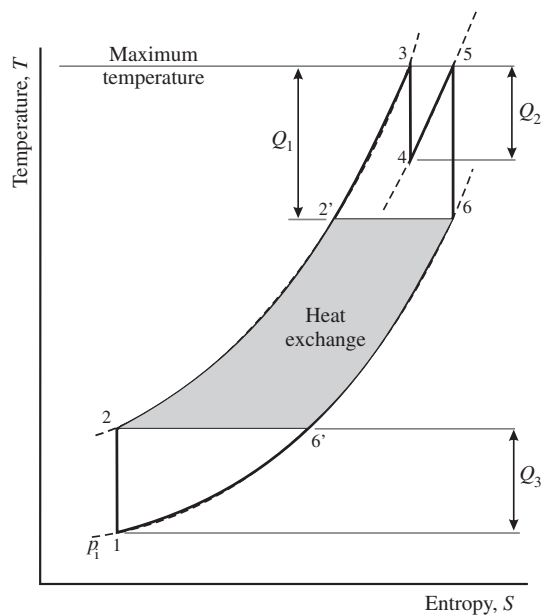
These relationships may be altered by the use of a heat exchanger. Figure 17.13 shows the effect of fitting a heat exchanger to a simple gas turbine. The curves were evaluated in the following way:

- the net work output is unaffected by the use of a heat exchanger;
- the energy addition is reduced by the heat exchanger;
- this increases the efficiency.

The energy addition, q_{34} , is evaluated in the following way. The heat exchanger effectiveness, ε , is defined as (see Fig. 17.9)

FIGURE 17.13

T - s diagram for gas turbine cycle with reheat and heat exchange.



$$\epsilon = \frac{T_3 - T_2}{T_5 - T_2}$$

Hence

$$T_3 = T_2 + \epsilon(T_5 - T_2) \quad (17.27)$$

$$= T_2(1 - \epsilon) + \epsilon T_5 \quad (17.28)$$

$$= T_2(1 - \epsilon) + \epsilon T_4 \left\{ 1 - \eta_T \left(1 - \frac{1}{\sigma_r} \right) \right\} \quad (17.29)$$

But

$$T_2 = T_1 \left\{ 1 + \frac{1}{\eta_C} (\sigma_r - 1) \right\} \quad (17.30)$$

Giving

$$T_3 = T_1 \left\{ \left[1 + \frac{1}{\eta_C} (\sigma_r - 1) \right] (1 - \epsilon) + \epsilon \gamma \left[1 - \eta_T \left(1 - \frac{1}{\sigma_r} \right) \right] \right\} \quad (17.31)$$

The energy addition

$$q_{34} = c_p (T_4 - T_3) \quad (17.32)$$

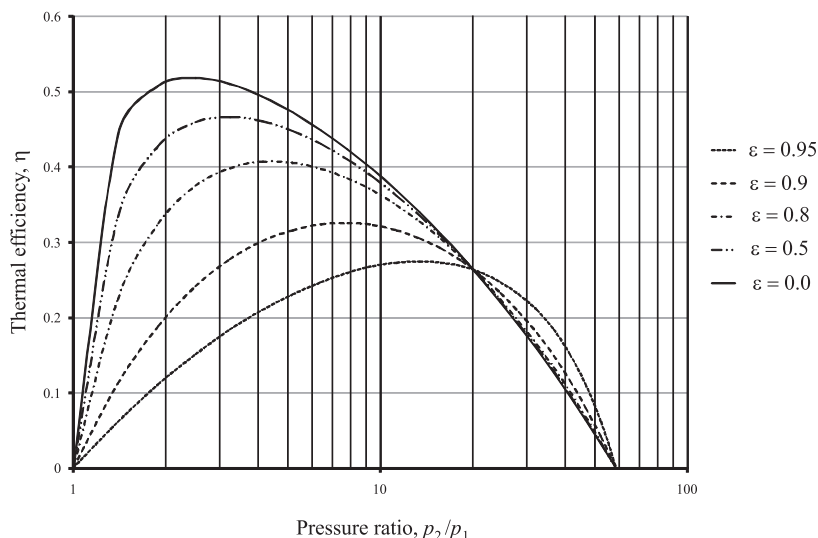


FIGURE 17.14

Variations of gas turbine efficiency with pressure ratio for a number of heat exchanger effectivenesses $\gamma = T_3/T_1 = 5$; $\eta_C = 0.8$; $\eta_T = 0.8$.

$$= c_p T_1 \left[\gamma - \left\{ \left[1 + \frac{1}{\eta_C} (\sigma_r - 1) \right] (1 - \varepsilon) + \varepsilon \gamma \left[1 - \eta_T \left(1 - \frac{1}{\sigma_r} \right) \right] \right\} \right] \quad (17.33)$$

If $\varepsilon = 0$ then the equation reduces to Eqn (17.26) above.

Figure 17.14 indicates the way thermal efficiency varies with both pressure ratio (this was chosen rather than σ_r because it is more relevant to an engineer) and heat exchanger effectiveness. The effectiveness values used were $\varepsilon = 0.95, 0.90, 0.80, 0.50$ and 0.0 . This graph shows that the pressure ratio for maximum efficiency decreases as the effectiveness of the heat exchanger increases. Also the efficiency is strongly affected by the effectiveness of the heat exchanger, going from about 28% with $\varepsilon = 0$ (i.e. no heat exchanger fitted) to 52% with an effectiveness of 0.95. Effectivenesses of up to 0.80 are typical of those achievable, and would result in a peak efficiency of about 40% with a pressure ratio of about 4:1. Without a heat exchanger the pressure ratio for maximum effectiveness is around 13:1. This is the area being addressed by the ICR turbine.

This analysis explains some of the differences between gas turbines designed for aircraft and those meant for road vehicles. The former turbines are not fitted with heat exchangers due to weight and bulk limitations – hence they operate at high pressure ratios. Turbines used in land applications can relatively easily accommodate a heat exchanger and usually operate on a low-pressure ratio cycle – although it must be recognised that the heat exchanger is relatively expensive to purchase and

maintain. Aircraft gas turbines use multistage axial compressors whereas automotive turbines can often achieve the required pressure ratio using a single stage centrifugal compressor.

It is interesting to examine what happens to efficiency and work ratio when $\varepsilon = 1$. The efficiency of the engine is

$$\eta = \frac{w_{\text{net}}}{q_{34}} = \frac{w_T - w_C}{q_{34}} \quad (17.34)$$

Substituting for w_{net} from Eqn (17.13), but also including η_C and η_T in the terms gives

$$\eta = \frac{c_p T_1 \left[\gamma \eta_T \left\{ 1 - \frac{1}{\sigma_r} \right\} - \frac{1}{\eta_C} \{ \sigma_r - 1 \} \right]}{c_p T_1 \left[\gamma - \left\{ \left[1 + \frac{1}{\eta_C} (\sigma_r - 1) \right] (1 - \varepsilon) + \varepsilon \gamma \left[1 - \eta_T \left(1 - \frac{1}{\sigma_r} \right) \right] \right\} \right]} \quad (17.35)$$

When $\varepsilon = 1$ Eqn (17.35) reduces to

$$\begin{aligned} \eta &= \frac{\left[\gamma \eta_T \left\{ 1 - \frac{1}{\sigma_r} \right\} - \frac{1}{\eta_C} \{ \sigma_r - 1 \} \right]}{\gamma \eta_T \left(1 - \frac{1}{\sigma_r} \right)} \\ &= 1 - \frac{\frac{1}{\eta_C} \{ \sigma_r - 1 \}}{\gamma \eta_T \left(1 - \frac{1}{\sigma_r} \right)} = r_w \end{aligned} \quad (17.36)$$

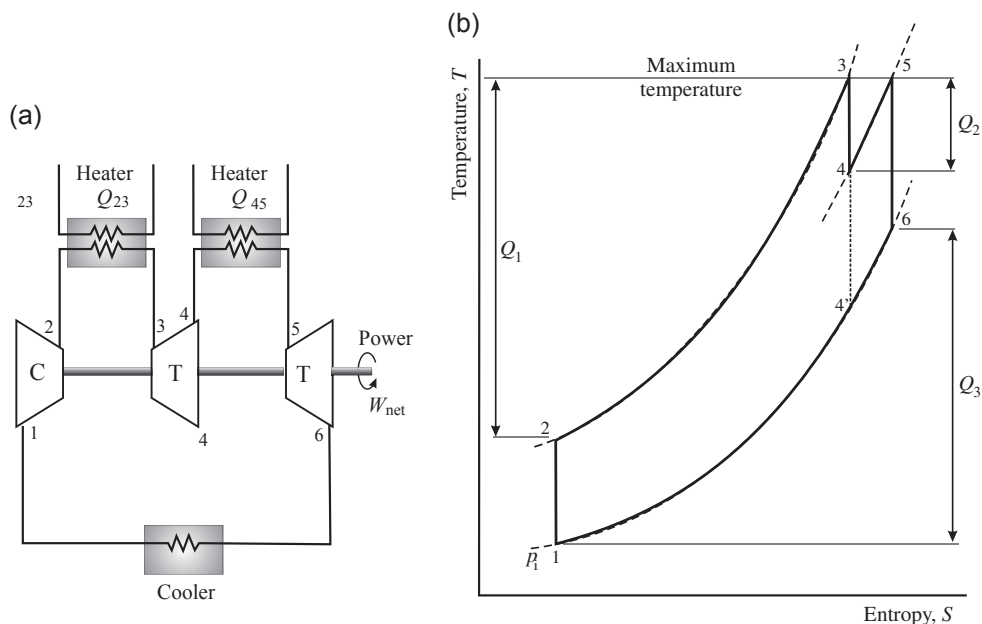
where r_w = work ratio. Hence, when a turbine is fitted with a perfect heat exchanger the work ratio and efficiency are equal.

17.2.3 REHEATING AND INTERCOOLING

It was shown above that a heat exchanger can raise the efficiency of a gas turbine by increasing the temperature of energy addition and decreasing the temperature of energy rejection. A similar effect can be achieved by introducing reheat and intercooling.

A cycle with reheat is shown in Fig. 17.15(a) and (b): the turbine is divided into two sections and the working fluid is withdrawn after the first turbine and reheated (up to approximately the peak temperature). The effect of reheating is to raise the mean temperature of energy addition but with the addition of extra energy and a reduced expansion ratio. The gas turbine cycle (Fig. 17.15(b)) with reheat can be considered to be two Joule cycles combined together. The cycles are 1234'1 and 4'4564'. The pressure ratio for the main cycle is the full compressor pressure ratio and the efficiency of this cycle is given by Eqn (17.8) as

$$\eta = 1 - \frac{1}{r_p^{\frac{\kappa-1}{\kappa}}}$$

**FIGURE 17.15**

(a) Schematic diagram of gas turbine with reheat, (b) T - s diagram for gas turbine with reheat.

The 'reheat cycle' has a lower pressure ratio but would again obey the same equation – hence it would have a lower efficiency. Hence the gas turbine cycle with reheat has a lower efficiency than a basic cycle even though the mean temperature of energy addition is higher.

The reason for this is that reheating has, in addition to increasing the mean temperature of energy addition, increased the mean temperature of energy rejection also. The latter effect is greater than the former. Hence, to regain any efficiency benefit from reheating it is necessary to attempt to lower the mean rejection temperature: this can be achieved by heat exchange. Such a cycle is shown in Fig. 17.13, and it can be seen that the mean temperature of energy addition is raised relative to a standard cycle while the mean temperature of energy rejection is reduced. This cycle is more efficient than the standard one, and it is also more efficient than the heat exchange cycle (Fig. 17.10).

A similar effect occurs with intercooling. Figure 17.16 shows a gas turbine cycle with intercooling between two stages of the compressor. The effect of intercooling is to increase the amount of energy rejected from the cycle but it is difficult to assess the actual effect on efficiency. The method of doing this is to subdivide the intercooled cycle into 'two cycles'. It can then be seen that intercooling effectively adds a low-pressure ratio cycle of low efficiency to the original cycle without intercooling – *hence the overall efficiency is lower but the total work output is greater*.

If a heat exchanger is fitted then the raising of the mean temperature of energy addition coupled with the lowering of the mean temperature of energy rejection brought about with the intercooler will raise the efficiency.

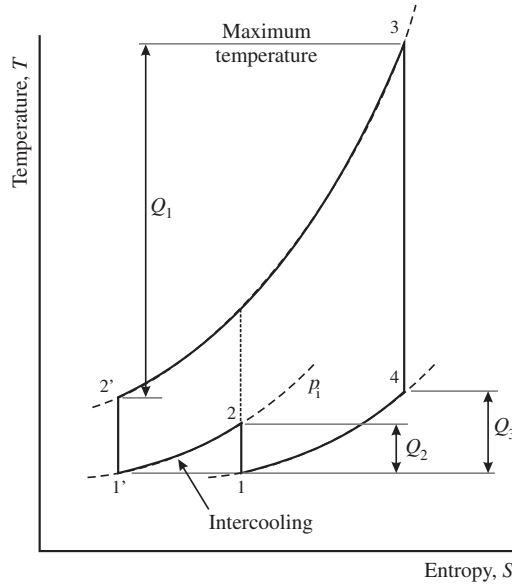


FIGURE 17.16

T-s diagram for gas turbine cycle with intercooling.

17.2.3.1 Optimum pressure ratio for reheating of gas turbines with heat exchange

In the same way as cycles were optimised previously to produce maximum work there must be an optimum pressure ratio at which reheating or intercooling should take place. This can be evaluated by consideration of the equations defining cycle efficiency.

Reheat cycle

Assume that reheat occurs at a pressure ratio given by

$$\sigma_R = \left(\frac{p_R}{p_1} \right)^{\frac{\kappa-1}{\kappa}} = \left(\frac{p_4}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \quad (17.37)$$

The efficiency of the cycle is given by Eqn (17.4):

$$\eta = \frac{w}{q_{in}}$$

and hence the maximum efficiency will occur when $\frac{\partial \eta}{\partial \sigma_R} = 0$.

Now

$$\frac{\partial \eta}{\partial \sigma_R} = \frac{1}{q_{in}} \frac{\partial w}{\partial \sigma_R} - \frac{w}{q_{in}^2} \frac{\partial q_{in}}{\partial \sigma_R} \quad (17.38)$$

i.e. when

$$\eta \frac{\partial q_{in}}{\partial \sigma_R} = \frac{\partial w}{\partial \sigma_R} \quad (17.39)$$

It will be assumed that reheat occurs to give $T_5 = T_3$ and also that $\eta_C = \eta_T = 1.0$. These assumptions simplify the problem.

Then energy added

$$q_{2/3} = c_p(T_3 - T_{2'}) \quad (17.40)$$

$$q_{45} = c_p(T_5 - T_4) \quad (17.41)$$

The heat exchanger effectiveness is given by Eqn (17.21):

$$\varepsilon = \frac{T_3 - T_2}{T_5 - T_2}$$

giving Eqn (17.28)

$$T_{2'} = T_2(1 - \varepsilon) + \varepsilon T_6$$

Let the pressure ratio of the plant be defined by

$$\sigma_r = (p_2/p_1)^{(\kappa-1)/\kappa} \quad (17.42)$$

and assume there are no pressure losses.

Then

$$T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{(\kappa-1)/\kappa} = T_1 \sigma_r \quad (17.43)$$

and

$$T_6 = T_5 \left(\frac{p_6}{p_5} \right)^{(\kappa-1)/\kappa} = \frac{T_5}{\sigma_R} \quad (17.44)$$

$$T_{2'} = T_1 \sigma_r (1 - \varepsilon) + \frac{\varepsilon T_5}{\sigma_R} = T_1 \left\{ \sigma_r (1 - \varepsilon) + \frac{\varepsilon \gamma}{\sigma_R} \right\} \quad (17.45)$$

This results in

$$\frac{q_{2/3}}{c_p T_1} = \gamma - \sigma_r (1 - \varepsilon) - \frac{\varepsilon \gamma}{\sigma_R} \quad (17.46)$$

Similarly

$$q_{45} = c_p(T_5 - T_4)$$

Now

$$T_4 = T_3 \left(\frac{T_4}{T_3} \right) = T_3 \left(\frac{p_4}{p_3} \right)^{\frac{\kappa-1}{\kappa}} = T_3 \left(\frac{p_4}{p_1} \frac{p_1}{p_3} \right)^{\frac{\kappa-1}{\kappa}} = T_3 \frac{\sigma_R}{\sigma_r} \quad (17.47)$$

$$q_{45} = c_p T_1 \left\{ \gamma - \frac{\gamma \sigma_R}{\sigma_r} \right\} \quad (17.48)$$

giving

$$\frac{q_{45}}{c_p T_1} = \gamma \left\{ 1 - \frac{\sigma_R}{\sigma_r} \right\} \quad (17.49)$$

Thus energy added per unit mass is,

$$\frac{q_{in}}{c_p T_1} = \frac{1}{c_p T_1} [q_{23} + q_{45}] \quad (17.50)$$

$$\begin{aligned} &= \gamma - \sigma_r(1 - \varepsilon) - \frac{\varepsilon\gamma}{\sigma_R} + \gamma \left\{ 1 - \frac{\sigma_R}{\sigma_r} \right\} \\ &= 2\gamma - \sigma_r(1 - \varepsilon) - \frac{\varepsilon\gamma}{\sigma_R} - \frac{\gamma\sigma_R}{\sigma_r} \end{aligned} \quad (17.51)$$

Differentiating with respect to σ_R .

$$\frac{1}{c_p T_1} \frac{\partial q_{in}}{\partial \sigma_R} = \frac{\varepsilon\gamma}{\sigma_R^2} - \frac{\gamma}{\sigma_r} \quad (17.52)$$

Considering now the work done per unit mass is

$$w_{34} = c_p(T_3 - T_4) = c_p T_1 \gamma \left(1 - \frac{\sigma_R}{\sigma_r} \right) \quad (17.53)$$

$$w_{56} = c_p(T_5 - T_6) = c_p T_1 \gamma \left(1 - \frac{1}{\sigma_R} \right) \quad (17.54)$$

$$w_{12} = c_p(T_1 - T_2) = -c_p T_1 (\sigma_r - 1) \quad (17.55)$$

Thus

$$\frac{w}{c_p T_1} = \gamma \left(1 - \frac{\sigma_R}{\sigma_r} \right) + \gamma \left(1 - \frac{1}{\sigma_R} \right) - (\sigma_r - 1) \quad (17.56)$$

Hence

$$\frac{1}{c_p T_1} \frac{\partial w}{\partial \sigma_R} = -\frac{\gamma}{\sigma_r} + \frac{\gamma}{\sigma_R^2} \quad (17.57)$$

Substituting in Eqn (17.39) gives

$$\eta \left(\frac{\varepsilon\gamma}{\sigma_R^2} - \frac{\gamma}{\sigma_r} \right) = -\frac{\gamma}{\sigma_r} + \frac{\gamma}{\sigma_R^2}$$

and rearranging, results in

$$\sigma_R^2 = \sigma_r \frac{(\varepsilon\eta - 1)}{(\eta - 1)} \quad (17.58)$$

If $\varepsilon = 1$ this equation reduces to $\sigma_R = \sqrt{\sigma_r}$ i.e.

$$\frac{p_4}{p_1} = \left(\frac{p_2}{p_1} \right)^{1/2} \quad (17.59)$$

Hence, the pressure ratio for most effective reheat equally splits the gas turbine pressure ratio. This results in equal work from each part of the turbine. If $\varepsilon \neq 1$ then the situation changes and the pressure ratio has to be evaluated iteratively. The pressure ratio can also be evaluated iteratively if $T_3 \neq T_5$ and if the compression and expansion are not isentropic.

17.2.3.2 Optimum pressure ratio for intercooling of gas turbines

The T - s diagram for an intercooled cycle is shown in Fig. 17.16. This cycle can be analysed in a similar way to the one with reheat to determine the optimum intermediate pressure for intercooling, p_i , in Fig. 17.16. This analysis is included in the tutorials as a problem for the student.

17.3 AIRCRAFT GAS TURBINES

These come in a number of variants as listed below:

1. turbojet
2. turbofan engine
3. turboprop engines

17.3.1 TURBOJET ENGINES

The previous sections have concentrated on gas turbines which produce a net shaft power output. The majority of turbines are probably used for aero applications: some of these produce shaft power to rotate a propeller but most (at present) produce a jet of hot gas which is then used for propulsion. Basically all aero engines operate by producing an airstream moving in the opposite direction to the aircraft. A propeller driven aircraft is propelled forwards by a large diameter, slow speed 'jet' produced by the propeller. A simple jet engine propels rearwards a small diameter, high-speed jet, whilst a turbofan engine produces a larger diameter, slower speed jet. It is instructive to consider why these different mechanisms are used in different applications.

The thrust produced by an aircraft jet engine, shown in Fig. 17.17, comes in two parts:

1. momentum thrust;
2. pressure thrust.

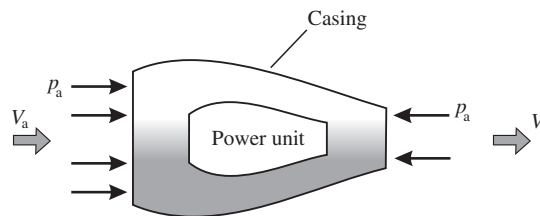


FIGURE 17.17

Schematic diagram of aircraft jet engine.

The total thrust is the sum of these two terms and is

$$F = \dot{m}(V_j - V_a) + A_j(p_j - p_a)$$

Now, in many engines the expansion in the nozzle is complete, and down to atmospheric pressure, p_a . This means that the pressure thrust is zero and the thrust then becomes

$$F = \dot{m}(V_j - V_a) \quad (17.60)$$

This thrust, at constant speed in level flight, must equal the drag on the aircraft. Hence it is possible to evaluate the *propulsive efficiency* (η_p) of the engine.

$$\begin{aligned} \eta_p &= \frac{\text{useful propulsive energy}}{\text{useful propulsive energy} + \text{K.E. of jet}} \\ &= \frac{mV_a(V_j - V_a)}{\dot{m} \left[V_a(V_j - V_a) + (V_j - V_a)^2/2 \right]} \\ &= \frac{2}{1 + V_j/V_a} \end{aligned} \quad (17.61)$$

This is sometimes referred to as the Froude efficiency.

Note:

- (1) The thrust (F) is maximum when $V_a = 0$ (i.e. static conditions) but $\eta_p = 0$.
- (2) η_p is maximum when $V_j/V_a = 1$, but $F = 0$.

Hence it is necessary for $V_j > V_a$ but the difference should be as small as possible to achieve the desired purpose.

The propulsive efficiency, η_p , is just a relationship between 'jet' and aircraft velocities and does not contain any information on the production of thrust as a function of the fuel flow. The efficiency of energy conversion, η_e , can be defined as

$$\eta_e = \frac{\dot{m}(V_j^2 - V_a^2)/2}{\dot{m}_f Q'_p} \quad (17.62)$$

which gives an overall efficiency, η_o , of

$$\eta_o = \frac{\dot{m}(V_j - V_a)V_a}{\dot{m}_f Q'_p} = \frac{FV_a}{\dot{m}_f Q'_p} \quad (17.63)$$

and

$$\eta_o = \eta_e \eta_p. \quad (17.64)$$

This shows that the efficiency of the engine in propelling the aircraft is the product of the engine and propulsion efficiencies.

It was shown that the ‘efficiency’ of an internal combustion engine could be defined by its brake specific fuel consumption (bsfc). It is not appropriate to use this parameter for all gas turbines because they do not necessarily produce shaft power. In the case of aircraft jet engines a more appropriate term is the fuel consumption per unit thrust, e.g. kg/hN, known as the specific fuel consumption (sfc).

Then

$$\text{sfc} = \frac{\dot{m}_f}{\dot{m}(V_j - V_a)} \quad (17.65)$$

and

$$\eta_o = \frac{V_a}{\text{sfc}} \frac{1}{Q'_p} \quad (17.66)$$

It is also possible to introduce a parameter which gives an indication of the amount of power obtained from a particular engine, somewhat similar to bmep for reciprocating engines. This is termed the specific thrust, F_s , which is the thrust per unit mass flow of air, i.e. $F_s = F/m$.

The performance of aircraft engines is normally defined at two operating conditions:

1. static performance at sea-level at maximum power (to give an indication of the power available at takeoff);
2. cruising performance at the cruising speed and altitude.

17.3.2 INTAKE AND PROPELLING NOZZLES

Intake ducts will not be discussed in detail here, except to point out that they are essential in decelerating the airflow from the aircraft forward velocity, V_a , to one acceptable to the compressor blades of the gas turbine (V_1). The design of nozzles for subsonic aircraft is much easier than for supersonic ones, in which a series of shocks are required to achieve the necessary deceleration. The processes occurring in the intake system are shown in Fig 17.18. The efficiency of the process can be defined in a similar manner to other isentropic efficiencies, giving

$$\eta_i = \frac{T_{01} - T_a}{T_{0a} - T_a} \quad (17.67)$$

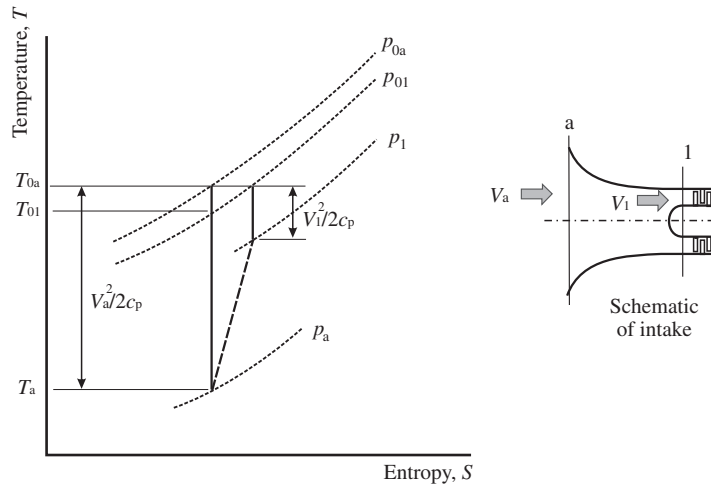
and this gives the pressure ratio across the intake as

$$\frac{p_{01}}{p_a} = \left(\frac{T_{01}}{T_a} \right)^{\frac{\kappa}{\kappa-1}} = \left\{ 1 + \eta_i \frac{V_a^2}{2c_p T_a} \right\}^{\frac{\kappa}{\kappa-1}} \quad (17.68)$$

where p_a and T_a are the ambient pressure and temperature respectively, η_i is the isentropic efficiency of the intake and V_a is the velocity of the air entering the intake (the cruising speed).

Propelling nozzles are an important feature of both subsonic and supersonic engines. The aim of these nozzles is to produce the best overall efficiency for the aircraft propulsion system. The propelling nozzle is the part of the engine aft of the last turbine stage, and may contain all the components shown in Fig. 17.19.

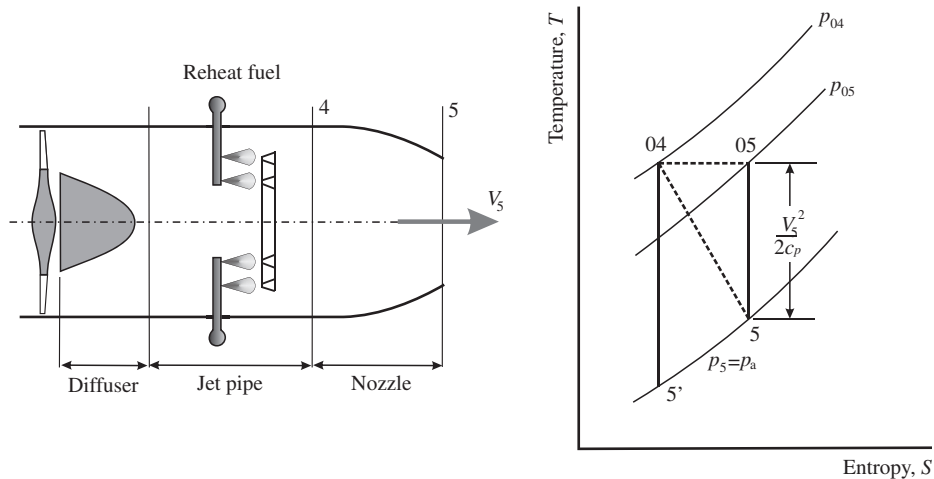
The diffuser slows down the stream of hot gas leaving the turbine, converting kinetic energy into a pressure rise. On combat aircraft reheat may be fitted and this consists of burning fuel at constant

**FIGURE 17.18**

'Intake' loss.

pressure in the nozzle system. Reheat gives a substantial increase in thrust, but a very low efficiency: it is used in combat aircraft for takeoff (to increase the payload that can be carried) and also for higher sprint performance. However, a 44% increase in thrust can require a 164% increase in fuel flow rate, so reheat has to be used sparingly otherwise range is reduced to unacceptable levels. Finally, the nozzle converts the slow moving gas into a jet which will propel the aircraft forward.

The propelling nozzle is usually a simple convergent one, even though the pressure ratio will often exceed the critical pressure ratio. Convergent-divergent nozzles are used on the high-pressure ratio

**FIGURE 17.19**

'Propelling nozzle' system.

engines which power supersonic aircraft: it is then often necessary to use variable area nozzles to limit the shock losses produced in the nozzle itself. This section will concentrate on convergent nozzles only because these are used on the majority of subsonic aircraft.

Two approaches can be used to define the performance of propelling nozzles:

1. isentropic efficiency, η_j ;
2. specific thrust coefficient, K_F .

This section will concentrate on the isentropic efficiency, η_j . The nozzle diagram is given in Fig. 17.19 and the value of η_j is

$$\eta_j = \frac{T_{04} - T_5}{T_{04} - T_5^*} \quad (17.69)$$

where T_{04} is the stagnation temperature downstream of the turbine (see Figs 17.19 and 17.20).

It is then possible to evaluate the temperature drop across the nozzle, using the notation on Fig. 17.19, as

$$T_{04} - T_5 = \eta_j T_{04} \left[1 - \left(\frac{1}{p_{04}/p_5} \right)^{\frac{\kappa-1}{\kappa}} \right] \quad (17.70)$$

this is also equivalent to $V_5^2/2c_p$, the kinetic energy term of the energy equation, because $T_{04} = T_{05}$.

If the pressure ratio across the nozzle is less than the *critical pressure ratio* then the flow at the nozzle exit is subsonic and the pressure at the exit plane of the nozzle equals the atmospheric pressure. If the pressure ratio is greater than the critical one then full expansion of the gas will not occur in the nozzle and the pressure at 5 will be greater than the ambient value. The critical pressure ratio, T_{04}/T_{05} , is one which results in $M_5 = 1$. This is achieved when

$$\frac{T_{04}}{T_c} = \frac{\kappa + 1}{2} \quad (\text{from the energy equation}),$$

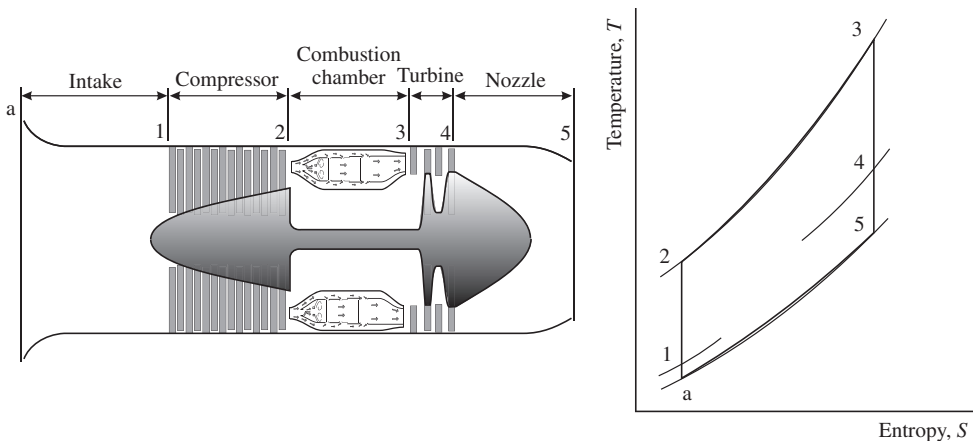


FIGURE 17.20

Simple turbojet engine and ideal cycle.

and this is the same for both isentropic and irreversible adiabatic flows. Figure 17.19 shows that, while the critical value of T_{04}/T_c results in sonic flow at station 5, it is also necessary to evaluate T_c , which is the temperature reached after *isentropic* expansion to p_c , viz.

$$T_{c'} = T_{04} - \frac{1}{\eta_j}(T_{04} - T_c) \quad (17.71)$$

and then

$$p_c = p_{04} \left(\frac{T_{c'}}{T_{04}} \right)^{\frac{\kappa}{\kappa-1}} = p_{04} \left[1 - \frac{1}{\eta_j} \left(1 - \frac{T_c}{T_{04}} \right) \right]^{\frac{\kappa}{\kappa-1}} \quad (17.72)$$

Hence

$$\frac{p_{04}}{p_c} = \frac{1}{\left[1 - \frac{1}{\eta_j} \left(\frac{\kappa-1}{\kappa+1} \right) \right]^{\frac{\kappa}{\kappa-1}}} \quad (17.73)$$

The area of the nozzle can be evaluated from the mass flow rate required at the throat density and gas velocity. Then

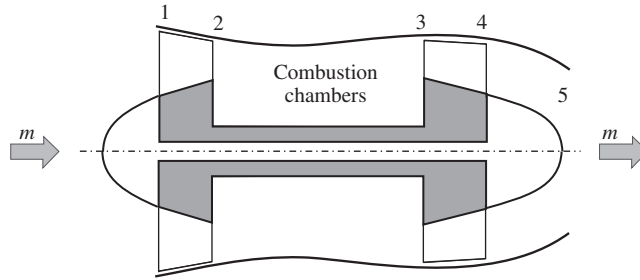
$$A_5 = \frac{\dot{m}}{\rho_c V_c}, \quad (17.74)$$

where $\rho_c = p_c/RT_c$ and $V_c = [2c_p(T_{04}-T_c)]^{1/2}$ or $(\kappa RT_c)^{1/2}$. The value obtained for A_5 will be approximate because there is a significant boundary layer built up in the nozzle which reduces the effective flow area. The value of η_j achieved is dependent on the design of the particular nozzle, but a typical one might be 0.95.

Example 1 (based on Saravanamutto et al. (2001))

Determine the specific thrust and sfc for the simple single spool turbojet engine, shown in Fig. 17.21, having the following component performance at the design point for which the cruising speed and altitude are 270 m/s and 5000 m respectively.

Compressor pressure ratio	8.0
Turbine inlet temperature	1200 K
Isentropic efficiency	
Of compressor, η_c	0.87
Of turbine, η_T	0.90
Of propelling nozzle, η_j	0.95
Mechanical transmission efficiency, η_m	0.99
Calorific value of fuel, Q'_p	44000 kJ/kg
Assume:	
c_p at engine inlet, c_{p_a}	1.005 kJ/kg K
c_p at turbine inlet, c_{p_e}	1.147 kJ/kg K
κ_a at engine inlet	1.4
κ_e at turbine inlet	1.33

**FIGURE 17.21**

Single spool turbojet.

Solution

From the international standard atmosphere table, at 5000 m

$$p_a = 0.5405 \text{ bar} \quad \text{and} \quad T_a = 255.7 \text{ K.}$$

The stagnation conditions after the inlet may be obtained as follows:

$$\frac{V_a^2}{2c_p} = \frac{270^2}{2 \times 1.005 \times 1000} = 36.3 \text{ K}$$

$$T_{01} = T_a + \frac{V_a^2}{2c_p} = 255.7 + 36.3 = 292 \text{ K}$$

$$p_{01} = p_a \left(\frac{T_{01}}{T_a} \right)^{\kappa/(\kappa-1)} = 0.8602 \text{ bar.}$$

At the outlet from the compressor

$$p_{02} = \left(\frac{p_{02}}{p_{01}} \right) p_{01} = 8.0 \times 0.8602 = 6.88 \text{ bar}$$

$$T_{02} - T_{01} = \frac{T_{01}}{\eta_c} \left(\left(\frac{p_{02}}{p_{01}} \right)^{(\kappa-1)/\kappa} - 1 \right) = \frac{292}{0.87} [8.0^{0.286} - 1] = 272.7 \text{ K}$$

$$T_{02} = 292 + 272.5 = 564.7 \text{ K}$$

$$w_T = w_c / \eta_m \quad \text{and hence}$$

$$T_{03} - T_{04} = \frac{c_{p_a}(T_{02} - T_{01})}{c_{p_g}} = \frac{1.005 \times 272.7}{1.147 \times 0.99} = 241.4 \text{ K}$$

$$T_{04} = 1200 - 241.4 = 958.6 \text{ K}$$

$$p_{04} = p_{03} \left(\frac{T_{04}}{T_{03}} \right)^{\kappa/(\kappa-1)} = 6.88 \left(\frac{958.6}{1200} \right)^4 = 2.501 \text{ bar.}$$

The nozzle pressure ratio is therefore

$$\frac{p_{04}}{p_a} = \frac{2.501}{0.5405} = 4.627$$

The critical pressure ratio, from Eqn (17.74), is

$$\frac{p_{04}}{p_c} = \frac{1}{\left(1 - \frac{1}{\eta_j} \left(\frac{\kappa - 1}{\kappa + 1}\right)\right)^{\kappa/(\kappa - 1)}} = \frac{1}{\left\{1 - \frac{1}{0.95} \left(\frac{0.333}{2.333}\right)\right\}^4} = 1.918$$

Since $p_{04}/p_a > p_{04}/p_c$ the nozzle is choked.

$$T_5 = T_c = \left(\frac{2}{\kappa + 1}\right) T_{04} = \frac{2 \times 958.6}{2.333} = 821.8 \text{ K}$$

$$p_5 = p_c = p_{04} \left(\frac{1}{p_{04}/p_c}\right) = \frac{2.501}{1.918} = 1.304 \text{ bar}$$

$$\rho_5 = \frac{p_c}{RT_c} = \frac{100 \times 1.304}{0.287 \times 821.8} = 0.5529 \text{ kg/m}^3$$

$$V_5 = (\kappa RT_c)^{1/2} = (1.333 \times 0.287 \times 821.8 \times 1000)^{1/2} = 560.7 \text{ m/s.}$$

$$\frac{A_5}{\dot{m}} = \frac{1}{\rho_5 V_5} = \frac{1}{0.5529 \times 560.7} = 0.003226 \text{ m}^2/\text{kg.}$$

The specific thrust is

$$\begin{aligned} F_s &= (V_5 - V_a) + \frac{A_5}{\dot{m}} (p_c - p_a) \\ &= (560.7 - 270) + 0.003226(1.304 - 0.5404) \times 10^5 \\ &= 290.7 + 246.3 = 537.0 \text{ Ns/kg.} \end{aligned}$$

Temperature rise in engine is

$$T_{03} - T_{02} = 1200 - 5647.7 = 635.3 \text{ K.}$$

Hence, using

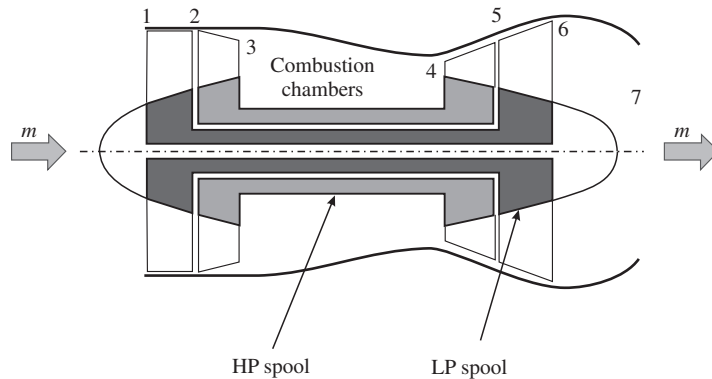
$$\begin{aligned} \Delta T &= \frac{\dot{m}_f Q'_p}{(\dot{m}_a + \dot{m}_f) c_{p_g}} \\ &= \frac{Q'_p}{(\varepsilon + 1) c_{p_g}} \end{aligned}$$

gives an air–fuel ratio,

$$\varepsilon = \frac{Q'_p}{c_{p_g} \Delta T} - 1 = 59.38.$$

This results in a sfc of

$$\frac{1}{\varepsilon F_s} = \frac{3600}{59.38 \times 537} = 0.1129 \text{ kg/hN.}$$

**FIGURE 17.22**

Twin-spool turbojet. LP, low pressure; HP, high pressure.

Figure 17.22 shows a schematic arrangement of a more complex turbojet engine in which two spools are used. These are free to rotate at speeds which balance the powers, mass flows and pressure ratios on each spool.

17.3.3 TURBOFAN ENGINES

The turbojet engine produces its thrust by means of a high-velocity jet of hot exhaust gas. This does not necessarily result in the best propulsion efficiency, defined in Eqn (17.61) as

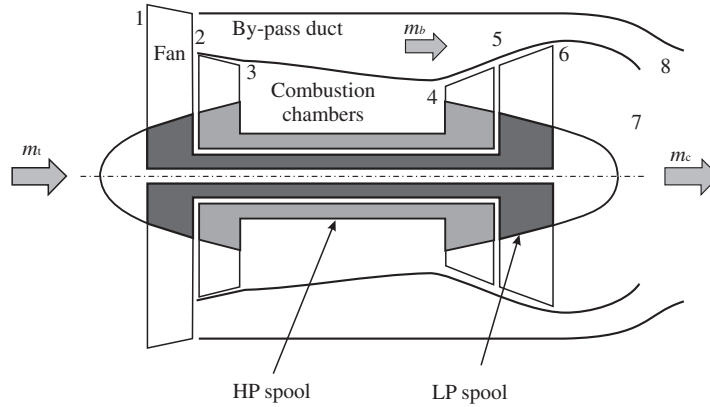
$$\eta = \frac{2}{1 + V_j/V_a}$$

where

V_j = jet velocity and
 V_a = velocity of aircraft.

The propulsion efficiency is zero when the aircraft velocity, V_a , is zero and this is the static thrust. Maximum efficiency occurs when $V_j = V_a$ but this results in no thrust. There must be a value of V_j/V_a which maximises the effectiveness of passing the aircraft through the air; it is found that values of V_j/V_a approaching unity are the most effective.

Appropriate values of V_j/V_a can be obtained by reducing the value of V_j and this can be achieved by increasing the mass flow through the engine to give the same jet momentum at reduced velocity. If the total airflow were passed through the combustion chamber then the air–fuel ratio would increase and the peak temperature would be reduced. This would reduce the thermal efficiency of the cycle. However, if the airflow through the engine were split so that the air–fuel ratio in the combustion chamber was maintained at a level which produced the maximum temperature, and the remainder was bypassed around the combustion chamber it would be possible to get the best of both arrangements. This is achieved by means of the turbofan engine.

**FIGURE 17.23**

Twin-spool turbofan engine. LP, low pressure; HP, high pressure.

Figure 17.23 shows a schematic arrangement of a turbofan engine; comparison with Fig. 17.22 shows that the arrangement is similar but the outside diameter is larger. It will be noticed that

1. some of the engine airflow is bypassed around the combustion chamber;
2. the engine has two (or more) shafts.

The turbofan engine has the following advantages over the turbojet engine:

1. the jet velocity is lower;
2. the overall efficiency of engine propulsion is higher;
3. the jet noise is lower.

It can be seen that the inflowing airstream ($\dot{m}_t$) is subdivided into a bypass stream ($\dot{m}_b$) and a combustion chamber stream ($\dot{m}_c$). A feature of importance for turbofan engines is the bypass ratio.

$$b = \frac{\dot{m}_b}{\dot{m}_c} \quad (17.75)$$

Then

$$\dot{m}_b = \frac{b\dot{m}_t}{b+1}; \quad \dot{m}_c = \frac{\dot{m}_t}{b+1} \quad \text{and} \quad \dot{m}_t = \dot{m}_b + \dot{m}_c \quad (17.76)$$

When the flows are both expanded to atmospheric pressure, i.e. the pressure thrust is zero, the net thrust of the engine is given by

$$F = (\dot{m}_b V_{jb} + \dot{m}_c V_{jc}) - \dot{m}_t V_a \quad (17.77)$$

The design of a turbofan engine requires the following data:

- overall pressure ratio and maximum turbine inlet temperature;
- bypass ratio (b) and fan pressure ratio (r_f).

Using these data the performance parameters can be calculated based on the following criteria:

- the pressure and temperature of the gas leaving the fan and entering the bypass duct;
- the mass flow along the bypass duct can be evaluated from the total flow and the bypass ratio;
- the thrust from the cold stream (bypass) can be evaluated;
- in a two-spool arrangement, the high-pressure (HP) turbine drives the HP compressor and a power balance must be achieved on that shaft; i.e. there is no net output;
- then the low-pressure (LP) turbine drives the fan according to following conditions

$$\dot{m}_t c_{p_a} \Delta T_{0_{12}} = \eta_m \dot{m}_c c_{p_g} \Delta T_{0_{56}} \quad (17.78)$$

thus

$$\Delta T_{0_{56}} = \frac{\dot{m}_t}{\dot{m}_c} \frac{c_{p_a}}{\eta_m c_{p_g}} \Delta T_{0_{12}} = (b + 1) \frac{c_{p_a}}{\eta_m c_{p_g}} \Delta T_{0_{12}} \quad (17.79)$$

The value of b can vary over a wide range ($0.3 < b < 10$) and hence it has a major effect on the temperature drop in the turbine driving the fan.

Once $\Delta T_{0_{56}}$ has been found it is possible to evaluate the other conditions in the turbines.

- If the hot and cold streams are mixed the resulting gas conditions should be evaluated from mass, enthalpy and momentum balances.

Example 2 (based on Saravanamuttoo et al. (2001))

The following data apply to a twin-spool turbofan engine, similar to Fig. 17.23, with the fan driven by the LP turbine and the compressor by the HP turbine. Separate cold and hot nozzles are used.

Overall pressure ratio	19.0
Fan pressure ratio, r_f	1.65
Bypass ratio m_b/m_c	3.0
Turbine inlet temperature	1300 K
Fan, compressor and turbine polytropic efficiencies, η_∞	0.90
Isentropic efficiency of each propelling nozzle	0.95
Mechanical efficiency of each spool	0.99
Combustion pressure loss	1.25 bar
Total air mass flow, $\dot{m}_t$	115 kg/s

Evaluate the thrust under sea level conditions where the ambient pressure and temperature are 1.0 bar and 288 K.

Solution

The values of $(n - 1)/n$ for the polytropic compression and expansion are for compression

$$\frac{n - 1}{n} = \frac{1}{\eta_{\infty C}} \left(\frac{\kappa - 1}{\kappa} \right)_a = \frac{1}{0.9 \times 3.5} = 0.3175$$

for expansion

$$\frac{n - 1}{n} = \eta_{\infty T} \left(\frac{\kappa - 1}{\kappa} \right)_g = \frac{0.9}{4} = 0.225.$$

Under static conditions $T_{01} = T_{0a}$ and $p_{01} = p_a$ so that, using the nomenclature of Fig. 17.23,

$$\frac{T_{02}}{T_{01}} = \left(\frac{p_{02}}{p_{01}} \right)^{(n-1)/n} \quad \text{and yields}$$

$$T_{02} = 288 \times 1.65^{0.3175} = 337.7 \text{ K}$$

$$T_{02} - T_{01} = 337.7 - 288 = 49.7 \text{ K}$$

$$\frac{p_{03}}{p_{02}} = \frac{19.0}{1.65} = 11.51$$

$$T_{03} = T_{02} \left(\frac{p_{03}}{p_{02}} \right)^{(n-1)/n} = 337.7 \times 11.51^{0.3175} = 734 \text{ K}$$

$$T_{03} - T_{02} = 734 - 337.7 = 396.3 \text{ K}.$$

The cold nozzle pressure ratio is

$$\frac{p_{02}}{p_a} = r_f = 1.65$$

and the critical pressure ratio for this nozzle is

$$\frac{p_{02}}{p_c} = \frac{1}{\left[1 - \frac{1}{\eta_j} \left[\frac{\kappa - 1}{\kappa + 1} \right] \right]^{\kappa/(\kappa - 1)}} = \frac{1}{\left[1 - \frac{1}{0.95} \left[\frac{0.4}{2.4} \right] \right]^{3.5}} = 1.965.$$

Thus the cold nozzle is not choked, so that $p_8 = p_a$ and the bypass thrust F_b is given simply by

$$F_b = \dot{m}_b V_8$$

The nozzle temperature drop, from Eqn (17.70), is

$$\begin{aligned} T_{02} - T_8 &= \eta_j T_{02} \left(1 - \left(\frac{1}{p_{02}/p_a} \right)^{\kappa - 1/\kappa} \right) \\ &= 0.95 \times 337.7 \left(1 - \left(\frac{1}{1.65} \right)^{1/3.5} \right) = 42.8 \text{ K}. \end{aligned}$$

and hence

$$V_8 = [2c_p(T_{02} - T_8)]^{1/2} = (2 \times 1.005 \times 1000 \times 42.8)^{1/2} = 293 \text{ m/s.}$$

Since the bypass ratio (b) is 3.0,

$$\dot{m}_b = \frac{\dot{m}_t}{b + 1} = \frac{115 \times 3.0}{4.0} = 86.25 \text{ kg/s}$$

$$F_b = 86.25 \times 293 = 25,300 \text{ N.}$$

Considering the work requirement of the HP rotor,

$$T_{04} - T_{05} = \frac{c_{pa}}{\eta_m c_{pg}} (T_{03} - T_{02}) = \frac{1.005 \times 396.3}{0.99 \times 1.147} = 350.3 \text{ K}$$

and for the LP rotor

$$T_{05} - T_{06} = (b + 1) \frac{c_{pa}}{\eta_m c_{pg}} (T_{02} - T_{01}) = \frac{4.0 \times 1.005 \times 49.7}{0.99 \times 1.147} = 176 \text{ K.}$$

Hence

$$T_{05} = T_{04} - (T_{04} - T_{05}) = 1300 - 350.3 = 949.7 \text{ K}$$

$$T_{06} = T_{05} - (T_{05} - T_{06}) = 949.7 - 176 = 773.7 \text{ K}$$

p_{06} may then be found as follows.

$$\frac{p_{04}}{p_{05}} = \left(\frac{T_{04}}{T_{05}} \right)^{n/(n-1)} = \left(\frac{1300}{949.7} \right)^{1/0.225} = 4.02$$

$$\frac{p_{05}}{p_{06}} = \left(\frac{T_{05}}{T_{06}} \right)^{n/(n-1)} = \left(\frac{949.7}{773.7} \right)^{1/0.225} = 2.48$$

$$p_{04} = p_{03} - \Delta p_{cc} = 19.0 \times 1.0 - 1.25 = 17.75 \text{ bar}$$

$$p_{06} = \frac{p_{04}}{(p_{04}/p_{05})(p_{05}/p_{06})} = \frac{17.75}{4.02 \times 2.48} = 1.78 \text{ bar}$$

Thus the hot nozzle pressure ratio is

$$\frac{p_{06}}{p_a} = 1.78$$

while the critical pressure ratio is

$$\frac{p_{06}}{p_c} = \frac{1}{\left[1 - \frac{1}{0.95} \left(\frac{0.333}{2.333} \right) \right]^4} = 1.914.$$

This nozzle is also unchoked, and hence $p_7 = p_a$.

$$T_{06} - T_7 = \eta_j T_{06} \left[1 - \left(\frac{1}{p_{06}/p_a} \right)^{(\kappa - 1)/\kappa} \right] = 0.95 \times 773.7 \left[1 - \left(\frac{1}{1.78} \right)^{1/4} \right] = 98.5 \text{ K}$$

$$V_7 = \left[2c_{p_g}(T_{06} - T_7) \right]^{1/2} = [2 \times 1.147 \times 1000 \times 98.5]^{1/2} = 476 \text{ m/s}$$

$$\dot{m}_c = \frac{\dot{m}_t}{b + 1} = \frac{115}{4.0} = 28.75 \text{ kg/s}$$

$$F_c = 28.75 \times 475 = 13700 \text{ N.}$$

Thus the total thrust is

$$F_t = F_b + F_c = 25300 + 13700 = 39000 \text{ N} = 39.0 \text{ kN.}$$

This example illustrates the method followed when a propelling nozzle is unchoked, while the example for the turbojet showed how to analyse a choked nozzle.

Note that at static conditions the bypass stream contributes approximately 65% of the total thrust. At a forward speed of 60 m/s which is approaching a normal takeoff speed, the momentum drag $\dot{m}V_a$ will be 115×60 or 6900 N; the ram pressure ratio and temperature rise will be negligible and thus the net thrust is reduced to 32,100 N. The drop in thrust during takeoff is even more marked for engines of higher bypass ratio and for this reason it is preferable to quote turbofan thrusts at a typical takeoff speed rather than at static conditions.

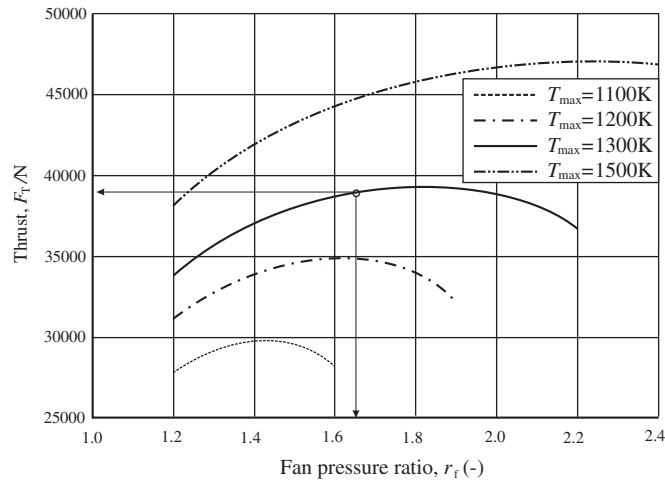
This engine would require a high pressure compressor with a pressure ratio of 11.5, which is rather higher than desirable and may lead to the problems of stability.

17.3.4 OPTIMIZATION OF TURBOFAN ENGINES

The equations developed above were programmed to allow investigation of a number of features of turbofan engine design and these will be discussed. When designing a turbojet engine the number of variable parameters is quite limited. The designer can vary the pressure ratio and the maximum cycle temperature to achieve a given efficiency. After that basic cycle design the mass flow rate can be chosen to give a particular thrust. In the case of the turbofan engine there are two additional variables: fan pressure ratio (r_f) and bypass ratio (b). Thus the problem of design becomes significantly more complex than for the turbojet because the operating envelope is defined by four independent variables:

- overall pressure ratio
- maximum cycle temperature
- fan pressure ratio
- bypass ratio

The effect of varying fan pressure ratio on the engine defined above will now be considered. Figure 17.24 shows the way in which the thrust varies with fan pressure ratio for a number of maximum temperatures. It can be seen that the thrust reaches a maximum at a particular fan pressure ratio for any temperature being considered. Also the fan pressure ratio for maximum thrust increases with increasing temperature. The reason for this maximisation of thrust is because the bypass thrust increases as the fan pressure ratio increases whereas the jet thrust decreases. Initially, when the fan pressure ratio is low the jet operates with its nozzle choked. In the middle of the range both the fan and jet are unchoked but when the fan pressure ratio gets high then the fan chokes. The change in thrust distribution also indicates the significant change in work balance that occurs in the engine. At low fan

**FIGURE 17.24**

Variation of total thrust with fan pressure ratio (r_f) for a turbofan engine. Overall pressure ratio: 19; bypass ratio (b): 3; (other parameters as Example 2).

pressure ratios the work done by the HP shaft is high but at high fan pressure ratios the LP shaft work increases rapidly. The final points on this graph are reached when the exit pressure (p_{06}) is less than atmospheric pressure.

The sfc varies in an inverse manner to the thrust and the minimum sfc coincides with maximum thrust. Surprisingly, the minimum sfc is not achieved with the maximum peak temperature and, in this case, a maximum temperature of 1100 K gives the lowest sfc at a fan pressure ratio, $r_f = 1.4$. Of course, at these conditions the thrust is significantly less than at other conditions: it must be remembered that the mass flow through the engine was maintained constant throughout this study.

17.4 COMBUSTION IN GAS TURBINES

Compared to other prime movers (such as diesel and reciprocating automobile engines), gas turbines are considered to produce very low levels of combustion pollution, as shown in Table 17.1 where they are compared to other power producing devices. The gas turbine emissions of major concern are unburned hydrocarbons, carbon monoxide, oxides of nitrogen (NO_x) and smoke. While the contribution of jet aircraft to atmospheric pollution is less than 1% of the total atmospheric emissions, their emissions are injected directly into the upper troposphere, and have doubled during 1970–1990 between the latitudes of 40–60° north, increasing ozone by about 20%. In the stratosphere, where supersonic aircraft fly, NO_x will deplete ozone. Both effects are harmful, so further NO_x reduction in gas turbine operation is a challenge for the twenty-first century.

Combustion in gas turbines takes place at essentially constant pressure, although there is a small pressure drop through the chamber of about 5–7% of the delivery pressure which should be taken into account when undertaking design. The overall air–fuel ratio in the combustion chamber will be around

Table 17.1 Pollution Order Table

	Coal-Fired Steam-Electric Generating Station	Natural Gas Fired Combined Cycle	Gasoline Automotive Engine	Diesel Engine
CO	2	1	8	2
UHC	1	~0	9	2
NO _x	10	4	10	10
SO _x	10	~0	1	3
Particulate	10	~0	2	10
Toxics Hazardous Air Pollutants	7	1	4	4
CO ₂ (GHG)	10	5	8	7
CH ₄ (GHG)	3 (coal mine CH ₄)	3 (extraction and transport)	~0	~0
N ₂ O (GHG and strato ozone depletion)	2 (fluidised bed combustors)	~0	~0	~0
CFCs (GHG and strato ozone depletion)	0	0	0	0
Summary	NO _x , SO _x and particulate are removed from the stack gases with specialized equipment. Toxics (e.g. Hg) are starting to be seriously examined for reduction.	The gas-fired combined cycle power plant is relatively clean, though NO _x is highly regulated. Emissions increase if the system is switched to oil-firing during the winter.	CO, UHC and NO _x emissions from the engine are significant. The exhaust emissions control catalyst removes about 90% of the pollutants.	Diesel emissions are relatively low, except for NO _x and black smoke (carbon particulate matter)

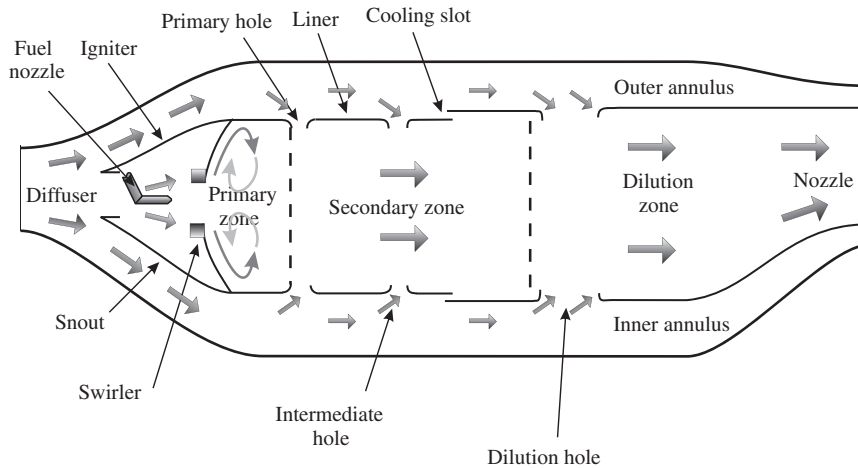
Aircraft gas turbines (kerosene): UHC and CO from ground operation (taxing); NO_x from takeoff and landing, and cruising (especially for stratospheric flight with supersonic transports).

Gas-fired (and propane-fired) residential furnaces and hot water heaters: CO and NO_x in moderate range. Cooking: the issue is indoor air pollution.

40:1, although there will be regions in which much richer mixtures exist. Figure 17.25 is a schematic section of an *annular combustion chamber*, which will be located circumferentially around the body of the gas turbine. Annular combustion chambers have advantages over the older types of tubular combustors in terms of pressure loss and compactness.

Table 17.1 summarises the problem. The rating scale varies from 0 (little significance) to 10 (great significance).

A successful combustor design must satisfy many requirements and the relative importance of each requirement varies with the application of the gas turbine: of course, some requirements are conflicting, necessitating design compromises be made. Most design requirements reflect concerns over

**FIGURE 17.25**

Section through aero gas turbine annular combustion chamber.

engine costs, efficiency and the environment. The basic design requirements can be classified as follows:

- High combustion efficiency at all operating conditions.
- Low levels of unburned hydrocarbons and carbon monoxide, low oxides of nitrogen at high power and no visible smoke for land-based systems. (Minimized pollutants and emissions.)
- Low pressure drop. Three to four percent is common.
- Combustion must be stable under all operating conditions.
- Consistently reliable ignition must be attained at very low temperatures, and at high altitudes (for aircraft).
- Smooth combustion, with no pulsations or rough burning.
- A low temperature variation for good turbine life requirements.
- Useful life (thousands of hours), particularly for industrial use.
- Multi-fuel use. Characteristically natural gas and diesel fuel are used for industrial applications and kerosene for aircraft.
- Length and diameter compatible with engine envelope (outside dimensions).
- Designed for minimum cost, repair and maintenance.
- Minimum weight (for aircraft applications).

The combustion chamber, shown in Fig. 17.25, has a number of elements which will now be described. The outer, air, casing contains the compressed air and bears its load. On entering the chamber the air passes through the diffuser, which slows the air from the compressor outlet velocity, which might reach 150 m/s or higher, to one that will sustain combustion. The diffuser also converts the dynamic head of the air into pressure, and delivers a smooth stable flow to the main chamber. This region also distributes the airflow between the primary air entering the snout and the secondary air entering the inner and outer annuli. After the diffuser, liquid fuel is injected, in droplet form, into the

airflow through an atomiser. There are many types of atomiser design and these will not be discussed here. However, the atomiser should possess the following characteristics:

- good atomisation over the entire range of fuel flows,
- rapid response to changes in throttle setting,
- freedom from flow instabilities,
- low susceptibility to blockage by contaminants,
- low susceptibility to gum formation by heat soakage,
- capability for scaling, to provide design flexibility,
- low cost, light weight, ease of manufacture and ease of removal,
- low susceptibility to damage during manufacture and installation.

It should also provide:

- an easily ignitable mixture,
- a ratio of maximum to minimum fuel flow that exceeds the ratio of maximum to minimum combustor airflow,
- controlled dispersion of the fuel throughout the primary combustion zone,
- an exit gas temperature distribution that is insensitive to variations in fuel flow rate.

The combustion volume shown in the annular chamber in Fig. 17.25 can be divided into three zones: primary, secondary and dilution. These zones will now be discussed.

Primary zone: the functions of the primary zone are to anchor the flame and to provide sufficient *time, temperature and turbulence* to achieve essentially complete combustion of the fuel. The *snout* imparts a high swirl into the flow to induce a strong recirculation region in the *primary zone*; this swirl enables the residence time in the primary zone to be lengthened without making this region excessively long. It also promotes good mixing through turbulence. And this mixing promotes efficient combustion and minimum pollutant formation. The fuel injector will be either a high-pressure spray atomiser or an air-blast injector. Sometimes a smaller pilot injector is used to assist ignition. Ignition is achieved by means of a powerful plasma jet igniter. In the *primary combustion zone* the air–fuel ratio will be approximately stoichiometric (15:1), and the adiabatic temperature rise will take the temperature up to about 2000 K, at which temperature NO_x will be formed. Jet-mixing processes play an important role in achieving satisfactory combustion performance. In the intermediate zone, rapid mixing of the injected air with the hot gases from the primary zone is needed to accelerate soot oxidation and to convert any dissociated species into normal products of combustion. Finally, the attainment of a satisfactory pattern factor at the combustor exit is dependent on thorough mixing of air and combustion products in the dilution zone.

Secondary zone: The gas enters here from the primary zone and is diluted with *secondary air* bleeding through the side walls of the chamber. This air will induce further turbulence, and supply more oxygen to complete the burning of the soot formed during the rich primary combustion. The secondary air will also lower the gas temperature to about 1800 K, and reduce the amount of NO_x produced. This zone must have sufficient length for the two main functions that it performs. At low altitudes it serves as a region in which dissociation losses in the gas flow can be recovered, and the burning of any imperfectly mixed fuel-rich pockets of gas can be completed. Dissociation has been discussed in Chapter 12, and this results in carbon dioxide (CO_2) dissociating to carbon monoxide (CO) and oxygen: to a lesser extent, there is also dissociation of water vapour. Reducing the gas

temperature to an intermediate level by the addition of a small amount of air allows the combustion of CO and partly burned fuel to proceed to completion. At high altitudes, the secondary zone serves principally as an extension of the primary zone.

Dilution zone: the dilution zone is the region where the air remaining after the combustion and wall cooling requirements have been met is admitted to the main chamber. This then provides an outlet stream with a mean temperature and a temperature distribution that is acceptable to the turbine. Finally the cooling air which has been passed down the outside of the combustion chamber will be mixed in with the hot gases, and the products will be passed to the turbine through the *nozzle*, which matches the flow from the combustion chamber to the requirements of the turbine.

A major requirement in the design of a gas turbine combustor is that combustion can be sustained over the entire range of operating conditions including the transient states of rapid acceleration and deceleration. For industrial engine combustors this presents no special problems, since the low velocities and high-pressure-loss factors employed in these systems are very conducive to stable combustion. The aircraft chamber, however, is called upon to operate at very low inlet temperatures and pressures and at fuel–air ratios that lie well outside the normal burning limits of hydrocarbon–air mixtures. Efficient combustion must be maintained in highly turbulent airstreams flowing at velocities that greatly exceed the normal burning velocity of the fuel.

The basic principle involved in flame stabilization is quite simple. If combustion is initiated in a flowing stream, and if the gas velocity U is higher than the flame speed S , the flame will move downstream at a speed of $U - S$ (flame blowout). If the burning velocity is higher, then the flame will move upstream with a speed of $S - U$. Only if $U = S$ will the flame be stationary. The function of the flameholder is to create a region in a high-speed gas stream whose velocity is lower than the burning velocity of the mixture. The primary design objective for good stability in any practical combustion device is to maximise the ratio of burning velocity to flow velocity. This, incidentally, is also a key requirement for high combustion efficiency. It is normally achieved by creating, at the upstream end of the liner, a sheltered zone of low velocity in which flame speeds are greatly enhanced by imparting a high level of turbulence to the primary air jets and by arranging for hot combustion products to recirculate and mix with the incoming air and fuel (see Fig. 17.25).

The stability performance of a combustor is usually expressed in the form of a stability plot that separates the regions of stable and unstable combustion. The traditional plot has equivalence ratio or fuel–air ratio as the ordinate, and some loading parameter, such as velocity or mass flow through the combustor, as the abscissa. These plots provide two basic kinds of information. First, for any given fuel–air ratio, they indicate the blowout velocity. Second, for any given combustor loading, they show the range of fuel–air ratios over which stable combustion can be achieved.

There are many reasons why combustion efficiency is of paramount importance for gas turbine combustors. First and foremost, combustion inefficiency represents a waste of fuel, which is clearly unacceptable in view of the world's dwindling oil supply and the rapid escalation of fuel costs. Also combustion inefficiency is manifested in the form of undesirable or harmful pollutant emissions, notably unburned hydrocarbons and carbon monoxide. Combustion efficiencies in excess of 99% at all operating conditions are demanded to meet emission regulations. For the aircraft engine, an additional requirement is that the level of combustion efficiency be fairly high, from 75% to 80%, when the combustion chamber is being used to accelerate the engine to its normal rotational speed after a flameout at high altitude. A high combustion efficiency is necessary when the engine is windmilling because the pressure and temperature of the air flowing through the combustor are close to the ambient values; at high altitudes, these are so low

that the stability limits are very narrow. This means that when the engine control system attempts to compensate for combustion inefficiency by supplying more fuel to the combustor, this extra fuel is liable to cause a 'rich extinction' of the flame. Thus, an important design requirement for an aircraft combustor is that it is sized large enough to ensure an adequate level of combustion efficiency during engine restart at the highest altitude at which relight capability is guaranteed.

17.5 CONCLUDING REMARKS

This chapter has developed the concepts introduced in Chapter 3, when the Joule cycle was introduced. It has shown that only the closed cycle gas turbines are heat engines, and most of the gas turbines encountered do not fall into that strictly defined category. However, it is possible to analyse the full range of gas turbine arrangements, and the basic parameters such as work (or power) output and efficiency can be evaluated for them. Again, the importance of the temperature range of operation has been emphasized, and the overriding importance of the mean temperatures of heat (energy) reception and rejection has been demonstrated. The fact that the working fluid in a gas turbine is a single phase gas is the biggest downfall of the device, because it results in a low work ratio: the situation is exacerbated at low loads when the difference between the turbine and compressor work reduces. The effects of reheating and intercooling were investigated, and it was found that in isolation these did not improve the efficiency of the device: regeneration (or heat exchange) was the way to improve efficiency in land-based engine.

Aircraft gas turbines were considered, and the differences between pure jet engines, turboprop and bypass engines were discussed. While the total spectrum of engines considered was limited to commercial applications, it was apparent that the use of bypass improved the sfc and propulsive efficiency of aircraft engines.

A brief description of combustion chambers showed that the basic parameters and principles used in their design relied on the underlying physics introduced in Chapter 15.

17.6 PROBLEMS

- P17.1** A gas turbine engine operates between minimum temperature T_1 and maximum temperature T_3 . Show that the optimum pressure ratio for maximum work output is

$$r_p = \left(\frac{T_3}{T_1} \right)^{\frac{\kappa}{2(\kappa - 1)}}$$

- P17.2** A gas turbine engine operates at temperature between 300 and 1200 K. The pressure ratio is 12 and the working fluid is CO_2 . Assume an isentropic process,

- (1) Determine the efficiency and work ratio of the cycle. Assume heat capacity ratio of CO_2 , $\kappa_{\text{CO}_2} = 1.3$.
- (2) Calculate the maximum net work. Assume $c_{p(\text{CO}_2)} = 0.9 \text{ kJ/kgK}$ [0.436, 0.556, 270 kJ/kg]

- P17.3** Assume the maximum pressure ratio. Determine the efficiency and work ratio of the cycle in P17.1. [0.75, 0.]

- P17.4** Air at 290 K flows into the compressor of a gas turbine engine. The temperature increases to 1350 K when it flows into the turbine. The pressure ratio is 15 and power output is 5 MW. Assume the whole process is isentropic, evaluate
1. Thermal efficiency.
 2. Fuel consumption. The lower calorific value of the fuel, Q'_p , is 44,000 kJ/kg.
 3. Ratio of turbine work and compressor work.
- Take heat capacity ratio, $\kappa_{\text{air}} = 1.38$; $c_p = 1.05$ kJ/kgK.
[0.526, 0.114 kg/s, 2.2]
- P17.5** A gas turbine operates at a pressure ratio of 8. The air flows into the compressor at 290 K and flows out of the combustion chamber at 1400 K. The efficiency of compressor and turbine are 0.8 and 0.9 respectively. A heat exchanger with effectiveness of 0.85 is used. Assuming an isentropic process, calculate the thermal efficiency and net power output of the engine. The mass flow rate is 1 kg/s. Take heat capacity ratio $\kappa_{\text{air}} = 1.38$; $c_p = 1.005$ kJ/kgK.
[0.61, 653.9 kW]
- P17.6** Prove that the optimum pressure ratio for intercooling of gas turbines with heat exchange is given below:

$$\frac{p_2}{p_1} = \frac{p_i}{p_1} = \left(\frac{p_2'}{p_1} \right)^{1/2}.$$

Assume that the processes in the turbine and compressor are both isentropic, and that the heat exchanger effectiveness, $\epsilon = 1.0$.

- P17.7** Air flows into the compressor of a gas turbine engine at 0.1 MPa, 300 K and is compressed to 0.8 MPa. The air is heated to a maximum temperature of 1100 K and then expanded through two stages each with a pressure ratio of 3. The intermediate reheating temperature is 1100 K. Assuming C_p is constant and independent of temperature, determine the cycle efficiency. Take heat capacity ratio $\kappa = 1.4$.
[0.41]
- P17.8** A turbojet is travelling at high Mach number and the ambient pressure, p_a , and temperature, T_a , are 0.5 bar and 220 K respectively. It is also known that the stagnation temperature at the inlet of the compressor is $T_{01} = 400$ K. If the intake nozzle isentropic efficiency, $\eta_i = 0.8$, find the pressure ratio, p_{01}/p_a .
[5.8]
- P17.9** If the compressor pressure ratio of the turbojet in P17.8 is 13.0 and the isentropic efficiency is 0.8, calculate the stagnation pressure p_{02} and the stagnation temperature T_{02} at the compressor outlet.
[37.7 bar, 940.5 K]
- P17.10** If the compressor (for the turbojet in P17.8 and P17.9) consumes 7500 kW of power, calculate the turbine temperature drop ($T_{03} - T_{04}$) and the mass flow rate of intake air. The mechanical transmission efficiency is 0.99 and the mass flow rate of the fuel is negligible.
[483.7 K, 13.74 kg/s]
- P17.11** Assume that the turbine inlet temperature T_{03} (for the engine considered in P17.8–P17.10) is 1700 K, and that the propelling nozzle has an inlet pressure p_{04} of 2.1 bar and an isentropic

efficiency of 0.95. Determine the specific thrust of the engine if the converging propelling nozzle is choked.

[285.9 m/s]

- P17.12** Consider a twin-spool turbofan engine with the fan driven by the LP turbine and the compressor by the HP turbine. Separate cold and hot exhaust nozzles are used. Calculate the total thrust under the following conditions.

Overall Pressure Ratio	25.0
Fan pressure ratio	1.8
Turbine inlet temperature	1500 K
Fan, compressor isentropic efficiency	0.9
Turbine isentropic efficiency	0.95
Isentropic efficiency of each nozzle	0.95
Mechanical efficiency of each spool	0.99
Combustion chamber pressure loss	1.3 bar
Mass flow rate of cold nozzle flow	130 kg/s
Mass flow rate of hot nozzle flow	32.5 kg/s

Assume sea level static conditions where the ambient pressure and temperature are 1.0 bar and 300 K, respectively.

[59.1 kN]

LIQUEFACTION OF GASES

18

If the temperature and pressure of a gas can be brought into the region between the saturated liquid and saturated vapour lines then the gas will become ‘wet’ and this ‘wetness’ will condense giving a liquid. Most gases existing in the atmosphere are extremely superheated, but are at pressures well below their critical pressures. Critical point data for common gases and some hydrocarbons are given in Table 18.1.

Figure 18.1 depicts qualitatively the state point of oxygen at ambient conditions and shows that it is a superheated gas at this pressure and temperature, existing at well above the critical temperature, but below the critical pressure. If it is desired to liquefy the gas, it is necessary to take its state point into the saturated liquid – saturated vapour region. This can be achieved in a number of ways. First, experience indicates that ‘heat’ has to be taken out of the gas. This can be done by two means:

1. cooling the gas by heat transfer to a cold reservoir, i.e. refrigeration;
2. expanding the gas in a reversible manner, so that it does work.

18.1 LIQUEFACTION BY COOLING – METHOD (I)

This method is satisfactory if the liquefaction process does not require very low temperatures. A number of common gases can be obtained in liquid form by cooling. Examples of these are the hydrocarbons butane and propane, which can both exist as liquids at room temperature if they are contained at elevated pressures. Mixtures of hydrocarbons can also be obtained as liquids and these include liquefied petroleum gas (LPG) and liquefied natural gas (LNG).

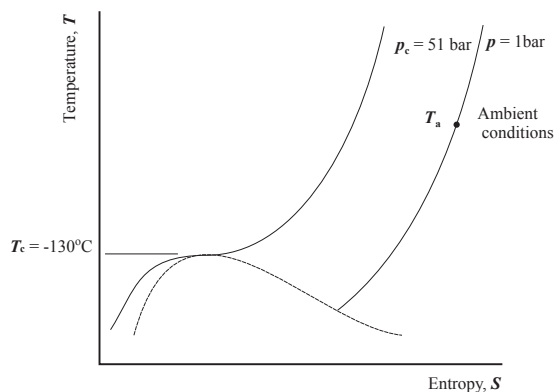
A simple refrigerator, and the refrigeration cycle, are shown in Fig. 18.2(a) and (b) respectively.

Consider the throttling process in Fig. 18.2, which is between 4 and 1. The working fluid enters the throttle at a high pressure in a liquid state, and leaves it at a lower pressure and temperature as a wet vapour. If the mass of working fluid entering the throttle is 1 kg then the mass of liquid leaving the throttle is $(1-x_1)$ kg. If this liquid were then withdrawn to a vessel, and the mass of fluid in the system were made up by adding $(1-x_1)$ kg of gas at state 3 then it would be possible to liquefy that gas. The liquefaction has effectively taken place because, in passing through the throttle the quality (dryness fraction) of the fluid has been increased, and the energy to form the vapour phase has been obtained from the latent heat of the liquid thus formed: the throttling process is an isenthalpic one, and hence energy has been conserved. If the working fluid for this cycle was a gas which it was desired to liquefy then the liquid could be withdrawn at state 1’ on Fig 18.2.

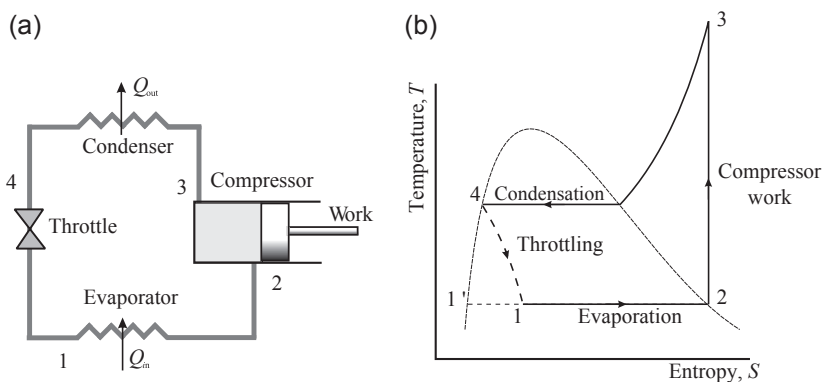
The simple refrigeration system shown in Fig. 18.2 might be used to liquefy substances which boil at close to the ambient temperature, but it is more common to use refrigeration plant in series, referred to as a *cascade*, to achieve reasonable levels of cooling. The cascade plant is also more cost-effective because it splits the temperature drop between two working fluids. Consider Fig. 18.2, the difference

Table 18.1 Critical temperatures and pressures for common substances

Substance	Critical Temperature, T_c °C [K]	Critical Pressure, p_c (bar)
Water (H ₂ O)	374 [647]	221.2
Methane (CH ₄)	−82 [191]	46.4
Ethane (C ₂ H ₆)	32 [305]	49.4
Propane (C ₃ H ₈)	96 [369]	43.6
Butane (C ₄ H ₁₀)	153 [426]	36.5
Carbon dioxide (CO ₂)	31 [304]	89
Oxygen (O ₂)	−130 [143]	51
Hydrogen (H ₂)	−243 [30]	13
Nitrogen (N ₂)	−147 [126]	34

**FIGURE 18.1**

State point of oxygen at ambient temperature and pressure.

**FIGURE 18.2**

A simple refrigerator (a) schematic of plant; (b) temperature–entropy (T – S) diagram.

between the top and bottom temperatures is related to the difference between the pressures. To achieve a low temperature, it is necessary to reduce the evaporator pressure, and this will increase the specific volume of the working fluid and hence the size of the evaporator. The large temperature difference will also decrease the coefficient of performance of the plant. The use of two plants in cascade enables the working fluid in each section to be optimised for the temperature range encountered. Two plants in cascade are shown in Fig. 18.3(a), and the T - s diagrams are depicted in Fig. 18.3(b).

In the cascade arrangement, the cooling process takes place in two stages: it is referred to as a binary cascade cycle. This arrangement is the refrigeration equivalent of the combined cycle power station. The substance to be liquefied follows cycle 1-2-3-4-1, and the liquid is taken out at state 1'. However, instead of transferring its waste energy, Q_2 , to the environment it transfers it to another refrigeration cycle which operates at a higher temperature level (see Chapter 19 for reference to pinch points). The working fluids in each cycle will be different, and that in the high temperature cycle, 5-6-7-8-5, will have a higher boiling point than the substance being liquefied. The two cycles can also be used to liquefy both of the working fluids, in which case liquid will also be taken out at state 5'.

The overall coefficient of performance of the two plants working in cascade can be evaluated by considering the heat flow through each section and is given by

$$\left(1 + \frac{1}{\beta'}\right) = \left(1 + \frac{1}{\beta'_1}\right) \left(1 + \frac{1}{\beta'_2}\right) \quad (18.1)$$

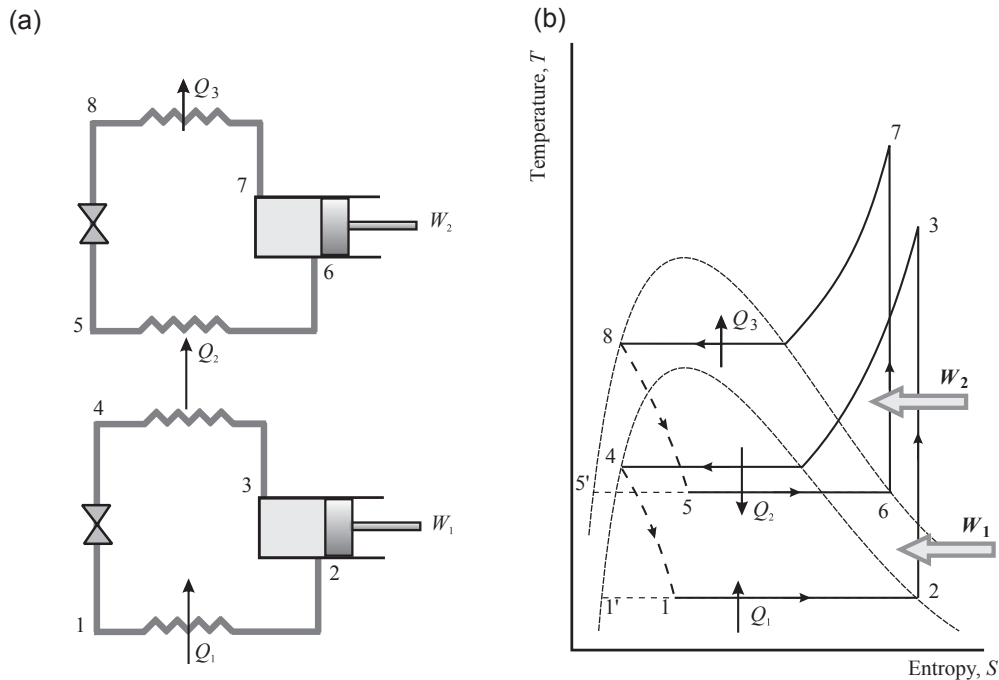


FIGURE 18.3

Cascade refrigeration cycle.

where β' is the overall coefficient of the combined plant, and β'_1 and β'_2 are the coefficients of performance of the separate parts of the cascade. The coefficient of performance of the overall plant is less than that of either individual part.

The liquefaction of natural gas is achieved by means of a ternary cascade refrigeration cycle, and the components are shown in Fig. 18.4. In this system, a range of hydrocarbons are used to cool each other. The longer chain hydrocarbons have higher boiling points than the shorter ones, and hence the alkanes can be used as the working fluids in the plant.

Another common gas that can be obtained in a nongaseous form is carbon dioxide (CO_2). This is usually supplied nowadays in a solid form called *dry ice*, although it was originally provided as a pressurised liquid. Dry ice is obtained by a modification of the refrigeration process, and the plant and

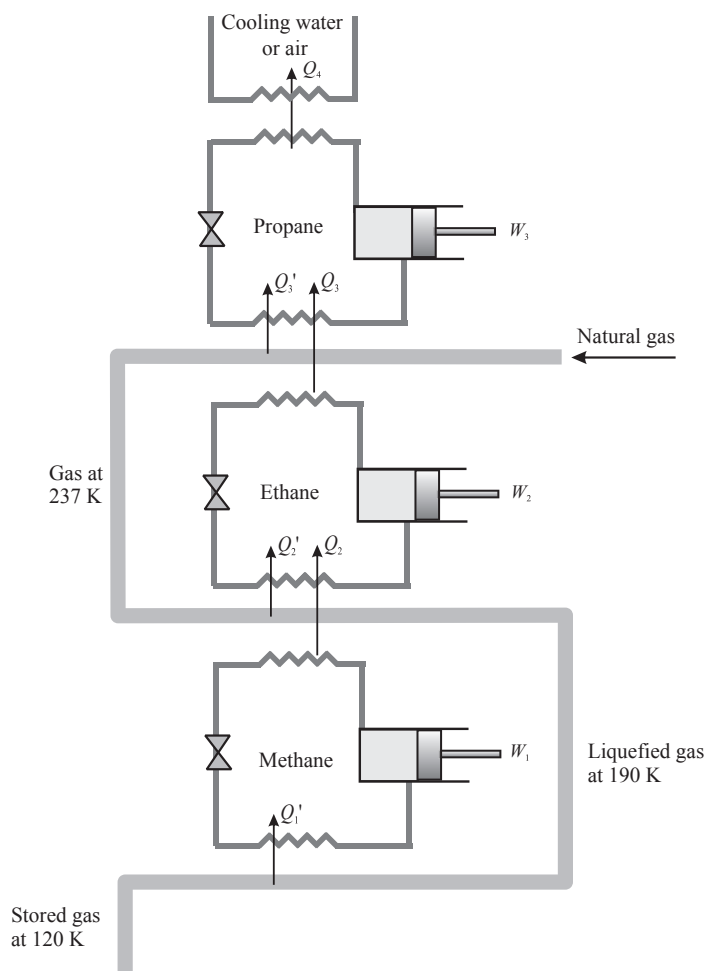


FIGURE 18.4

Plant for liquefaction of natural gas.

relevant T - s diagrams are shown in Fig. 18.5(a) and (b) respectively. This is like a ternary cascade system, but in this case, the working fluid passes through all the stages of the plant. The carbon dioxide gas enters the plant at state 'a', and passes through the final stage, referred to as the snow chamber, because by this stage the gas has been converted to dry ice. Heat is transferred from the carbon dioxide to the final product causing some evaporation: this evaporated product is passed back to the first compressor. The fluid then passes through the first compressor, where it is compressed to state 'c'. It is then passed into a *flash tank*, where it is cooled by transferring heat with liquid already in there: this again causes some evaporation of the product, which is passed back into the second compressor, along with the working fluid. In the example shown the process has three stages, and the final stage must be at

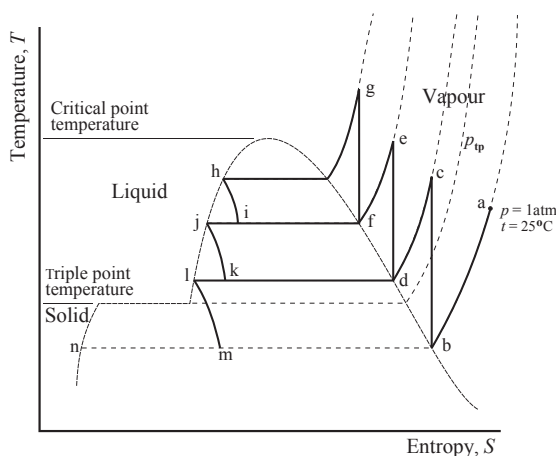
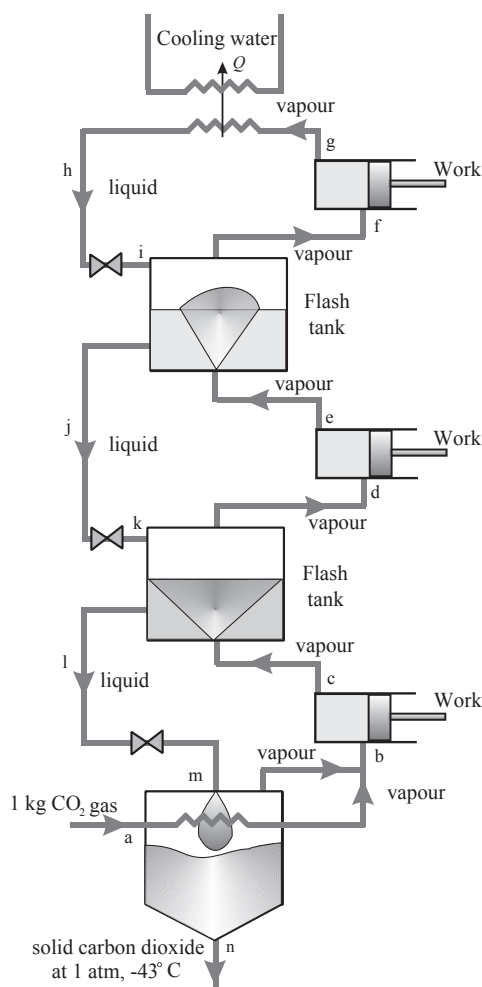


FIGURE 18.5

Plant for manufacture of dry ice (solid carbon dioxide).

a pressure high enough to enable the condensation to occur by heat transfer to a fluid at close to atmospheric temperature, depicted by point 'h' on Fig. 18.5(b); the pressure must also be below the critical pressure for condensation to occur. The liquid that is produced at 'j' passes through the series of throttles to obtain the refrigeration effect necessary to liquefy the carbon dioxide. In the last chamber, the liquid is expanded below the triple point pressure, and the phase change enters the solid–gas region. Carbon dioxide cannot exist as a liquid at atmospheric pressure, because its triple point pressure is 5.17 bar: hence it can either be a pressurised liquid or a solid. Dry ice is not in equilibrium with its surroundings, and is continually evaporating. It could only be in a stable state, if the ambient temperature was dropped to the equivalent of the saturated temperature for the solid state at a pressure of 1 bar.

18.2 LIQUEFACTION BY EXPANSION – METHOD (II)

If the gas does work against a device (e.g. a turbine) whilst expanding adiabatically then the internal energy will be reduced and liquefaction may ensue. A cycle which includes such an expansion process is shown in the Fig. 18.6. The gas, for example oxygen, exists at state 1 when at ambient temperature and pressure: it is in a superheated state, but below the critical pressure. If the gas is then compressed isentropically to a pressure above the critical pressure it will reach state 2. The temperature at state 2 is above the ambient temperature, T_a , but heat transfer to the surroundings allows the temperature to be reduced to state point 2a. If the liquefaction plant is a continuously operating plant, then there will be available a supply of extremely cold gas or liquid and this can be used, by a suitable arrangement of heat exchangers, to further cool the gas to state point 3. If the gas is now expanded isentropically through the device from state 3 down to its original pressure, it will condense out as a liquid at state 4. Hence, the processes defined on Fig. 18.6 can be used to achieve liquefaction of a gas by use of a device taking energy out of the substance by producing work output. It should be noted that if the gas

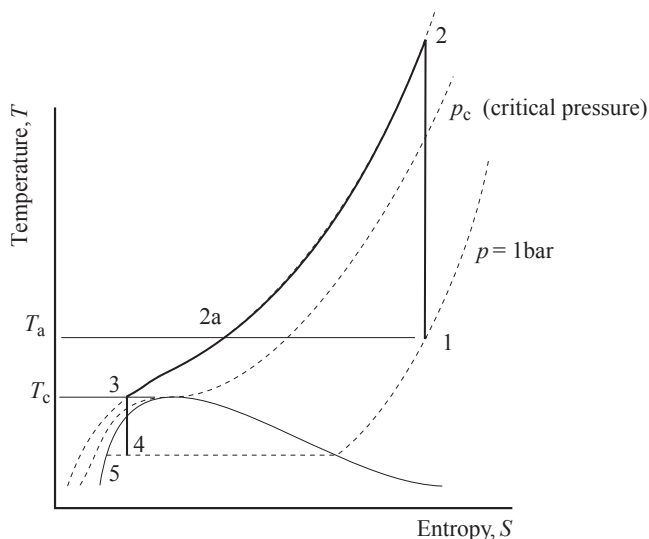


FIGURE 18.6

A method for liquefying a gas.

was a *supercritical vapour* at ambient conditions, it would be impossible to obtain it in liquid form at atmospheric pressure.

In the liquefaction process described above, the gas may be expanded from state 3 to state 4 either by a reciprocating machine or against an expansion turbine. Both these machines suffer the problem that the work done in the expansion process is a function of the initial temperature because the temperature drop across the turbine is

$$\Delta T = T_3 \eta_T \left\{ 1 - \left(\frac{p_4}{p_3} \right)^{\frac{\kappa - 1}{\kappa}} \right\} \quad (18.2)$$

It can be seen from Eqn (18.2) that as T_3 becomes very small the temperature drop achieved by the expansion gets smaller, which means that pressure ratio to obtain the same temperature drop has to be increased for very low critical temperatures. Another major problem that occurs at very low temperatures is that lubrication becomes extremely difficult. For this reason, the turbine is a better alternative than a reciprocating device because it may have air bearings, or gas bearings of the same substance as that being liquefied, thus reducing contamination.

Fortunately another method of liquefaction is available which overcomes many of the problems described above. This is known as the Joule–Thomson effect and it can be evaluated analytically. The Joule–Thomson effect is the result of relationships between the properties of the gas in question.

18.2.1 THE JOULE–THOMSON EFFECT

The Joule–Thomson effect was discovered in the mid-nineteenth century when experiments were being undertaken to define the First Law of Thermodynamics. Joule had showed that the specific heat at constant volume was not a function of volume, and a similar experiment was developed to ascertain the change of enthalpy with pressure. The experiment consisted of forcing a gas through a porous plug by means of a pressure drop. It was found that, for some gases, at a certain entry temperature, there was a temperature drop in the gas after it had passed through the plug. This showed that, for these gases, *the enthalpy of the gas was a function of both temperature and pressure* (see also Chapter 1).

A suitable apparatus for conducting the experiment is shown in Fig. 18.7.

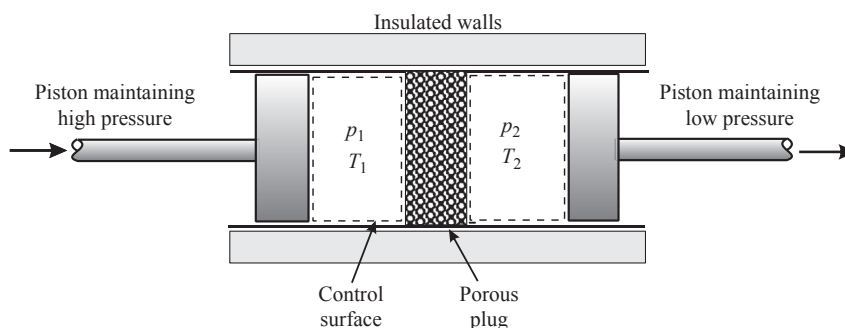
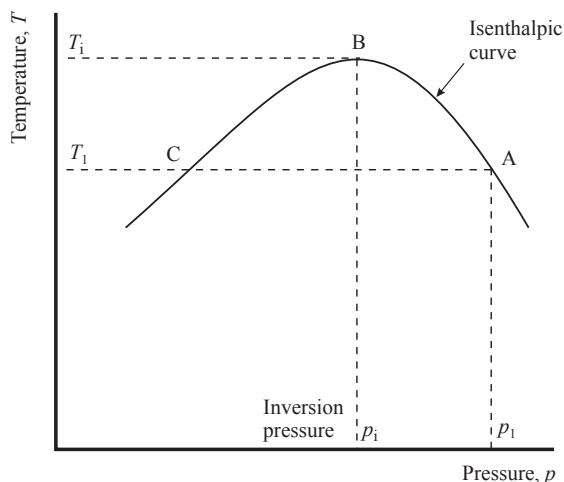


FIGURE 18.7

Porous plug device for Joule–Thomson experiment.

FIGURE 18.8

Isenthalpic curve for flow through a porous plug.



If the upstream pressure and temperature are maintained constant, and the downstream pressure is varied the temperature measured follows a trace of the form shown in Fig. 18.8.

Line ABC in Fig. 18.8 *does not show the change of temperature as the gas flows through the porous plug*: it is made up of results from a series of experiments and shows the effect of lowering the back pressure on the downstream temperature. It is very difficult to evaluate the variation of temperature along the plug, and this will not be attempted here. However, as the pressure, p_2 , is decreased below p_1 the temperature increases until point B is reached: after this the temperature decreases with decreasing pressure, p_2 . Eventually a point is reached, denoted C on the diagram, where $T_2 = T_1$, and after this $T_2 < T_1$. The maximum temperature on this isenthalpic curve is referred to as the *inversion temperature*, T_i , and point B is called the *inversion point*.

The process shown in Fig. 18.8 may be analysed by applying the Steady Flow Energy Equation (see Chapter 1) across control volume, when

$$\dot{Q} - \dot{W} = \dot{m} \left(h_2 - h_1 + \frac{V_2^2}{2} - \frac{V_1^2}{2} \right) \quad (18.3)$$

where

$\dot{Q}$ = rate of heat transfer,

$\dot{W}$ = rate of work transfer,

$\dot{m}$ = mass flow rate,

h_1, h_2 = enthalpy upstream and downstream of plug,

V_1, V_2 = velocity upstream and downstream of plug.

Now $\dot{Q} = 0$, $\dot{W} = 0$, $V_2 \approx V_1$. Hence $h_2 = h_1$, and the enthalpy along line ABC is constant: thus ABC is an *isenthalpic line*. The most efficient situation from the viewpoint of obtaining cooling is achieved if p_1 and T_1 are at B, the *inversion point*. If state (p_1, T_1) is to the right of B then T_2 depends on the pressure drop, and it could be greater than, equal to, or less than, T_1 . If the upstream state (p_1, T_1) is

at B then the downstream temperature, T_2 , will always be less than T_1 . It is possible to analyse whether heating or cooling will occur by evaluating the sign of the derivative $(\partial T/\partial p)_h$. This term is called the *Joule–Thomson Coefficient*, μ .

If $\mu < 0$, then there can be either heating or cooling depending on whether the downstream pressure is between A and C, or to left of C. If $\mu > 0$, then the gas will be cooled on passing through the plug. (i.e. the upstream state point defined by (p_1, T_1) is to the left of B on the isenthalpic line.)

This situation can be analysed in the following way. From the Second Law of Thermodynamics

$$dh = Tds + vdp. \quad (18.4)$$

But for this process $dh = 0$, and thus, from Eqn (18.4),

$$0 = T \left(\frac{\partial s}{\partial p} \right)_h + v. \quad (18.5)$$

If it is assumed that entropy is a continuous function of pressure and temperature, i.e. $s = s(p, T)$ then

$$ds = \left(\frac{\partial s}{\partial p} \right)_T dp + \left(\frac{\partial s}{\partial T} \right)_p dT \quad (18.6)$$

which can be rearranged to give

$$\left(\frac{\partial s}{\partial p} \right)_h = \left(\frac{\partial s}{\partial p} \right)_T + \left(\frac{\partial s}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_h \quad (18.7)$$

Hence, substituting this expression into Eqn (18.5) gives

$$0 = T \left\{ \left(\frac{\partial s}{\partial p} \right)_T + \left(\frac{\partial s}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_h \right\} + v \quad (18.8)$$

Now, from thermodynamic relationships (Eqn (7.24)),

$$T \left(\frac{\partial s}{\partial T} \right)_p = c_p$$

and, from the Maxwell relationships (Eqn (7.19(d)))

$$\left(\frac{\partial s}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p.$$

Thus

$$0 = -T \left(\frac{\partial v}{\partial T} \right)_p + c_p \left(\frac{\partial T}{\partial p} \right)_h + v \quad (18.9)$$

which may be rearranged to give

$$\left(\frac{\partial T}{\partial p} \right)_h = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] = \mu. \quad (18.10)$$

This can be written in terms of the coefficient of expansion $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p$, and Eqn (18.10) becomes

$$\mu = \frac{v}{c_p} [\beta T - 1]. \quad (18.11)$$

At the inversion temperature

$$\left(\frac{\partial T}{\partial p} \right)_h = 0, \text{ giving } T_i = \frac{1}{\beta}. \quad (18.12)$$

It is possible to evaluate the Joule–Thomson coefficient for various gases from their state equations. For example the Joule–Thomson coefficient for a perfect gas can be evaluated by evaluating μ from Eqn (18.10) by differentiating the perfect gas equation

$$pv = RT \quad (18.13)$$

Now,

$$\mu = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right].$$

and, from Eqn (18.13) the derivative

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p} \quad (18.14)$$

Hence,

$$\mu = \frac{1}{c_p} \left[T \frac{R}{p} - v \right] = 0.$$

This means that it is not possible to cool a perfect gas by the Joule–Thomson effect. This is what would be expected, because the enthalpy of an ideal gas is not a function of pressure. However, it does not mean that gases which obey the ideal gas law at normal atmospheric conditions (e.g. oxygen, nitrogen, etc.) cannot be liquefied using the Joule–Thomson effect, because they cease to obey this law close to the saturated vapour line. The possibility of liquefying a gas obeying the van der Waals equation is considered below.

Van der Waals equation for air may be written, using a and b for air as 1.358 bar (m³/kmol)² and 0.0364 m³/kmol respectively,

$$p = \frac{0.083143T}{(v - 0.0364)} - \frac{1.358}{v^2} \quad (18.15)$$

To assess whether a van der Waals gas can be liquefied using the Joule–Thomson effect, it is necessary to evaluate the Joule–Thomson coefficient, μ . This is related to $(\partial v / \partial T)_p$, which can be evaluated in the following way.

From Eqn (18.15), in general form

$$T = \left(p + \frac{a}{v^2} \right) \frac{(v - b)}{\Re} \quad (18.16)$$

$$\begin{aligned} \text{and hence, } \left(\frac{\partial T}{\partial v}\right)_p &= \frac{1}{\Re} \left(p + \frac{a}{v^2}\right) - \left(\frac{v-b}{\Re}\right) \left(\frac{2a}{v^3}\right), \\ \text{giving } \left(\frac{\partial v}{\partial T}\right)_p &= \frac{\Re}{\left(p + \frac{a}{v^2}\right) - (v-b) \left(\frac{2a}{v^3}\right)} \end{aligned} \quad (18.17)$$

Thus, from Eqn (18.17), the Joule–Thomson coefficient for a van der Waals gas is not zero at all points, being given by

$$\mu = \frac{1}{c_p} \left[\frac{\Re T}{\left(p + \frac{a}{v^2}\right) - (v-b) \left(\frac{2a}{v^3}\right)} - v \right] \quad (18.18)$$

18.2.2 MAXIMUM AND MINIMUM INVERSION TEMPERATURES

The general form of Van der Waals equation, Eqn (18.15), can be rewritten as

$$T = \left(p + \frac{a}{v^2}\right) \frac{(v-b)}{\Re}. \quad (18.16)$$

The inversion temperature is defined as

$$T_i = v \left(\frac{\partial T}{\partial v}\right)_p \quad (18.19)$$

which can be evaluated from Eqn (18.16) in the following way.

$$\begin{aligned} \left(\frac{\partial T}{\partial v}\right)_p &= \frac{1}{\Re} \left(p + \frac{a}{v^2}\right) - \left(\frac{v-b}{\Re}\right) \left(\frac{2a}{v^3}\right), \\ \text{giving } v \left(\frac{\partial T}{\partial v}\right)_p &= \frac{1}{\Re} \left\{ v \left(p + \frac{a}{v^2}\right) - (v-b) \left(\frac{2a}{v^2}\right) \right\} \end{aligned} \quad (18.20)$$

It is now necessary to solve for v in terms of T_i alone, and this can be achieved by multiplying Eqn (18.16) by v and Eqn (18.20) by $(v-b)$. This gives

$$vT_i = \left(p + \frac{a}{v^2}\right) \frac{v(v-b)}{\Re}, \quad (18.21)$$

$$\text{and } (v-b)T_i = \frac{v(v-b)}{\Re} \left(p + \frac{a}{v^2}\right) - \frac{(v-b)^2}{\Re} \frac{2a}{v^2} \quad (18.22)$$

Subtracting Eqns (18.21) and (18.22) gives

$$\left(\frac{v-b}{v}\right) = \sqrt{\frac{\Re b T_i}{2a}} = x = 1 - \frac{b}{v} \quad (18.23)$$

Substituting Eqn (18.23) in Eqn (18.15) gives

$$p = \frac{a}{b^2} \left(1 - \sqrt{\frac{\Re b T_i}{2a}} \right) \left(3\sqrt{\frac{\Re b T_i}{2a}} - 1 \right) \quad (18.24)$$

The maximum and minimum inversion temperatures are achieved when the pressure, p , is zero. This gives

$$\hat{T}_i = \frac{2a}{\Re b}, \quad \text{and} \quad \check{T}_i = \frac{2a}{9\Re b} = \frac{\hat{T}_i}{9} \quad (18.25)$$

The value of the critical temperature for a van der Waals gas is

$$T_c = \frac{8a}{27\Re b}, \quad (18.26)$$

and hence

$$\begin{aligned} \frac{\hat{T}_i}{T_c} &= \frac{\text{Maximum inversion temperature}}{\text{Critical temperature}} = 6.75 \\ \frac{\check{T}_i}{T_c} &= \frac{\text{Minimum inversion temperature}}{\text{Critical temperature}} = 0.75 \end{aligned} \quad (18.27(a, b))$$

These equations will now be applied to air: van der Waals equation for air was given as Eqn (18.15). Substituting these values of coefficients into Eqn (18.24), which can be solved as a quadratic equation in T_i , gives the diagram shown in Fig. 18.9. This shows that it is not possible to liquefy air, if it is above a pressure of about 340 bar.

The maximum pressure for which inversion can occur is when $dp/dT = 0$. This can be related to Van der Waals equation in the following way, using the expression for x introduced in Eqn (18.23).

$$\begin{aligned} \frac{dp}{dT} &= \frac{dp}{dx} \frac{dx}{dT}, \quad \text{and since } \frac{dx}{dT} \text{ is a simple single term expression, } \frac{dp}{dT} = 0 \quad \text{when} \quad \frac{dp}{dx} = 0. \\ \frac{dp}{dx} &= \frac{a}{b^2} \left\{ 3(1-x) - (3x-1) \right\} \end{aligned} \quad (18.28)$$

Equation (18.28) is zero when $3(1-x) - (3x-1) = 0$, i.e. when $x = 2/3$.

Hence the maximum pressure at which inversion can occur is

$$p = \frac{a}{b^2} \left(1 - \frac{2}{3} \right) \left(3 \times \frac{2}{3} - 1 \right) = \frac{a}{3b^2} = 9p_c \quad (18.29)$$

Thus the maximum pressure at which a Van der Waals gas can be liquefied using the Joule–Thomson effect is nine times the critical pressure. Substituting for a and b in Eqn (18.29) gives the maximum pressure as 341.6 bar.

Figure 18.9 indicates that it is not possible to cool air using the Joule–Thomson effect, if it is at a temperature of greater than 900 K, or at one less than about 100 K. Similar calculations for hydrogen

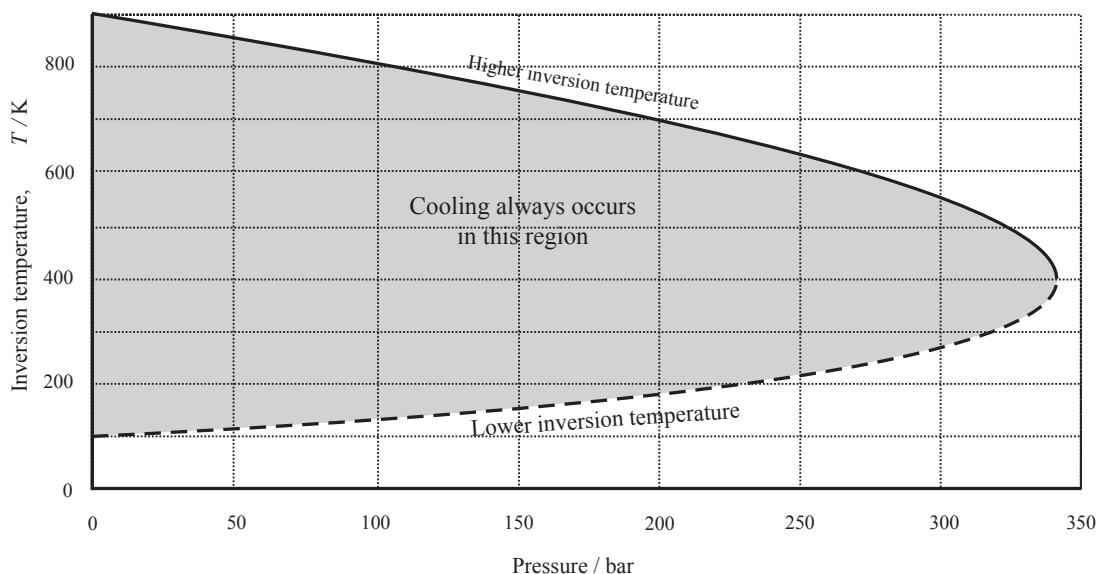


FIGURE 18.9

Higher and lower inversion temperatures for air.

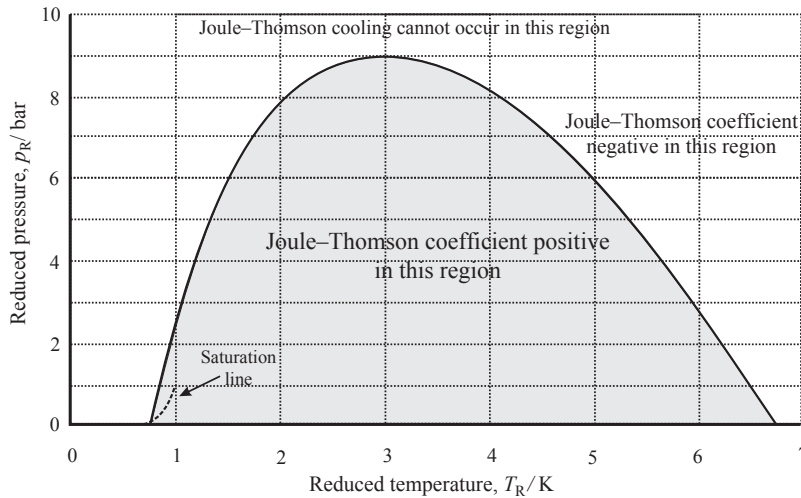
give 224 K and 24.9 K respectively for the maximum and minimum inversion temperatures. The maximum pressure at which inversion can be achieved is 117 bar.

The inversion curve goes through the lines of constant enthalpy at the point where $(\partial T / \partial p)_h = 0$. To the left of the inversion curve cooling always occurs; to the right heating or cooling occurs depending on the values of the pressure.

Figure 18.9 may be drawn in a more general manner by replotting it in terms of the reduced pressure (p_R) and temperature (T_R) used in the Law of Corresponding States (see Chapter 8, Section 8.3). This generalised diagram is shown in Fig. 18.10. Also shown on that diagram is the saturation line for water plotted in nondimensional form. For a gas to be cooled using the Joule–Thomson effect, it is necessary that its state lies in the region shown on Fig. 18.10. Consideration of Table 18.1 shows that for oxygen and nitrogen at atmospheric temperature the values of reduced temperature are 2.10 and 2.38 respectively. Hence, these gases can both be liquefied at pressures up to $8p_c$, i.e. approximately 400 and 270 bar respectively. However, hydrogen at atmospheric temperature has a T_R value of 10, and lies outside the range of the Joule–Thomson effect. To be able to liquefy hydrogen by this method, it is necessary to precool it by using another fluid, e.g. liquid nitrogen when the value of T_R could become as low as 4.2, which is well within the range of inversion temperatures.

18.2.3 LINDE LIQUEFACTION PLANT

Many gases are liquefied using the Joule–Thomson effect. This approach is embodied in the Linde liquefaction process, and a schematic of the equipment is shown in Fig. 18.11(a), while the thermodynamic processes are depicted in Fig. 18.11(b). The Linde process is similar to a refrigerator

**FIGURE 18.10**

Inversion region in terms of reduced pressure ($p_R = p/p_c$) and reduced temperature ($T_R = T/T_c$). Note the saturation line.

operating on a vapour compression cycle (i.e. the typical refrigeration cycle), except that it includes a heat exchanger to transfer energy equal to Q_A and Q_B from the high-temperature working fluid to that which has already been cooled through throttling processes. The two throttling processes depicted in Fig. 18.11(a) both bring about cooling through the Joule–Thomson effect. The operating processes in the Linde plant will now be described: it will be assumed that the plant is already operating in steady state and that a supply of liquefied gas exists. The gas is supplied to a compressor at state 1 and make-up gas is supplied at state 11, which is the same as state 1. This is then compressed to a high, supercritical pressure (which might be hundreds of atmospheres) by a multistage reciprocating compressor with interstage cooling. The gas finally reaches state 2, and it is then passed through a heat exchanger which cools it to state 3. At this point it is throttled for the first time, and is cooled by the Joule–Thomson effect to state 4 and passed into a receiver. Some of the gas entering the receiver is passed back to the compressor via the heat exchanger, and the remainder is passed through a second throttle until it achieves state 6. At this stage it is in the liquid–vapour region of the state diagram, and liquid gas can be removed at state 9. The yield of liquid gas is y , defined by the quality of state point 6 on the T – s diagram.

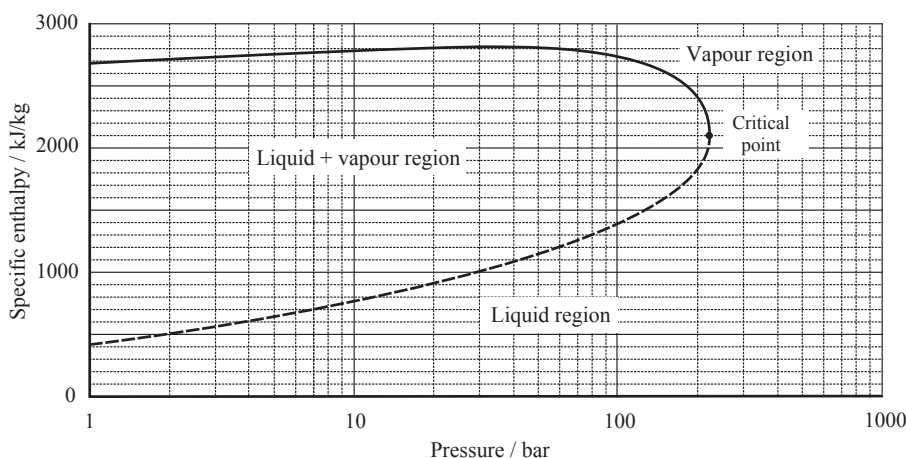
18.2.4 INVERSION POINT ON p – v – T SURFACE FOR WATER

The Joule–Thomson effect for water was met early in the study of thermodynamics (see Chapter 1, Section 1.5.8.3.2*). It was shown that the quality (dryness fraction) of water vapour could be increased by passing the wet vapour through a throttle. This process is an isenthalpic one in which the pressure decreases. The liquid–vapour boundary for water is shown in Fig. 18.12, and it can be seen that the

*<http://booksite.elsevier.com/9780444633736/>



enthalpy of the vapour peaks at a value of about 2800 kJ/kg. If water vapour at 20 bar, with an enthalpy of 2700 kJ/kg is expanded through a throttle then its quality increases; this means that it would not be possible to liquefy the water vapour by the Joule–Thomson effect, and hence this point must be below the minimum inversion temperature. Using the van der Waals relationship and substituting for the critical temperature gives $\bar{T}_i = 0.75 \times T_c = 212^\circ\text{C}$. This is equivalent to a pressure of about 20 bar, which is close to that defining the maximum enthalpy on the saturation line. This point of minimum inversion temperature can also be seen on the Mollier (h – s) diagram for steam, and is where the saturation curve peaks in enthalpy value. If the pressure was, say, 300 bar and the enthalpy was 2700 kJ/kg then an isenthalpic expansion would result in the gas becoming wetter, and liquefaction could occur.

**FIGURE 18.12**

Variation of enthalpy on the saturated liquid and vapour lines with pressure for steam.

EXAMPLE

(based on Haywood (1980))

A simple Linde liquefaction plant is shown in Fig. 18.13. This is similar to that in Fig. 18.11 except that the liquefaction takes place in a single process, and the cascade is omitted. The plant is used to liquefy air, which is fed to the compressor at 1 bar and 17 °C, and compressed isothermally to 200 bar. The compressed air then transfers heat in a counterflow heat exchanger, which has no external heat losses or friction, with the stream leaving the flash chamber, and the inlet temperature of the hot stream equals the outlet temperature of the cold stream. Using the table of properties for air at low temperatures and high pressures, Table 18.2, and taking the dead state conditions for energy as 1 bar and 290 K, evaluate

1. the yield of liquid air per kg of compressed fluid;
2. the temperature of the compressed air before the Joule–Thomson expansion process;
3. the minimum work required per kg of liquid air;
4. the actual work required per kg of liquid air;
5. the rational efficiency of the plant and the irreversibilities introduced by the heat exchanger and the throttle.

Considering the heat exchanger: since it is adiabatic

$$H_2 - H_3 = H_7 - H_6 \quad (18.30)$$

Substituting for specific enthalpies in Eqn (18.30) gives

$$m_2(h_2 - h_3) = m_6(h_7 - h_6) \quad (18.31)$$

Now

$$m_6 = m_2(1 - y) \quad (18.32)$$

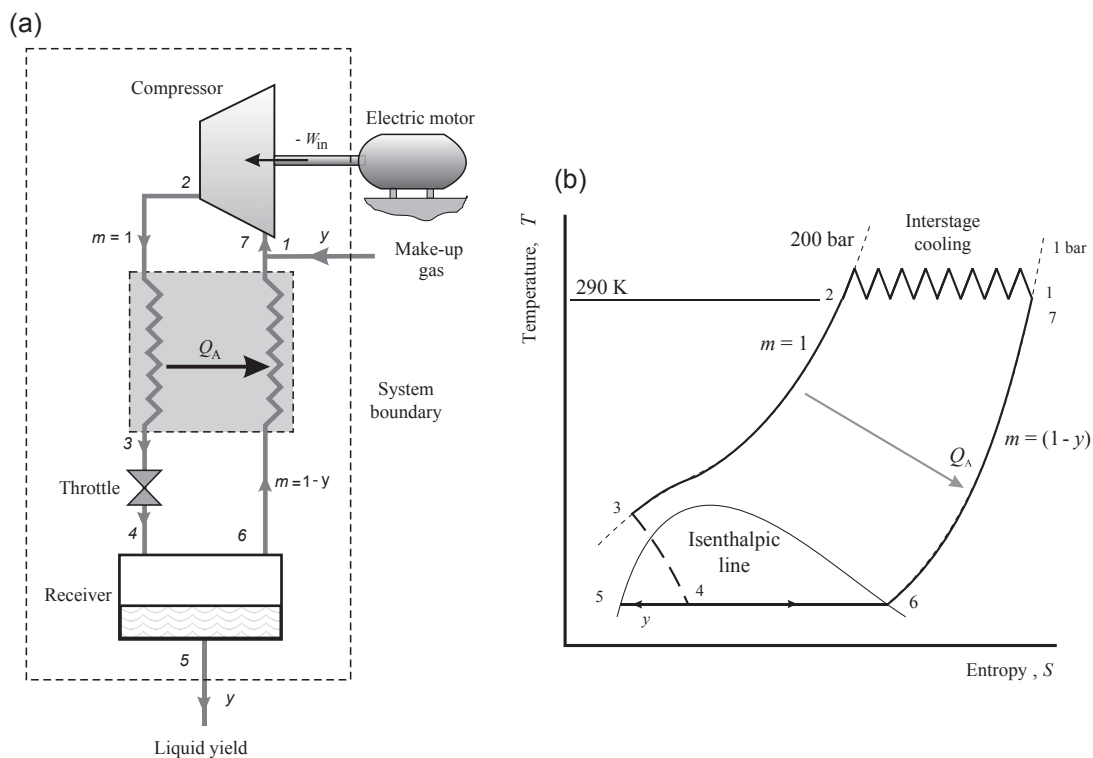


FIGURE 18.13

Simplified Linde gas-liquefaction plant. (a) Schematic diagram of simplified plant; (b) T - s diagram for liquefaction process.

1. yield of liquid per kg of compressed fluid

At point 1, $p_1 = 1\text{ bar}$; $T_1 = 290\text{ K}$; $h_1 = 12097\text{ kJ/kmol}$; $s_1 = 111.63\text{ kJ/kmol K}$

at point 2, $p_2 = 200\text{ bar}$; $T_2 = 290\text{ K}$; $h_2 = 11025\text{ kJ/kmol}$; $s_2 = 64.09\text{ kJ/kmol K}$

and hence

$$h_2 - h_3 = (1 - y)(h_7 - h_6), \quad (18.33)$$

giving $h_3 = h_2 - (1 - y)(h_7 - h_6)$

The process from 3 to 4 is isenthalpic, and is a Joule–Thomson process, thus

$$h_4 = h_3 \quad (18.34)$$

But

$$h_4 = x_4 h_g + (1 - x_4) h_f = (1 - y) h_6 + y h_5 \quad (18.35)$$

Table 18.2 Properties of air (based on Haywood, 1972)

Pressure (Atmosphere)	Temperature T_s (K)	Enthalpy (kJ/kmol)		Entropy (kJ/kmol K)		
		h_f	h_g	s_f	s_g	
1	81.7	0	5942	0.00	74.00	
5	98.5	917	6249	10.33	65.09	
10	108.1	1537	6284	16.24	60.55	
20	119.8	2506	6127	24.51	54.93	
30	127.8	3381	5760	31.17	49.87	
35	131.1	3884	5433	35.08	46.92	
37.66	(T_c) 132.5	4758	4758	41.39	41.39	
Properties of air on the saturated liquid and saturated vapour lines						
Pressure (Atmospheres)	1	30	40	50	200	400
Temperature (K)						
90	h 6190 s 76.9					
100	h 6493 s 80.09					
110	h 6795 s 82.97					
120	h 7092 s 85.53	2343	2187	2114	2086	
125	h 7243 s 86.78	22.85	21.38	20.48	15.3	
130	h 7393 s 87.96	2994	2719	2595	2428	
135	h 7541 s 89.09	28.14	25.69	24.41	18.11	
140	h 7691 s 90.16	5976	3405	3159	2770	
145	h 7842 s 91.20	51.54	31.07	28.81	20.8	
150	h 7993 s 92.28	6355	4816	3847	3111	
160	h 8290 s 94.2	54.44	41.74	33.99	23.38	
170	h 8582 s 95.95	6664	6048	4698	3451	
180	h 8877 s 97.62	56.66	50.68	40.19	25.86	
		6928	6468	5597	3789	
		58.52	53.63	46.54	28.24	
		7168	6786	6231	4123	
		60.14	55.77	50.85	30.51	
		7602	7309	6974	4779	4944
		62.94	59.15	55.65	34.75	29.98
		7995	7761	7509	5409	5439
		65.31	61.90	58.89	38.57	32.98
		8365	8168	7966	6006	5915
		67.42	64.24	61.52	41.98	35.87

Table 18.2 Properties of air (based on Haywood, 1972)—cont'd

Pressure (Atmospheres)	1	30	40	50	200	400
190	<i>h</i> 9172	8718	8546	8380	6583	6390
	<i>s</i> 99.21	69.33	66.16	63.75	45.21	38.44
200	<i>h</i> 9464	9056	8909	8761	7116	6858
	<i>s</i> 100.7	71.07	68.02	65.69	47.93	40.84
250	<i>h</i> 10925	10671	10581	10491	9427	9074
	<i>s</i> 107.3	78.27	75.61	73.44	58.28	50.73
290	<i>h</i> 12097	11912	11848	11784	11025	10738
	<i>s</i> 111.63	82.79	80.2	78.14	64.09	56.75
300	<i>h</i> 12364	12212	12154	12094	11405	11133
	<i>s</i> 112.6	83.91	81.34	79.28	65.52	58.23

Properties of superheated air at low temperatures and high pressures.
h: kJ/kmol.
s: kJ/kmol K.
m_w: = 28.9.

Combining Eqns (18.33) and (18.34) gives

$$y = \frac{h_2 - h_7}{h_7 - h_5} = \frac{12097 - 11025}{12097 - 0} = 0.08862 \quad (18.36)$$

Hence, the yield of liquid air per kg of compressed air is 0.08862 kg.

2. the temperature before the Joule–Thomson process

This is the temperature of the gas at point 3. From Eqns (18.34) and (18.35)

$$\begin{aligned}
 h_3 = h_4 &= x_4 h_g + (1 - x_4) h_f = (1 - y) h_6 + y h_5 \\
 &= (1 - 0.08862) \times 5942 = 5415 \text{ kJ/kmol}
 \end{aligned} \quad (18.37)$$

This value of enthalpy at 200 bar is equivalent to a temperature of 170 K.

3. minimum work required per kg liquid yield

Consideration of the control system in Fig. 18.13 shows that only three parameters cross the system boundary; these are the make-up gas, the liquid yield, and the work input to the compressor. Hence, the minimum work required to achieve liquefaction of the gas is

$$\widetilde{W}_{\text{net}} = y(b_1 - b_5), \text{ giving the work per unit mass of liquid as } \widetilde{w}_{\text{net}} = \frac{\widetilde{W}_{\text{net}}}{y} = b_1 - b_5 \quad (18.38)$$

In this case $b_5 = 0$ because point 5 (the liquid point at 1 bar) was chosen as the datum for properties, hence

$$\widetilde{w}_{\text{net}} = h_1 - T_0 s_1 - 0 = 12097 - 290 \times 111.63 = -20275 \text{ kJ/kmol liquid}$$

$$= \frac{-20275}{28.9} = -701.6 \text{ kJ/kg liquid}$$

4. work required per liquid yield

The compression process is an isothermal one, and hence the work done is

$$w = p_1 v_1 \ln \frac{v_2}{v_1} = -p_1 v_1 \ln \frac{p_2}{p_1} = -\Re T_1 \ln \frac{p_2}{p_1} \quad (18.39)$$

Substituting the values gives

$$\begin{aligned} w &= -\Re T_1 \ln \frac{p_2}{p_1} = -8.3143 \times 290 \times \ln \frac{200}{1} = -12775 \text{ kJ/kmol gas} \\ &= \frac{-12775}{28.9} = -442 \text{ kJ/kg gas} = \frac{-442}{0.08863} = -4987 \text{ kJ/kg liquid} \end{aligned}$$

5. rational efficiency

The rational efficiency of the plant is defined as

$$\eta_R = \frac{\widetilde{w}_{\text{net}}}{w} = \frac{-701}{-4987} = 0.1406 \quad (18.40)$$

Hence, the plant is only 14.1% as efficient as it could be if all the energy transfers were reversible. It is instructive to examine where the irreversibilities occur.

18.2.4.1 The heat exchanger

The irreversibility of the heat exchanger is

$$\begin{aligned} I_{\text{HE}} &= (1 - y)(b_7 - b_6) - (b_2 - b_3) \\ &= 0.91137 \times \{-20275 - (-15518)\} - \{-7561 - (-5776)\} \\ &= -2550 \text{ kJ/kmol gas} \end{aligned}$$

This is equivalent to 20.0% of the work required to compress the gas.

18.2.4.2 The throttle to achieve liquefaction

The irreversibility of the throttle is

$$I_{\text{throttle}} = b_4 - b_3 = 0.91137 \times (-15518) - (-5776) = -8366 \text{ kJ/kmol gas}$$

This is equivalent to 65.5% of the work used to compress the gas.

Hence, the work required to liquefy the gas is

$$w = \widetilde{w}_{\text{net}} + I_{\text{HE}} + I_{\text{throttle}}$$

18.3 CONCLUDING REMARKS

It has been shown that gases can be liquefied in a number of ways. Gases which are liquids at temperatures close to ambient can be liquefied by cooling in a simple refrigeration system. Carbon dioxide, which cannot be maintained as a liquid at ambient pressure, is made into dry ice which is not in equilibrium at room temperature and pressure.

If it is necessary to achieve extremely low temperatures to bring about liquefaction, the Joule–Thomson effect is employed. It is possible to analyse such liquefaction plant using equilibrium thermodynamics and suitable equations of state. The efficiency of liquefaction plant has been calculated and the major influences of irreversibilities in the processes have been illustrated.

18.4 PROBLEMS

P18.1 Show that the Joule–Thomson coefficient, μ , is given by

$$\mu = \frac{1}{c_p} \left(T \left(\frac{\partial v}{\partial T} \right)_p - v \right).$$

Hence or otherwise show that the inversion temperature (T_i) is

$$T_i = \left(\frac{\partial T}{\partial v} \right)_p v.$$

The equation of state for air may be represented by

$$p = \frac{\Re T}{v_m - 0.0367} - \frac{1.368}{v_m^2}$$

where p = pressure (bar), T = temperature (K), and v_m = molar volume (m^3/kmol).

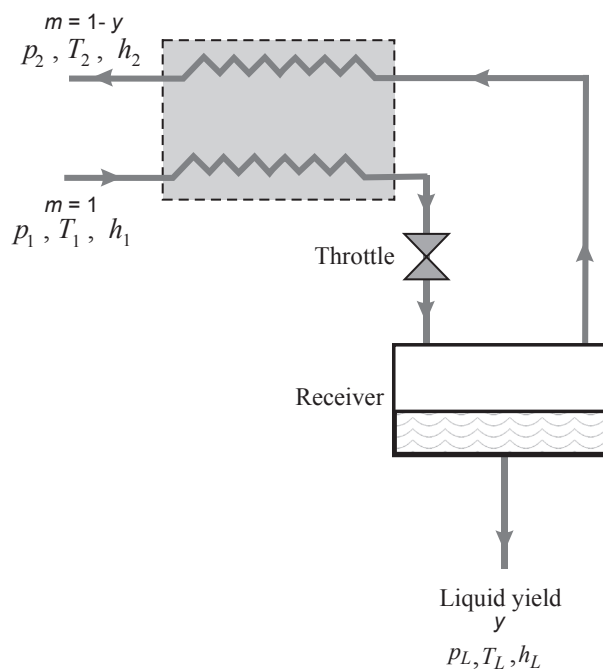
Determine the maximum and minimum inversion temperature and the maximum inversion pressure for air.

[896 K; 99.6 K; 339 bar]

P18.2 The last stage of a liquefaction process is shown in diagrammatic form in Fig. P18.2. Derive the relationship between p_1 and T_1 for the maximum yield of liquid at conditions p_L , T_L , h_L for a gas obeying the state equation

$$\left(p + \frac{1.368}{v_m^2} \right) (v_m - 0.0367) = \Re T$$

where p is pressure (bar), v_m is the molar volume (m^3/kmol), and T is temperature (K).

**FIGURE P18.2**

Final stage of liquefaction plant.

Calculate the pressure for maximum yield at a temperature of 120 K.

$$\left[p = \frac{a}{b^2} \left(1 - \sqrt{\frac{\Re b T_i}{2a}} \right) \left(3 \sqrt{\frac{\Re b T_i}{2a}} - 1 \right); 62.8 \text{ bar} \right]$$

P18.3 The equation of state for a certain gas is

$$v_m = \frac{\Re T}{p} + \frac{k}{\Re T}$$

where k is a constant. Show that the variation of temperature with pressure for an isenthalpic process from 1 to 2 is given by

$$T_1^2 - T_2^2 = -\frac{4k}{c_p \Re} (p_1 - p_2)$$

If the initial and final pressures are 50 bar and 2 bar respectively and the initial temperature is 300 K, calculate

- the value of the Joule–Thomson coefficient at the initial state, and
- the final temperature of the gas, given that

$$k = -11.0 \text{ kJ m}^3/(\text{kmol})^2$$

$$c_{p,m} = 29.0 \text{ kJ/kmol K.}$$

$$[3.041 \times 10^7 \text{ m}^3 \text{ K/J; } 298.5 \text{ K}]$$

P18.4 A gas has the equation of state

$$\frac{pv_m}{RT} = 1 + Ap(T^3 - 9.75T_cT^2 + 9T_c^2T) + Bp^2T$$

where A and B are positive constants and T_c is the critical temperature. Determine the maximum and minimum inversion temperatures, expressed as a multiple of T_c .

$$[6T_c; 0.5T_c]$$

P18.5 A gas has the equation of state

$$\frac{pv_m}{RT} = 1 + Np + Mp^2$$

where N and M are functions of temperature. Show that the equation of the inversion curve is

$$p = -\frac{dN}{dT} \bigg/ \frac{dM}{dT}$$

If the inversion curve is parabolic and of the form

$$(T - T_0)^2 = 4a(p_0 - p)$$

where T_0 , p_0 and a are constants, and if the maximum inversion temperature is five times the minimum inversion temperature, show that $a = \frac{T_0^2}{9p_0}$ and give possible expressions for N and M .

$$\left[M = T; N = -p_0T + \frac{(T - T_0)^3}{12a} + c \right]$$

P18.6 In a simple Linde gas-liquefaction plant (see Fig. 18.13), air is taken in at the ambient conditions of 1 bar and 300 K. The water-jacketed compressor delivers the air at 200 bar and 300 K and has an *isothermal efficiency* of 70%. There is zero temperature difference at the warm end of the regenerative heat exchanger (i.e. $T_2 = T_7$). Saturated liquid air is delivered at a pressure of 1 bar. Heat leakages into the plant and pressure drops in the heat exchanger and piping can be neglected.

Calculate the yield of liquid air per unit mass of air compressed, the work input per kilogram of air liquefied, and the *rational efficiency* of the liquefaction process.

$$[7.76\%; 8.39 \text{ MJ/kg; } 8.84\%].$$

PINCH TECHNOLOGY

19

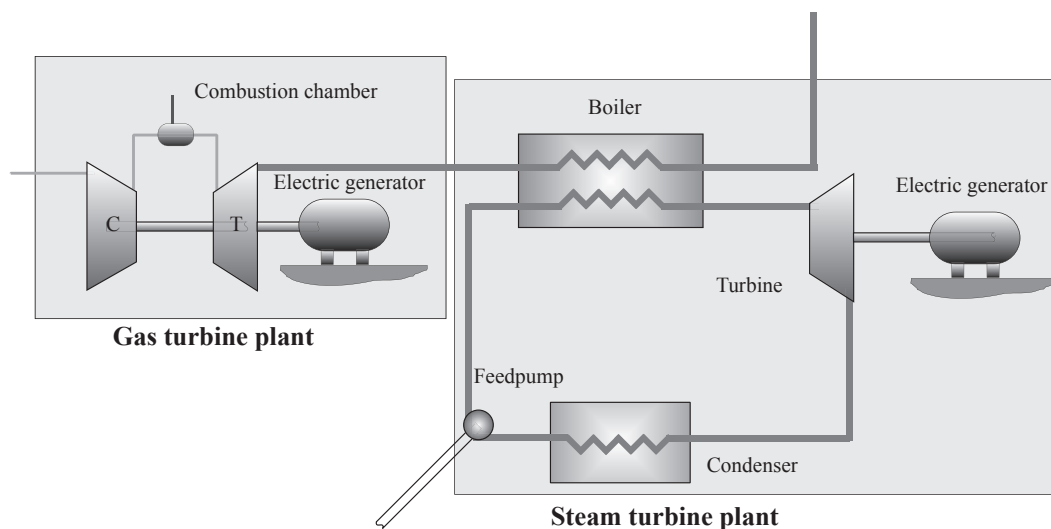
In recent years, a new technology for minimising the energy requirements of process plant has been developed: this has been named *pinch technology* or *process integration* by its major proponent, Linnhoff (Linnhoff and Senior (1983); Linnhoff and Turner (1981); Smith (1995)). Process plant, such as oil refineries or major chemical manufacturing plant, requires that heating and cooling of the feed stock take place as the processes occur. Obviously it would be beneficial to use the energy from a stream which requires cooling to heat another which requires heating; in this way the energy which has to be supplied from a high temperature source (or utility) is reduced, and the energy which has to be rejected to a low temperature sink (or utility) is also minimised. Both of these external transfers incur a cost in running the plant. Pinch technology is an approach which provides a mechanism for automating the design process, and *minimising the external heat transfers*.

Pinch situations also occur in power generation plant; for example, in a combined cycle gas turbine (CCGT) plant (see Fig. 19.1) energy has to be transferred from the gas turbine exhaust to the working fluid in the steam turbine. A T - s diagram of a CCGT plant is shown in Fig. 19.2, where the heat transfer region is shown: the pinch is the closest approach in temperature between the two lines. It is defined as the minimum temperature difference between the two streams for effective heat transfer, and is due to the difference in the properties of the working fluids during the heat transfer process (viz. the exhaust gas from the gas turbine cools down as a single phase but the water changes phase when it is heated) – this limits the amount of energy that can be taken from the hot fluid. The heat transfer processes are shown on a Temperature – Enthalpy (T – H) transfer diagram in Fig. 19.3, where the pinch is obvious.

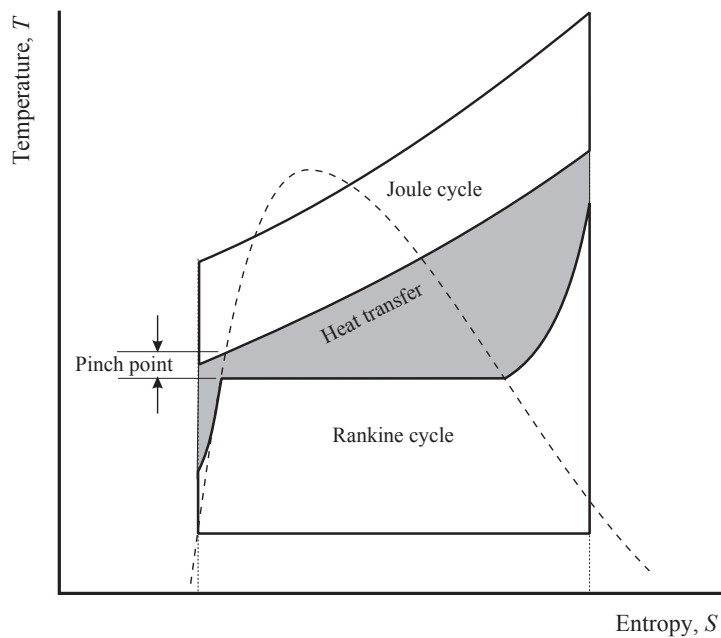
Perhaps the easiest way of gaining an understanding of pinch techniques is to consider some simple examples.

19.1 HEAT TRANSFER NETWORK WITHOUT A PINCH PROBLEM

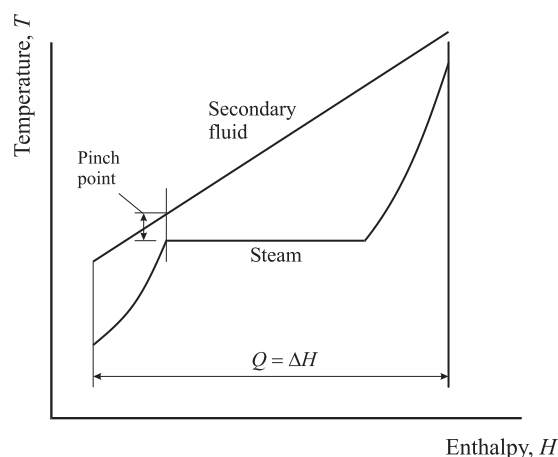
This example has a total of seven streams, three hot and four cold, and it is required to use the heating and cooling potential of the streams to minimise the heat transfer from high-temperature utilities, and the heat transfer to low-temperature utilities. The parameters for the streams involved in the processes are given in Table 19.1. The supply temperature, T_S , is the initial temperature of the stream, and the target temperature, T_T , is the target final temperature that must be achieved by heat transfer. The heat flow capacity, mC , is the product of the mass flow and the specific heat of the particular stream, and the heat load is the amount of energy that is transferred to or from the streams.

**FIGURE 19.1**

Schematic diagram of combined cycle gas turbine (CCGT) power plant.

**FIGURE 19.2**

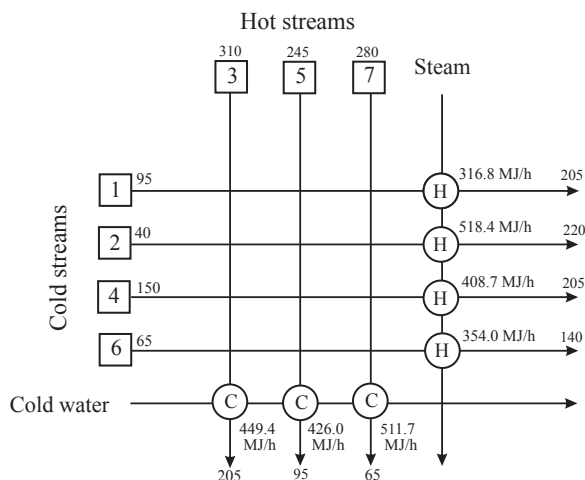
Temperature – entropy ($T-s$) diagram for a (combined cycle gas turbine) CCGT.

**FIGURE 19.3**

Temperature – enthalpy ($T - H$) diagram for a (combined cycle gas turbine) CCGT.

Stream No	Stream Type	Supply Temperature $T_S/(^{\circ}\text{C})$	Target Temperature $T_T/(^{\circ}\text{C})$	Heat Flow Capacity $mC/(\text{MJ/hK})$	Heat Load $Q/(\text{MJ/h})$
1	Cold	95	205	2.88	316.8
2	Cold	40	220	2.88	518.4
3	Hot	310	205	4.28	–449.4
4	Cold	150	205	7.43	408.7
5	Hot	245	95	2.84	–426.0
6	Cold	65	140	4.72	354.0
7	Hot	280	65	2.38	–511.7

In this case, there are three streams of fluid which require cooling (the hot streams) and four streams of fluid which require heating (the cold streams). The simplest way of achieving this is cool the hot streams by transferring heat directly to a cold water supply, and to heat the cold streams by means of a steam supply; this approach is shown in Fig. 19.4. This means that the hot utility (the steam supply) has to supply 1597.9 MJ of energy, while the cold utility (a cold water supply) has to remove 1387.1 MJ of energy. Both of these utilities are a cost on the process plant. The steam has to be produced by burning a fuel, and use of the cold water will be charged by the water authority. In reality a *minimum net heat supply* of $1597.9 - 1387.1 = 210.8$ MJ/h could achieve the same result, if it were possible to transfer all the energy available in the hot streams to the cold streams. This problem will now be analysed.

**FIGURE 19.4**

Direct heat transfer between the fluid streams and the hot and cold utilities.

If heat is going to be transferred between the hot and cold streams there must be a temperature difference between the streams: assume in this case that the minimum temperature difference ($\delta T_{\min}$) is 10 °C.

The method of tackling this problem proposed by Linnhoff and Turner (1981) is as follows.

19.2 STEP 1: TEMPERATURE INTERVALS

Evaluate the temperature intervals defined by the ‘interval boundary temperatures’. These can be defined in the following way: the unadjusted temperatures of the cold streams can be used, and the hot stream temperatures can be adjusted by subtracting $\delta T_{\min}$ from the actual values. In this way, the effect of the minimum temperature difference has been included in the calculation. This results in Table 19.2.

The parameters defining the streams can also be shown on a diagram of temperature against heat load (enthalpy transfer), see Fig. 19.5. This diagram has been evaluated using the data in Table 19.2, and is based on the unadjusted temperatures. The hot stream line is based on the *composite* temperature – heat load data for the hot streams, and is evaluated using Eqn (19.2); the cold stream line is evaluated by applying the same equation to the cold streams. It can readily be seen that the two lines are closest at the temperature axis, when they are still 25 °C apart: this means that there is no ‘pinch’ in this example because the temperature difference at the pinch point is greater than the minimum value allowable. Hence, the problem reduces to transferring energy from the hot streams to the cold streams, and finally adding 210.8 MJ/h from a hot utility. The mechanism for allocating the energy transfers will now be introduced.

Having defined the temperature intervals it is possible to consider the problem as shown in Fig. 19.6. The energies flowing into and out of the combined systems, Q_h and Q_c are those which have

Stream No	Stream Type	Supply Temperature $T_S/(^{\circ}\text{C})$	Target Temperature $T_T/(^{\circ}\text{C})$	Adjusted Temperatures		Order
1	Cold	95	205	95	205	T_9 T_5
2	Cold	40	220	40	220	T_{13} T_4
3	Hot	310	205	300	195	T_1 T_6
4	Cold	150	205	150	205	T_7 Duplicate
5	Hot	245	95	235	85	T_3 T_{10}
6	Cold	65	140	65	140	T_{11} T_8
7	Hot	280	65	270	55	T_2 T_{12}

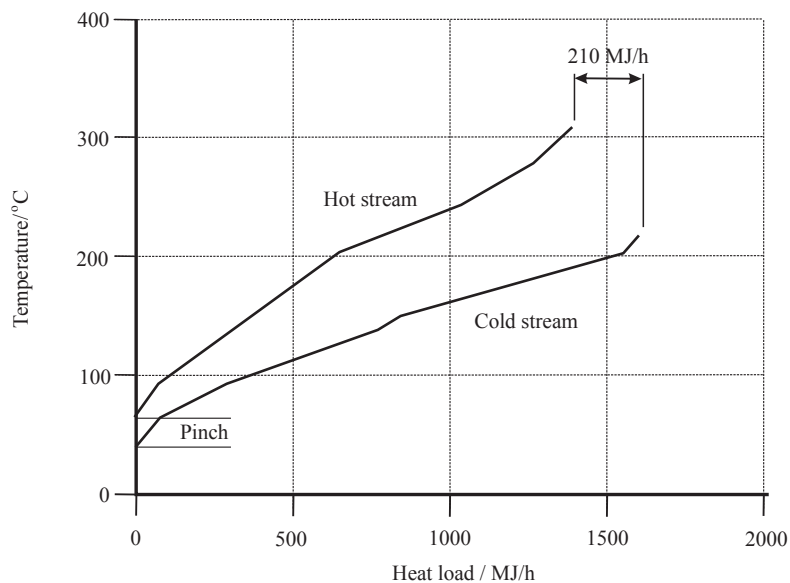
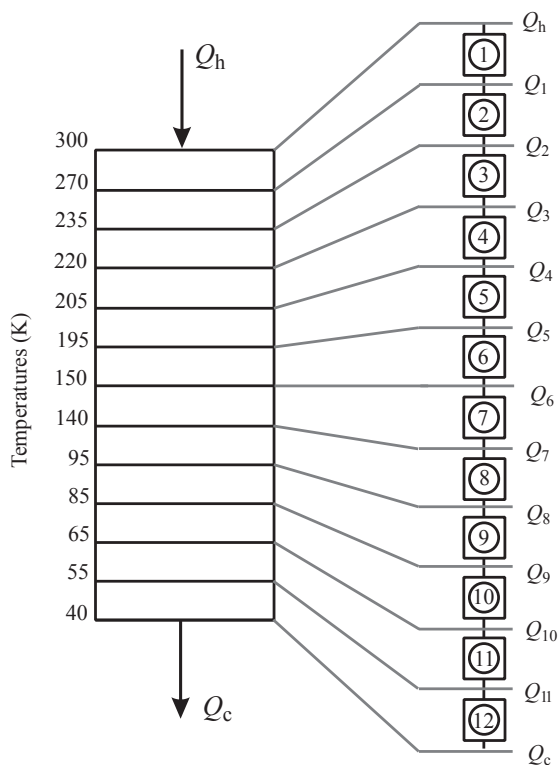


FIGURE 19.5

Temperature – heat load diagram.

**FIGURE 19.6**

Temperature intervals for heat transfer network.

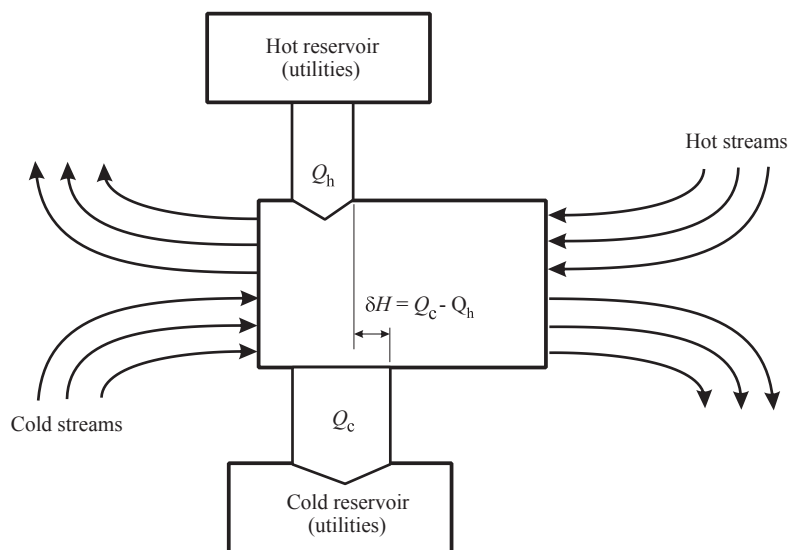
to be supplied by or lost to the external reservoirs respectively. It is also apparent that the difference between these values is the difference between the enthalpies of the hot and cold streams, i.e.

$$Q_c - Q_h = \delta H \quad (19.1)$$

Consideration will show that δH is constant, because the difference between the enthalpies of the hot and cold streams is constant, and this means that any additional energy added from the high-temperature supplies must be compensated by an equal amount of energy being rejected to the low-temperature sinks: hence energy will have just flowed wastefully through the overall system. The heat transfer network can be shown schematically as in Fig. 19.7. The heat flows through each of the temperature intervals can be evaluated as shown in the next step.

19.3 STEP 2: INTERVAL HEAT BALANCES

Table 19.2 includes the effect of the minimum temperature difference between the streams, $\delta T_{\min}$, and hence the intervals have been established so that full heat transfer is possible between the hot and cold streams. It is now necessary to apply the First Law to examine the enthalpy balance between the streams, when

**FIGURE 19.7**

Overall energy balance for heat transfer network.

$$\delta H_i = \left(\sum_{\text{Hot}} (mC)_{h,i,i+1} - \sum_{\text{Cold}} (mC)_{c,i,i+1} \right) (T_i - T_{i+1}) \quad (19.2)$$

where

i = initial temperature of the interval

$i + 1$ = final temperature of the interval

Applying this equation to this example results in the heat flows shown by the $\delta H = mC\delta T$ values in Fig. 19.8.

It can be seen from Fig. 19.8 that the individual heat transfers are positive (i.e. from the hot streams to the cold streams) in the first four intervals. In the fifth interval, the amount of energy required by the cold streams exceeds that available from the hot streams in that temperature interval, but the energy can be supplied from that available in the higher temperature intervals. However, by the eighth interval the demands of the cold streams exceed the total energy available from the hot streams, and it is at this point that the energy should be added from the hot utility because this will limit the temperature required in the hot utility. In reality, the 210.8 MJ could be provided from the hot utility at any temperature above 140 °C, but the higher the temperature of the energy the more will be the irreversibility of the heat transfer process. It is now useful to look at the way in which the heat can be transferred between the hot and cold streams.

The streams available for the heat transfer processes are shown in Fig. 19.9. First, it should be recognised that there is no heat transfer to the cold utility, and thus all the heat transfers from the hot

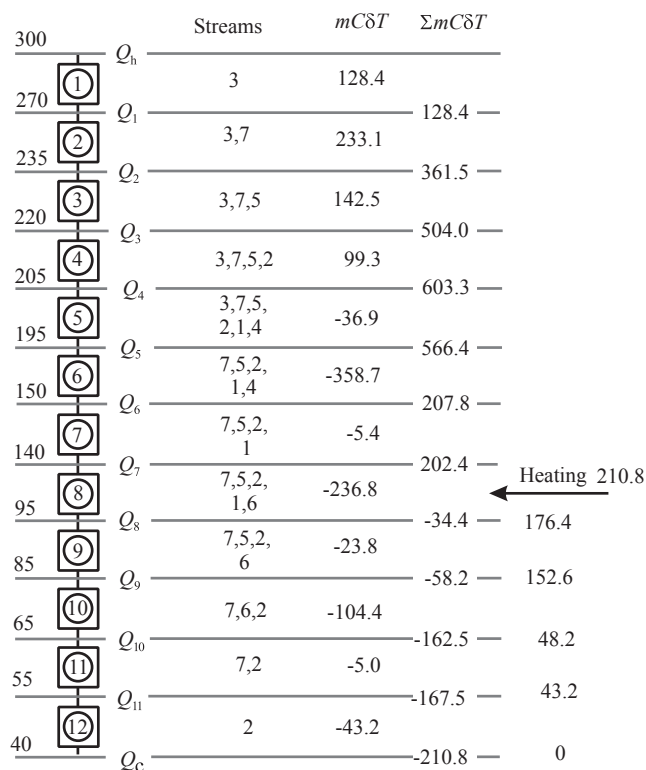


FIGURE 19.8

Heat flows.

streams must be to cold streams. This constrains the problem to ensure that there is always a stream cold enough to receive heat from the hot sources. This means that the temperature of stream 7 must be cooled to its target temperature of 65 °C by transferring heat to a colder stream: the only one available is stream 2. Hence, the total heat transfer from stream 7 is passed to stream 2: An energy balance shows that the temperature of stream 2 is raised to 218 °C, and there is a residual heat capacity of 6.7 MJ before the stream reaches its target temperature. In a similar manner, it is necessary for stream 5 to be matched to stream 6 because this is the only stream cold enough to bring its temperature down to 95 °C. In this way, it is possible to remove streams 6 and 7 from further consideration because they have achieved their target temperatures: Streams 2 and 5 must be left in the network because they still have residual energy before they achieve their targets. Fig. 19.9 can be modified to Fig. 19.10.

Streams 2 and 5 are represented in this diagram by their residual energies, and by the temperatures that were achieved in the previous processes. It is possible to cool streams 3 and 5 by transferring energy with either cold streams 1 or 4. The decision in this case is arbitrary, and for this case stream 3 will be matched with stream 4, and stream 5 will be matched with stream 1. This results in the heat transfers shown in Fig. 19.10, and by this stage streams 5 and 4 can be removed from further consideration. This results in another modified diagram, Fig. 19.11.

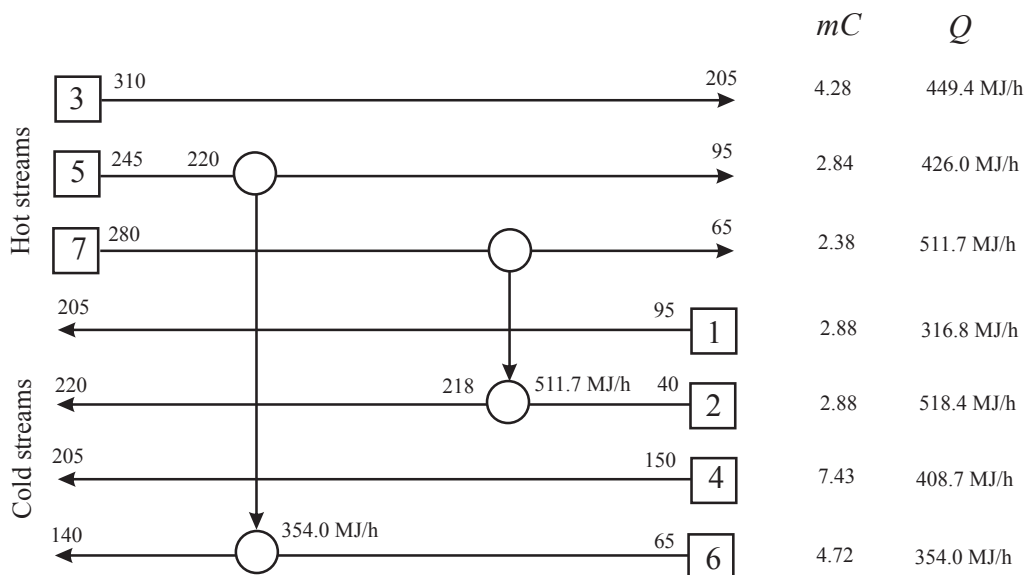


FIGURE 19.9

Initial heat transfer: heat transfer from streams 5 to 6, and 7 to 2.

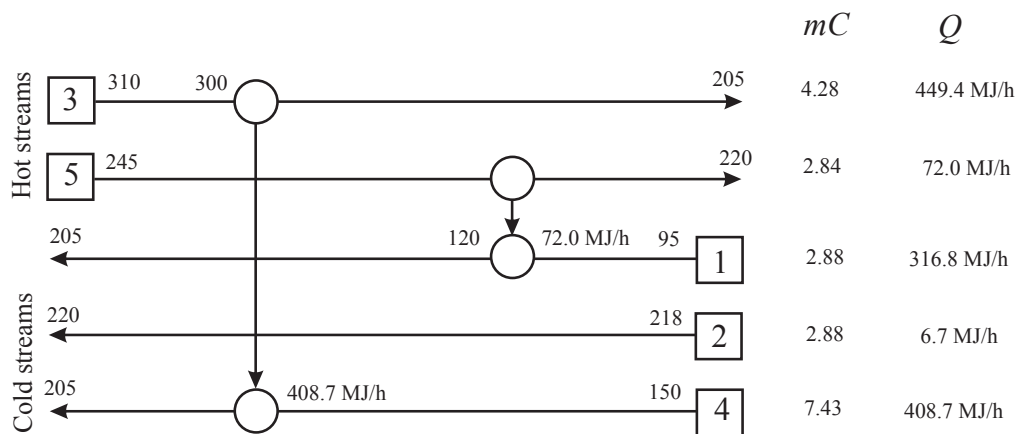


FIGURE 19.10

Removing the residuals for streams 2 and 5.

By this stage, it is necessary to consider adding the heat from the hot utility. In this case, the temperature at which this energy is added is relatively arbitrary, and the heat should be transferred at as low a temperature as possible. This is indicated by the 210.8 MJ heat transfer in Fig. 19.11.

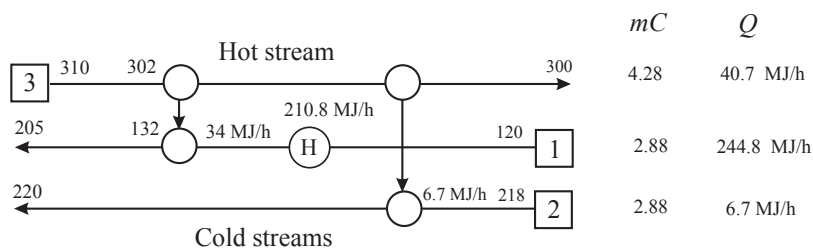


FIGURE 19.11

Completing the heat transfer network.

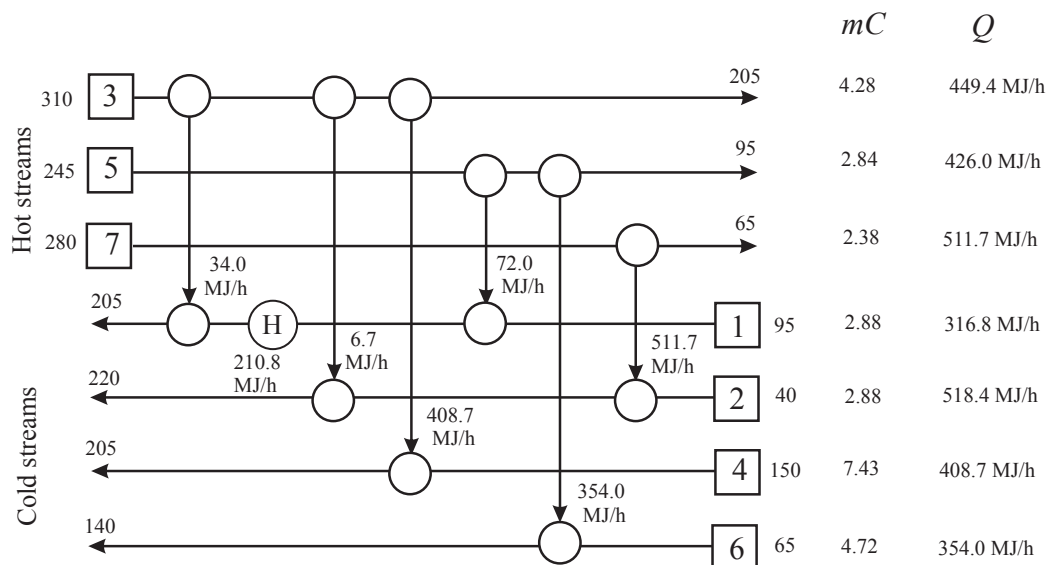


FIGURE 19.12

Composite diagram for heat exchange network.

The previous analysis has considered the problem in discrete parts, but it is now possible to combine all these subsections into a composite diagram, and this is shown in Fig. 19.12.

The diagram given in Fig. 19.12 suggests that seven heat exchangers are required, but the diagram is not the most succinct representation of the network problem, which is better displayed as shown in Fig. 19.13, which grows directly out of the original arrangement shown in Fig. 19.4.

This case was a relatively straightforward example of a heat exchanger network in which it was always relatively easy to match the streams, because there was always sufficient temperature difference to drive the heat transfer processes. The next example shows what happens when there is not sufficient temperature difference to drive the heat transfer processes.

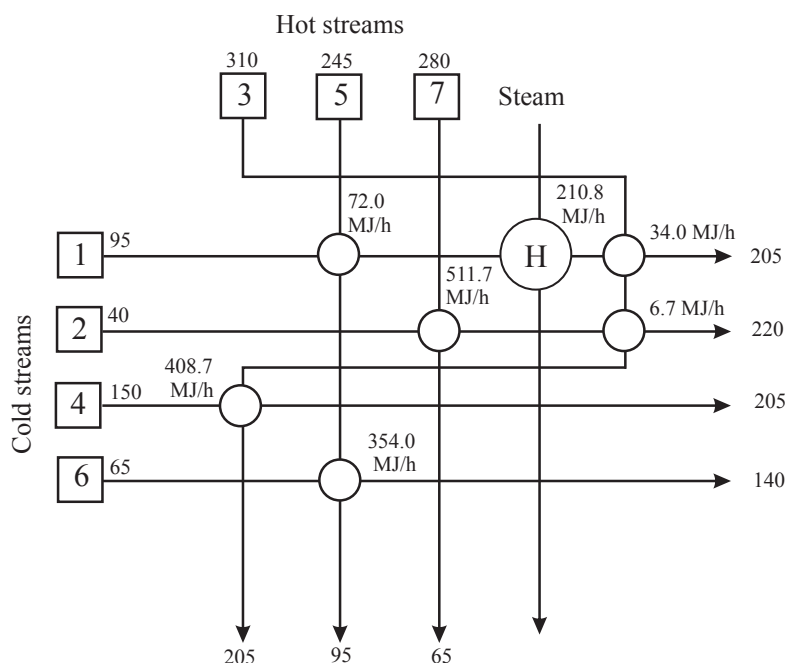


FIGURE 19.13

Diagram showing minimum number of heat exchangers to achieve heat transfer.

Table 19.3 Characteristics of Streams					
Process Stream		Supply Temperature, $T_S/(^{\circ}\text{C})$	Target Temperature $T_T/(^{\circ}\text{C})$	Heat Capacity Flowrate, $mC/(\text{MJ/hK})$	Heat Load $ mC(T_S - T_T) $ $/(\text{MJ/h})$
Number	Type				
1	Cold	50	110	2.0	120
2	Hot	130	70	3.0	180
3	Cold	80	115	4.0	140
4	Hot	120	55	1.5	97.5

19.4 HEAT TRANSFER NETWORK WITH A PINCH POINT

Consider there are four streams of fluid with the characteristics given in Table 19.3. Assume that the minimum temperature difference between any streams to obtain acceptable heat transfer is 5°C , i.e. $\delta T_{\min} = 5^{\circ}\text{C}$. This value of $\delta T_{\min}$ is referred to as the *pinch point* because it is the closest that the temperatures of the streams are allowed to come. The temperatures of the streams can be ordered in a manner similar to the first case, and the results of this are shown in Table 19.4.

Stream No	Stream Type	$T_S/(^{\circ}\text{C})$	$T_T/(^{\circ}\text{C})$	Adjusted Temperatures		Order
1	Cold	50	110	50	110	T_6 T_3
2	Hot	130	70	125	65	T_1 T_5
3	Cold	80	115	80	115	T_4 T_2
4	Hot	120	55	115	50	Duplicate Duplicate

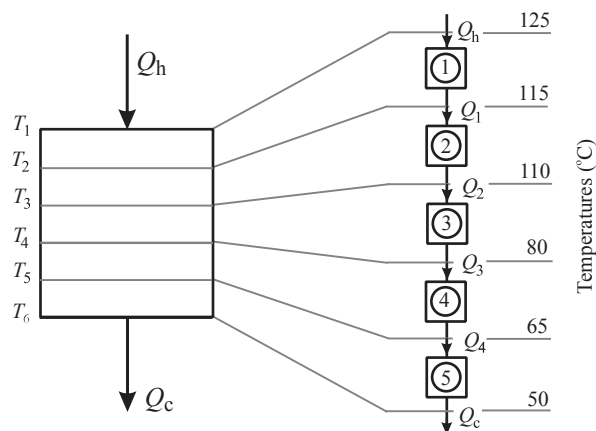


FIGURE 19.14

Temperature intervals for heat transfer network.

These temperature intervals can be depicted graphically as shown in Fig. 19.14. It can be seen that there are five intervals in this case, as opposed to the twelve in the first case.

It is now possible to draw the temperature – heat load diagram for this problem, and this is shown in Fig. 19.15. It can be seen that the basic cold stream is too close to the hot stream and there will not be sufficient temperature difference to drive the heat transfer processes. The modified cold stream line has been drawn after undertaking the following analysis, and does produce sufficient temperature difference at the pinch.

19.5 STEP 3: HEAT CASCADING

This step is an additional one to those introduced previously, and consideration will show why it comes about. Fig. 19.16 indicates the heat flows in the various intervals and, in the left-hand column of figures, shows that if the heat flow from the hot utility (or heat source) is zero then there will be a

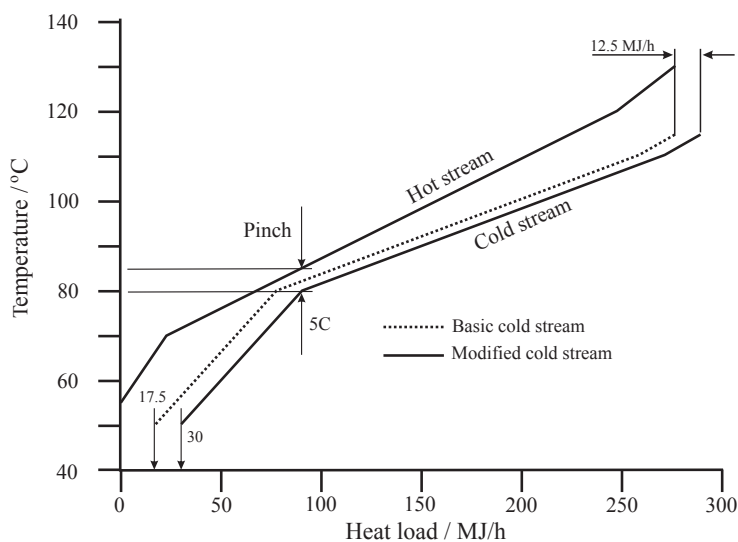


FIGURE 19.15

Temperature – heat load diagram, indicating pinch point.

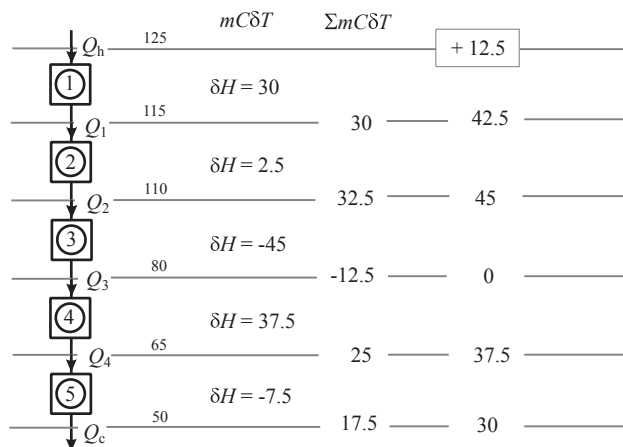


FIGURE 19.16

Temperature intervals and heat loading.

negative heat flow of -12.5 units in temperature interval 3 between 110°C and 80°C . Consideration will show that *this is impossible because it means that the heat will have been transferred against the temperature gradient*. Such a situation can be avoided if sufficient energy is added to the system to make the largest negative heat flow zero in this interval. The result of this is shown in the right-hand

column of figures in Fig. 19.16, which has been achieved by adding 12.5 units of energy to the system. It can be seen that in both cases the difference between Q_h and Q_c is 17.5 units of energy. If an energy balance is applied to the streams defined in Table 19.3 then

$$\begin{aligned}\sum \delta H_i &= 3 \times (130 - 70) + 1.5 \times (120 - 55) - 2 \times (110 - 50) - 4 \times (115 - 80) \\ &= 17.5\end{aligned}\quad (19.3)$$

Hence, as stated previously, the energies obey the steady flow energy equation for the system shown in Fig. 19.16.

There is now a point in the temperature range where the heat flow is zero: this point is called *the pinch*. In this example it is at 80 °C, which means that the pinch occurs at a cold stream temperature of 80 °C and a hot stream temperature of 85 °C. There are three important constraints regarding the pinch:

1. Do not transfer heat across the pinch. Any heat flow across the pinch results in the same amount of heat being added to every heat flow throughout the system, and hence increases Q_h and Q_c .
2. Do not use the cold sink above the pinch. If the system has been designed for minimised heat flow, it does not reject any heat from itself. (see Fig. 19.16, where the heat rejection has been made zero at the pinch.)
3. Do not use the hot source below the pinch. If the system has been designed for minimised heat flow, it does not absorb any heat below the pinch.

It is hence possible to reduce the problem into two parts: above the pinch and below the pinch, as shown in Fig. 19.17, which is a modification of Fig. 19.7.

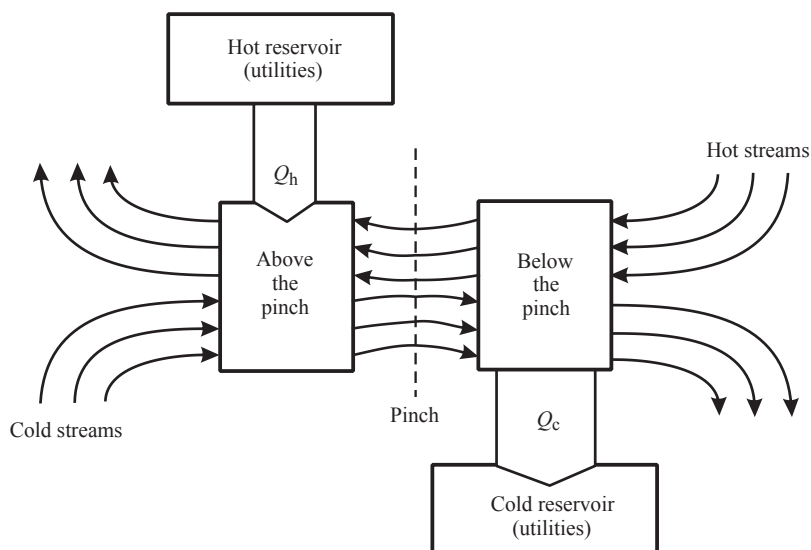


FIGURE 19.17

Breaking the problem at the pinch point.

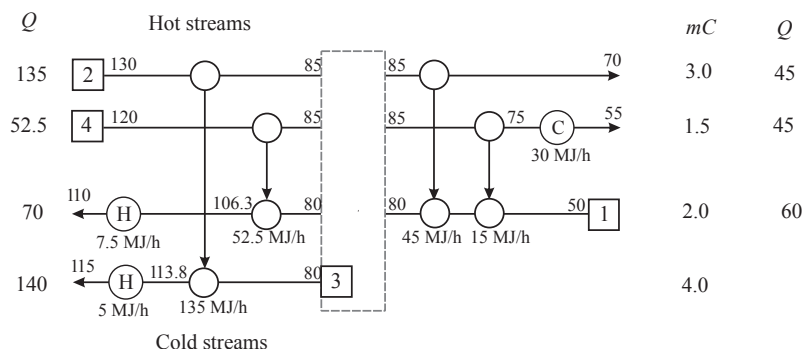


FIGURE 19.18

Hot and cold streams with pinch.

It is now necessary to break the problem at the pinch, and this results in Fig. 19.18, which is the equivalent of Fig. 19.9 for the first example.

Now the problem can be analysed, bearing in mind the restrictions imposed by the pinch point. This means that cooling to the utility stream is not allowable above the pinch, and hence the only transfer can be with the hot utility above the pinch. It is now necessary, as far as possible, to match the hot and cold streams above the pinch.

1. Consider stream 2 is matched with stream 1, and stream 4 is matched with stream 3. Then stream 2 can transfer 70 MJ/h to stream 1, and enable stream 1 to achieve its target temperature, while reducing its temperature to 106.7 °C. Also stream 4 can transfer its energy to stream 3, and this will raise the temperature of stream 3 to 93.1 °C. This shows that there is not sufficient energy available in these streams to achieve the target temperatures. The reason for this being an unsuitable approach is because the heat capacity flowrate for stream 1 above the pinch is greater than that of the cold stream above the pinch. Since both streams have the same temperature at the pinch point, then the high temperature of the cold stream would have to be higher than that of the hot stream to achieve an energy balance: this would result in an impossible heat transfer situation. Hence, for the result to be possible

$$mC_{\text{cold}} \geq mC_{\text{hot}} \quad (19.4)$$

above the pinch point.

2. If the alternative match is used, viz., stream 2 matched to stream 3, and stream 4 matched to stream 1, then the answer shown in Fig. 19.19 is obtained. The heat transfers are shown on the diagram. It can be seen that it is not possible to match the hot and cold streams either above or below the pinch. This means that utility heat transfers are required from the hot utility above the pinch, and heat transfers to the cold utility are required below the pinch. This proposal does obey inequality Eqn (19.4), and is hence acceptable.
3. It can be seen that, above the pinch point, energy has to be added to the system from the hot utility. This obeys the rules proposed above, and the total energy added is 12.5 MJ/h, which is in agreement with the value calculated in Fig. 19.16.

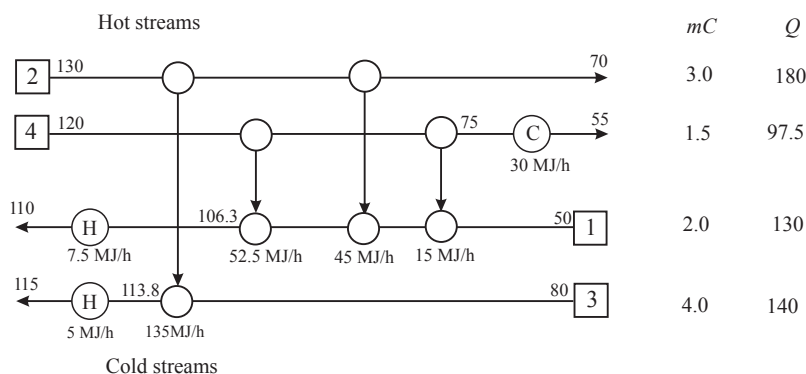


FIGURE 19.19

Composite diagram for heat transfer network in example 2.

4. Considering the heat transfers below the pinch, it can be seen that stream 1 can be heated by energy interchange with streams 2 and 4: neither stream has sufficient capacity alone to bring stream 1 to its target temperature. However, it is feasible to bring about the heating because

$$mC_{\text{hot}} \geq mC_{\text{cold}} \quad (19.5)$$

which is the equivalent of inequality Eqn (19.4) for the transfers below the pinch. In this case, it was chosen to transfer all the energy in stream because this results in a lower temperature for heat transfer to the cold utility. The 30 MJ/h transferred to the cold utility is in line with that calculated in Fig. 19.16.

These diagrams can now be joined together to give the composite diagram in Fig. 19.19.

The heat load against temperature diagram for this problem, before heat transfer from the utilities has been supplied, is shown in Fig. 19.15, and was discussed previously. It is now possible to consider the modified diagram, when it can be seen that the energy transfers have produced sufficient temperature difference to satisfy the constraints of the problem.

19.6 PROBLEMS

- P19.1** A process plant has two streams of hot fluid and two streams of cold fluid, as defined in Table P19.1. It is required to minimise the energy which must be transferred to hot and cold utilities by transferring energy between the streams. If the minimum temperature difference for effective heat transfer is 20 °C, design a network which achieves the requirement, and minimises the transfers to the utilities. Is there a pinch point in this problem, and at what temperature does it occur? Calculate the minimum heat transfers to and from the cold and hot utilities.

$$[105\text{ °C (cold stream)}; Q_{\text{H}_{\min}} = 90\text{ MJ/h}; Q_{\text{C}_{\min}} = 140\text{ MJ/h}]$$

Stream No	Stream Type	Supply Temperature $T_S/(^{\circ}\text{C})$	Target Temperature $T_T/(^{\circ}\text{C})$	Heat Flow Capacity $mC/(\text{MJ/hK})$
1	Hot	205	65	2.0
2	Hot	175	75	4.0
3	Cold	45	180	3.0
4	Cold	105	155	4.5

- P19.2** Some stream data have been collected from a process plant, and these are listed in Table P19.2. Assuming the minimum temperature difference between streams, $\Delta T_{\min} = 10^{\circ}\text{C}$
- calculate the data missing from Table P19.2;
 - analyse this data to determine the minimum heat supplied from the hot utility, the minimum heat transferred to the cold utility, and the pinch temperatures;
 - draw a schematic diagram of the heat transfer network.

Stream No	Stream Type	Supply Temperature $T_S/(^{\circ}\text{C})$	Target Temperature $T_T/(^{\circ}\text{C})$	Enthalpy Change, $\Delta H/(\text{kW})$	Heat Flow Capacity $mC/(\text{kW/K})$
1	Cold	60	180	?	3
2	Hot	180	40	?	2
3	Cold	30	130	220	?
4	Hot	150	40	440	?
5	Cold	60	80	40	?

[360 kW; 280 kW; 2.2 kW/K; 4.0 kW/K; 2.0 kW/K; $Q_{H_{\min}} = 60 \text{ kW}$; $Q_{C_{\min}} = 160 \text{ kW}$; $T_{C_{\text{pinch}}} = 140^{\circ}\text{C}$]

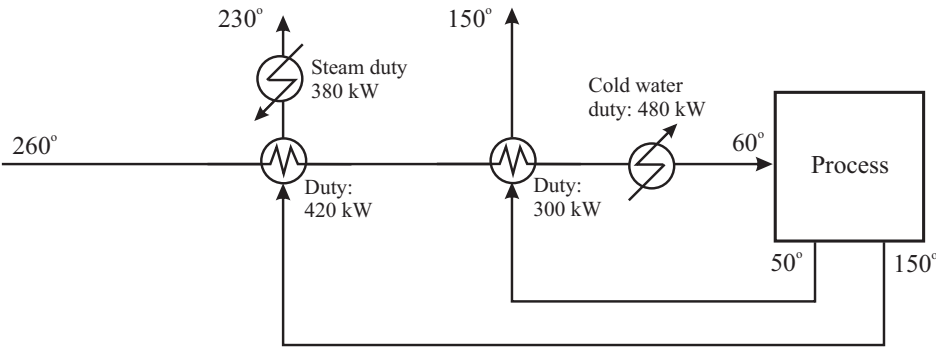


FIGURE P19.3

Network for problem P19.3.

P19.3 Figure P19.3 shows a network design using steam, cooling water and some heat recovery.

(a) Does this design achieve the minimum energy target for $\Delta T_{\min} = 20^\circ\text{C}$?

(b) If the current network does not achieve the targets, show a network design that does.

[(a) $T_{C_{\text{pinch}}} = 150^\circ\text{C}$; $T_{H_{\text{pinch}}} = 170^\circ\text{C}$; $Q_C = 480\text{ kW}$; $Q_H = 380\text{ kW}$;

(b) $Q_{C_{\min}} = 360\text{ kW}$; $Q_{H_{\min}} = 260\text{ kW}$]

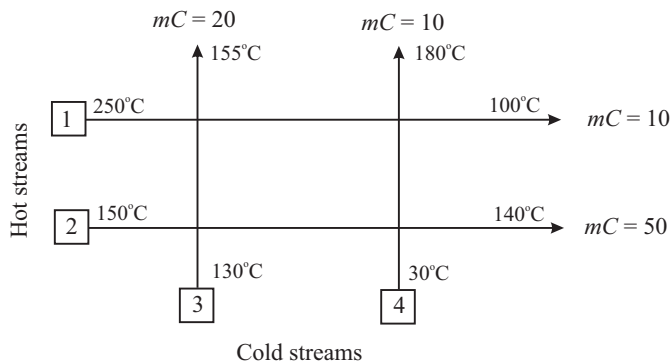


FIGURE P19.4

Network for problem P19.4.

P19.4 Figure P19.4 shows two hot streams and two cold streams for heat integration (subject to $\Delta T_{\min} = 20^\circ\text{C}$).

(i) What are the energy targets?

(ii) Show a network design achieving these targets.

[$Q_{H_{\min}} = 0$; $Q_{C_{\min}} = 0$]

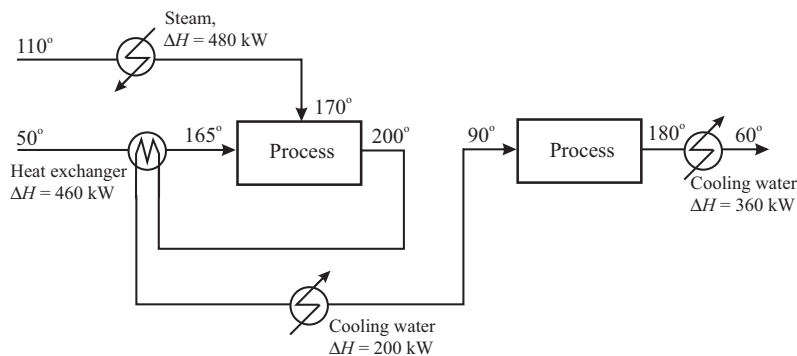


FIGURE P19.5

Network for problem P19.5.

P19.5 Figure P19.5 shows an existing design of a process plant, containing two exothermic processes. These require streams of reactants as shown in the diagram, and produce products at the temperatures shown. The plant achieves the necessary conditions by providing 480 kW of heat from a steam source, and rejects a total of 560 kW of energy to cold water utilities; only 460 kW is transferred between the streams. Show

- that there is a pinch point, and evaluate the temperature;
- that the existing plant is inefficient in its use of the energy available;
- calculate the energy targets for $\Delta T_{\min} = 20^\circ\text{C}$ and show a design that achieves these targets.

[(a) $T_{C_{\text{pinch}}} = 110^\circ\text{C}$; $T_{H_{\text{pinch}}} = 130^\circ\text{C}$; (b) $Q_C = 560\text{ kW}$; $Q_H = 480\text{ kW}$; (c) $Q_{C_{\min}} = 210\text{ kW}$; $Q_{H_{\min}} = 130\text{ kW}$]

P19.6 Recalculate the problem in P19.5 using a $\Delta T_{\min} = 10^\circ\text{C}$. Comment on the effect of reducing the minimum temperature difference.

[(a) $T_{C_{\text{pinch}}} = 110^\circ\text{C}$; $T_{H_{\text{pinch}}} = 120^\circ\text{C}$; (b) $Q_C = 560\text{ kW}$; $Q_H = 480\text{ kW}$; (c) $Q_{C_{\min}} = 120\text{ kW}$; $Q_{H_{\min}} = 40\text{ kW}$]

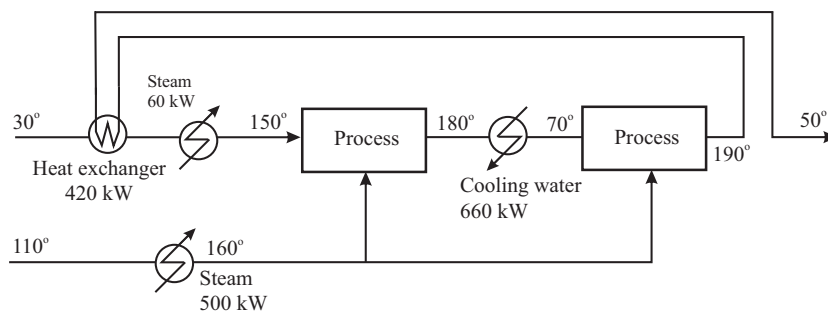


FIGURE P19.7

Network for problem P19.7.

P19.7 A network for a process plant is shown in Fig P19.7.

- Calculate the energy targets for $\Delta T_{\min} = 10^\circ\text{C}$ and show a design that achieves these targets.
- Explain why the existing network does not achieve the energy targets.

[(a) $Q_{C_{\min}} = 190\text{ kW}$; $Q_{H_{\min}} = 90\text{ kW}$; (b) there is transfer across the pinch]

IRREVERSIBLE THERMODYNAMICS

20

Classical thermodynamics deals with transitions from one equilibrium state to another and since it does not analyse the changes between state points it could be called *thermostatics* (see Tribus (1961)). The term *thermodynamics* will be reserved, in this chapter, for dynamic nonequilibrium processes.

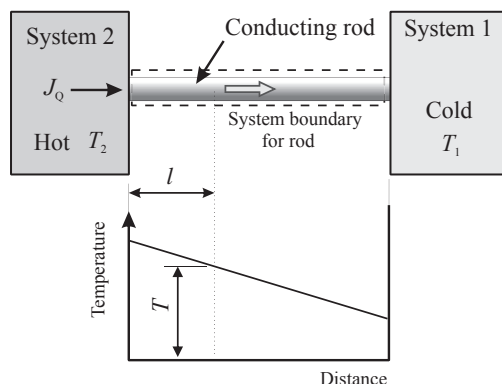
Phenomenological laws should have been met previously which describe irreversible processes in the form of proportionalities, e.g. Fourier's law of heat conduction, Ohm's law relating electrical current and potential gradient, Fick's law relating flow of matter (Fick, 1856) and concentration gradient etc. When two of these phenomena occur simultaneously they interfere, or couple, and give rise to new effects. One such cross-coupling is the reciprocal effect of thermoelectricity and electrical conduction: the Peltier effect (evolution or absorption of heat at a junction due to the flow of electrical current) and thermoelectric force (due to maintenance of the junctions at different temperatures). It is necessary to formulate coupled equations to deal with these phenomena, which are 'phenomenological' inasmuch as they are experimentally verified laws but are not a part of the comprehensive theory of irreversible processes.

It is possible to examine irreversible phenomena by statistical mechanics and the kinetic theory but these methods are on a molecular scale and do not give a good macroscopic theory of the processes. Another method of considering nonequilibrium processes is based on 'pseudo-thermodynamic theories'. Here the laws of thermostatics are applied to a part of the irreversible process which is considered to be reversible and the rest of the process is considered as irreversible and not taken into account. Thomson applied the Second Law of thermostatics to thermoelectricity by considering the Thomson and Peltier effects to be reversible and the conduction effects to be irreversible. The method was successful as the predictions were confirmed by experiment but it has not been possible to justify Thomson's hypothesis from general considerations.

A systematic macroscopic and general thermodynamics of irreversible processes can be obtained from a theorem published by Onsager (1931a, b). This was developed from statistical mechanics and the derivation will not be shown but the results will be used. The theory, based on Onsager's theorem, also shows why the incorrect thermostatic methods give correct results in a number of cases.

20.1 DEFINITION OF IRREVERSIBLE OR STEADY-STATE THERMODYNAMICS

All previous work on macroscopic 'thermodynamics' has been related to equilibrium. A system was said to be in equilibrium when no spontaneous process took place and all the thermodynamic properties remained unchanged. The macroscopic properties of the system were spatially and temporally invariant.

**FIGURE 20.1**

Steady-state conduction of heat along a bar.

Consider the system shown in Fig. 20.1, in which a thermally insulated rod connects two reservoirs at temperatures T_2 and T_1 respectively. Heat flows between the two reservoirs by conduction along the rod. If the reservoirs are very large the conduction of energy out of, or into, them can be considered not to affect them. A state will be achieved when the rate of heat flow, dQ/dt , entering the rod equals the rate of heat flow, $-dQ/dt$, leaving the rod. If a thermometer was inserted at any point in the rod the reading would not change with time, but it would be dependent on position. If the rod was of uniform cross-section, the temperature gradient would be linear. (This is the basis of the Searle's bar conduction experiment.)

The temperature in the bar is therefore a function of position but is independent of time. The overall system is in a 'stationary' or 'steady' state but not in 'equilibrium' for that requires that the temperature be uniform throughout the system. If the metal bar was isolated from all the influences of the surroundings and from the heat sources, i.e. if it is made an *isolated system* the difference between the *steady state* and *equilibrium* becomes obvious. In the case where the system was in *steady state*, processes would occur after the isolation (equalisation of temperature throughout the bar); where the system was already in *equilibrium*, they would not.

20.2 ENTROPY FLOW AND ENTROPY PRODUCTION

Still considering the conduction example given above. If the heat flows into the left-hand end of the bar due to an infinitesimal temperature difference, i.e. the process is reversible, the left-hand reservoir loses entropy at the rate

$$\frac{dS_2}{dt} = -\frac{1}{T_2} \frac{dQ}{dt} \quad (20.1)$$

Similarly the right-hand reservoir gains entropy at the rate

$$\frac{dS_1}{dt} = \frac{1}{T_1} \frac{dQ}{dt} \quad (20.2)$$

Thus, the total change of entropy for the whole system is

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} = \frac{dQ}{dt} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{dQ}{dt} \left[\frac{T_2 - T_1}{T_2 T_1} \right] \quad (20.3)$$

Now $T_2 > T_1$ and therefore the rate of change of entropy, $\frac{dS}{dt} > 0$.

To understand the meaning of this result, it is necessary to consider a point in the bar. At the point ℓ from the left-hand end, the thermometer reading is T . This reading is independent of time and is the reading obtained on the thermometer *in equilibrium* with the particular volume of the rod in contact with it. Hence, the thermometer indicates the ‘temperature’ of that volume of the rod. Since the temperature is constant, the system is in a ‘steady state’ and at each point in the rod, the entropy is invariant with time. However, there is a net transfer of entropy from the left-hand reservoir to the right-hand reservoir, i.e. entropy is ‘flowing’ along the rod. The total entropy of the composite system is increasing with time and this phenomenon is known as ‘entropy production’.

20.3 THERMODYNAMIC FORCES AND THERMODYNAMIC VELOCITIES

It has been suggested that for systems not far removed from equilibrium, the development of the relations used in the thermodynamics of the steady state should proceed along analogous lines to the study of the dynamics of particles, i.e. the laws should be of the form

$$J = LX \quad (20.4)$$

where

J is the thermodynamic velocity or flow;

X is the thermodynamic force; and

L is a coefficient independent of X and J and is scalar in form, while both J and X are vector quantities.

The following simple relationships illustrate how this law may be applied.

Fourier’s equation for one-dimensional conduction of heat along a bar is

$$\frac{dQ}{dt} = -kA \frac{dT}{d\ell}, \quad (20.5)$$

where Q = quantity of energy (heat); T = temperature; A = area of cross-section; ℓ = length; k = thermal conductivity.

Ohm’s law for flow of electricity along a wire, which is also one-dimensional, is

$$I = \frac{dq_\ell}{dt} = -\lambda A \frac{de}{d\ell} \quad (20.6)$$

where I = current; q_ℓ = charge (coulomb); e = potential difference (voltage); A = area of cross-section of wire; ℓ = length; λ = electrical conductivity.

Fick’s law for the diffusion due to a concentration gradient is, in one dimension,

$$\frac{dn_i}{dt} = -k \frac{dC_i}{d\ell} \quad (20.7)$$

where n_i = amount of substance, i , C_i = concentration of component, i , and k = diffusion coefficient. It will be shown later that this equation is not as accurate as one proposed by Hartley, in which the gradient of the ratio of chemical potential to temperature is used as the driving potential.

Other similar relationships occur in physics and chemistry but will not be given here. The three equations given above relate the flow of one quantity to a difference in potential: hence, there is a flow term and a force term as suggested by Eqn (20.4). It will be shown that although Eqns (20.5)–(20.7) appear to have the correct form, they are not the most appropriate relationships for some problems. Equations (20.5)–(20.7) also define the relationship between individual fluxes and potentials, whereas in many situations the effects can be coupled.

20.4 ONSAGER'S RECIPROCAL RELATION

If two transport processes are such that one has an effect on the other, e.g. heat conduction and electricity in thermoelectricity; heat conduction and diffusion of gases; etc., then *the two processes are said to be coupled*. The equations of coupled processes may be written as

$$\left. \begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \right\} \quad (20.8)$$

Equation (20.8) may also be written in matrix form as

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \quad (20.8a)$$

It is obvious that in this equation the basic processes are defined by the diagonal coefficients in the matrix, while the other processes are defined by the off-diagonal terms.

Consider the situation, where diffusion of matter is occurring with a simultaneous conduction of heat. Each of these processes is capable of transferring energy through a system. The diffusion process achieves this by mass transfer, i.e. each molecule of matter carries some energy with it. The thermal conductivity process achieves the transfer of heat by the molecular vibration of the matter transmitting energy through the system. Both achieve a similar result of redistributing energy but by different methods. The diffusion process also has the effect of redistributing the matter throughout the system, in an attempt to achieve the equilibrium state in which the matter is evenly distributed with the minimum of order (i.e. the maximum entropy or minimum chemical potential). It can be shown, by a more complex argument that thermal conduction will also have an effect on diffusion. First, if each process is considered in isolation the equations can be written

$$J_1 = L_{11}X_1 \quad \text{the equation of conduction without any effect due to diffusion;}$$

$$J_2 = L_{22}X_2 \quad \text{the equation of diffusion without any effect due to conduction.}$$

Now, the diffusion of matter has an effect on the flow of energy because the individual, diffusing, molecules carry energy with them, and hence an effect for diffusion must be included in the term for thermal flux, J_1 .

Hence

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (20.9)$$

where L_{12} is the *coupling coefficient* showing the effect of mass transfer (diffusion) on energy transfer.

In a similar manner, because conduction has an effect on diffusion, the equation for mass transfer can be written

$$J_2 = L_{21}X_1 + L_{22}X_2 \quad (20.10)$$

where L_{21} is the coupling coefficient for these phenomena.

A general set of coupled linear equations is

$$J_i = \sum_k L_{ik}X_k \quad (20.11)$$

The equations are of little use unless more is known about the forces X_k and the coefficients L_{ik} . This information can be obtained from *Onsager's reciprocal relation*. There is considerable latitude in the choice of the forces X , but Onsager's relation chooses the forces in such a way that when each flow J_j is multiplied by the appropriate force X_j the sum of these products is equal to the rate of creation of entropy per unit volume of the system, θ , multiplied by the temperature, T .

Thus

$$T\theta = J_1X_1 + J_2X_2 + \dots = \sum_i J_iX_i \quad (20.12)$$

Equation (20.12) may be rewritten

$$\theta = \sum_i J_i x_i \quad (20.13)$$

where

$$x_i = \frac{X_i}{T}.$$

Onsager further showed that if the abovementioned condition was obeyed then, in general,

$$L_{ik} = L_{ki} \quad (20.14)$$

This means that the *coupling matrix* in Eqn (20.8a) is *symmetric*, i.e. $L_{12} = L_{21}$ for the particular case given above. The significance of this is that the effect of parameters on each other is equivalent irrespective of which is judged to be the most, or least, significant parameter. Consideration will show that if this was not true then it would be possible to construct a system which disobeyed the laws of thermodynamics. It is not proposed to derive Onsager's relation which is obtained from molecular considerations, it will be assumed to be true.

In summary, the thermodynamic theory of an irreversible process consists of first finding the *conjugated fluxes and forces*, J_i and x_i , from Eqn (20.13) by calculating the entropy production. Then a study is made of the phenomenological Eqn (20.11) and Onsager's reciprocal relation (20.14) is used to solve these. The whole procedure can be performed within the realm of macroscopic theory and is valid for any process.

20.5 THE CALCULATION OF ENTROPY PRODUCTION OR ENTROPY FLOW

In Section 20.2, the concept of entropy flow was introduced. At any point in the bar, ℓ , the entropy flux, J_S , may be defined as the entropy flow rate per unit cross-sectional area. At ℓ , the entropy flow rate will be the following:

$$\frac{dS}{dt} = \frac{d}{dt} \left(\frac{Q}{T} \right) = \frac{1}{T} \frac{dQ}{dt} \quad (20.15)$$

and the entropy flux is

$$J_S = \frac{1}{A} \frac{dS}{dt} = \frac{1}{A} \left(\frac{1}{T} \frac{dQ}{dt} \right) \quad (20.16)$$

The heat flow rate J_Q is defined as

$$J_Q = \frac{dQ/dt}{A} \quad (20.17)$$

Hence

$$J_S = \frac{J_Q}{T} \quad (20.18)$$

The rate of production of entropy per unit volume, θ , is

$$\theta = \frac{d}{dV} \left(\frac{dS}{dt} \right) = \frac{d}{d\ell} \left(\frac{dS/dt}{A} \right) = \frac{d}{d\ell} \left(\frac{1}{A} \frac{dS}{dt} \right)$$

i.e.

$$\theta = \frac{dJ_S}{d\ell} \quad (\text{from Eqn (20.16)}) \quad (20.19)$$

Substituting from Eqn (20.18) for J_S gives

$$\theta = \frac{d}{d\ell} \left(\frac{J_Q}{T} \right) = - \frac{J_Q}{T^2} \frac{dT}{d\ell} \quad (20.20)$$

Equation (20.20) is the rate of production of entropy per unit volume at point ℓ in the rod, where the temperature is T . This equation was derived for thermal conduction *only*.

If the rod was at a uniform temperature, i.e. in equilibrium, $\frac{dT}{d\ell} = 0$ and $\theta = 0$. For conduction $\frac{dT}{d\ell} < 0$ thus θ is positive, i.e. entropy is produced not dissipated.

A similar calculation may be made for the flow of electricity along a wire. The wire may be considered to be in contact along its length with a reservoir at temperature T . If an electric current density, $J_I (= I/A)$, flows due to a potential difference $d\epsilon$, and since the wire is at constant temperature T because of its contact with the reservoir, then the electrical work must be equal to the heat transferred from the wire.

The rate of doing electrical work (power) is $-J_I A d\epsilon$, and the total rate of heat production is $\dot{Q}$. Hence

$$\dot{Q} = -J_I A d\epsilon \quad (20.21)$$

The total change in entropy in volume dV is

$$\theta dV = - \frac{J_I A d\varepsilon}{T}. \quad (20.22)$$

Hence, the rate of production of entropy per unit volume is, because $dV = Ad\ell$

$$\theta = - \frac{J_I}{T} \frac{d\varepsilon}{d\ell}. \quad (20.23)$$

Equation (20.23) applies for electrical flow with *no* heat conduction.

20.6 THERMOELECTRICITY – THE APPLICATION OF IRREVERSIBLE THERMODYNAMICS TO A THERMOCOUPLE

20.6.1 THERMOELECTRIC PHENOMENA

As an aid to understanding the analysis which follows a summary will be given of the effects involved in a thermocouple. A thermocouple consists of two junctions of dissimilar metals one held at a high temperature the other at a low temperature, as shown in Fig. 20.2.

Two different wires A and B are joined to form a loop with two junctions, each placed in a heat reservoir. A perfectly reversible motor is inserted in wire B. If the temperatures of the two reservoirs are different then not only will heat be transported along the wires A and B but also a flow of electrical current will occur. The following phenomena may be isolated.

1. If the entire system is kept at a uniform temperature and the motor is driven as a generator then a current will flow round the circuit. It is found that under these circumstances heating occurs at one junction and cooling at the other. This is known as the *Peltier Effect* and the heating (or cooling) is equal to πI where π = Peltier coefficient and I is the current. Because of the resistance of the wires, it is necessary to do work to drive the generator. This work is equal to the product of current and potential difference across the wire and is called *Joule heating*; this is the $I^2 R$ loss, which is dissipated in the reservoirs.
2. If the reservoirs are put at different temperatures, a potential difference is set up even when no electric current flows. This is called the *Seebeck effect*. *Fourier conduction* will also occur along the wires.

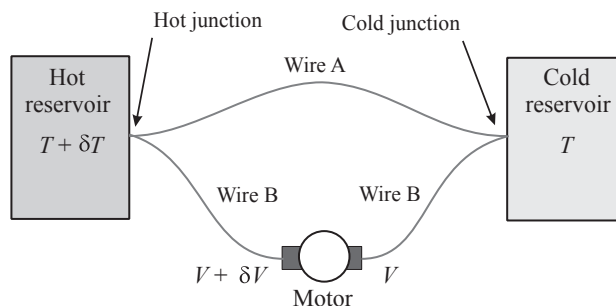


FIGURE 20.2

Schematic diagram of a thermocouple being used to drive an electric motor.

3. If both a temperature difference and electric current occur simultaneously, then a third effect occurs. This is called the *Thomson heat* and occurs in a wire carrying a current of electricity along a temperature gradient. Consider a wire in a temperature field in the absence of an electric current. At each point in the wire there will exist a temperature as shown in Fig. 20.1. Now suppose an electrical current flows. It is found that a flow of heat is required to keep the wire at the same temperature as previously. This effect is additional to Joulean heating and is proportional to the temperature gradient. The heat flux is given by

$$\frac{d\dot{Q}}{d\ell} = \sigma I \frac{dT}{d\ell} \quad (20.24)$$

where $\dot{Q}$ = rate of heat transfer; I = current; $dT/d\ell$ = temperature gradient in direction of I ; and σ = Thomson Coefficient.

The above laws are purely phenomenological. The various coefficients defined in them can be used in engineering practice. It is impossible to measure some of these effects in isolation. For example, if it is attempted to measure the potential difference between two points not at the same temperature, the measuring instrument and the electrical wires used to make the connections will constitute part of a thermocouple circuit. When making connections, it is necessary that the measuring points are in an isothermal region. These connections will still give rise to contact and thermally induced voltages but these are usually negligibly small.

It is not possible to measure the thermoelectric characteristics of a single material, except for the Thomson effect, because they are junction effects. Hence, *the Seebeck and Peltier coefficients are the properties of pairs of metals*, not single metals.

20.6.2 UNCOUPLED EFFECTS IN THERMOELECTRICITY

Consider the two possible types of uncoupled flow. Let suffix 1 refer to heat flow processes and suffix 2 refer to electrical flow processes.

Heat flow

For uncoupled heat flow, the rate of entropy production per unit volume is, from Eqns (20.13) and (20.20)

$$\theta = \frac{J_1 X_1}{T} = \frac{J_Q X_1}{T} = -\frac{J_Q}{T^2} \frac{dT}{d\ell} \quad (20.25)$$

where

$$X_1 = -\frac{1}{T} \frac{dT}{d\ell} \quad (20.26)$$

Electrical flow

For uncoupled electrical flow, from Eqns (20.13) and (20.23)

$$\theta = \frac{J_2 X_2}{T} = \frac{J_I X_2}{T} = -\frac{J_I}{T^2} \frac{d\varepsilon}{d\ell} \quad (20.27)$$

$$X_2 = -\frac{d\varepsilon}{d\ell} \quad (20.28)$$

20.6.3 THE COUPLED EQUATIONS OF THERMOELECTRICITY

The Onsager relations as given by Eqn (20.8) may be applied.
i.e.

$$\left. \begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \right\}$$

These become, in this case

$$\text{for heat flow } J_Q = -\frac{L_{11}}{T} \frac{dT}{d\ell} - L_{12} \frac{d\varepsilon}{d\ell} \quad (20.29)$$

$$\text{for electrical flow } J_I = -\frac{L_{21}}{T} \frac{dT}{d\ell} - L_{22} \frac{d\varepsilon}{d\ell} \quad (20.30)$$

From Eqn (20.18), the entropy flux J_S is given by $J_S = \frac{J_Q}{T}$, and hence Eqn (20.29) may be written

$$J_S = -\frac{L_{11}}{T^2} \frac{dT}{d\ell} - \frac{L_{12}}{T} \frac{d\varepsilon}{d\ell} \quad (20.31)$$

It has been assumed that both the electrical and heat flow phenomena may be represented by empirical laws of the form $J = LX$.

At constant temperature, Ohm's law states $I = -\lambda A \frac{d\varepsilon}{d\ell}$, giving

$$J_I = \frac{I}{A} = -\lambda \frac{d\varepsilon}{d\ell} \quad (20.32)$$

where λ is the electrical conductivity of the wire at constant temperature.

If dT is set to zero in Eqn (20.30), i.e. the electrical current is flowing in the absence of a temperature gradient, then

$$-\lambda \frac{d\varepsilon}{d\ell} = -L_{22} \frac{d\varepsilon}{d\ell}, \text{ which gives } L_{22} = \lambda \quad (20.33)$$

If the *entropy flux* in the wire is divided by the *electrical current flowing at constant temperature* and this ratio is called the *entropy of transport* S^* , then

$$S^* = \left(\frac{J_S}{J_I} \right)_T = \left(-\frac{L_{12}}{T} \frac{d\varepsilon}{d\ell} \right) / \left(-\lambda \frac{d\varepsilon}{d\ell} \right) = \frac{L_{12}}{TL_{22}} \quad (20.34)$$

The entropy of transport is basically the rate at which entropy is generated per unit energy flux in an *uncoupled process*. It is a useful method for defining the cross-coupling terms in the coupled equations.

Thus

$$L_{12} = TL_{22}S^* = \lambda TS^* \quad (20.35)$$

By Onsager's reciprocal relation

$$L_{21} = L_{12} = \lambda TS^* \quad (20.36)$$

Substituting for L_{22} , L_{12} and L_{21} in Eqns (20.29) and (20.30) gives

$$J_Q = -\frac{L_{11}}{T} \frac{dT}{d\ell} - \lambda TS^* \frac{d\varepsilon}{d\ell} \quad (20.37)$$

and

$$J_I = -\frac{\lambda TS^*}{T} \frac{dT}{d\ell} - \lambda \frac{d\varepsilon}{d\ell} \quad (20.38)$$

Now if there is zero current flow (i.e. $J_I = 0$), Fourier's law of heat conduction may be applied giving

$$J_Q = \frac{dQ/dt}{A} = -k \frac{dT}{d\ell} \quad (20.39)$$

However, if $J_I = 0$ then Eqn (20.38) gives

$$\frac{d\varepsilon}{d\ell} = -S^* \frac{dT}{d\ell} \quad (20.40)$$

Substituting this value for $d\varepsilon/d\ell$ in Eqn (20.37) gives

$$J_Q = -\frac{k dT}{d\ell} = -\frac{L_{11}}{T} \frac{dT}{d\ell} + \lambda S^{*2} T \frac{dT}{d\ell} \quad (20.41)$$

Hence

$$L_{11} = (k + \lambda TS^{*2}) T \quad (20.42)$$

Substituting the coefficients into Eqns (20.29) and (20.30) gives the following:

$$\text{for heat flow } J_Q = -\left(k + \lambda TS^{*2}\right) \frac{dT}{d\ell} - \lambda TS^* \frac{d\varepsilon}{d\ell} \quad (20.43)$$

$$\text{for electrical flow } J_I = -\lambda S^* \frac{dT}{d\ell} - \lambda \frac{d\varepsilon}{d\ell} \quad (20.44)$$

The entropy flux is obtained from Eqn (20.31).

$$J_S = -\frac{(k + \lambda TS^{*2})}{T} \frac{dT}{d\ell} - \lambda S^* \frac{d\varepsilon}{d\ell} \quad (20.45)$$

It is possible to define another parameter, the heat of transport Q^* , where $Q^* = \left(\frac{J_Q}{J_I}\right)_T$. This is basically the 'thermal energy' which is transported by a flow of electrical energy when there is no temperature gradient, and indicates the magnitude of the off-diagonal terms in the cross-coupling matrix in Eqn (20.8a).

From Eqns (20.43) and (20.44), when $dT = 0$

$$\left(\frac{J_Q}{J_I}\right)_T = \left(-\lambda TS^* \frac{d\varepsilon}{d\ell}\right) / \left(-\lambda \frac{d\varepsilon}{d\ell}\right) = TS^* \quad (20.46)$$

Hence

$$Q^* = TS^* \quad (20.47)$$

Equation (20.47) is interesting because it retains the basic generic form relating ‘heat’, temperature, and ‘entropy’, namely that entropy is evaluated by dividing a heat transfer term by a temperature term.

It is now possible to relate the equations derived above to the various physical phenomena observed in experiments. Previously the Seebeck effect was defined as the potential difference set up in a wire due to a temperature gradient without any current flow (i.e. $(d\epsilon/dT)_{J=0}$). From Eqn (20.44), if there is zero current flow

$$-S^* \frac{dT}{d\ell} = \frac{d\epsilon}{d\ell} \quad \text{or} \quad \frac{d\epsilon}{dT} = -S^* \quad (20.48)$$

Hence, S^* is a measure of the magnitude of the Seebeck effect, and the value of S^* for most materials is nonzero.

If the wire is kept at a constant temperature, a flow of heat (thermal energy) will occur due to the electrical potential difference. From Eqn (20.43)

$$J_Q = -\lambda TS^* \frac{d\epsilon}{d\ell} \quad (20.49)$$

This transport of thermal energy due to an electrical field is known as the Thomson effect.

20.6.4 THE THERMOCOUPLE

A thermocouple is a device for recording temperature at a point. It can be represented diagrammatically as shown in Fig. 20.3.

The thermocouple consists of two wires X and Y of dissimilar metals forming a junction at a . The ends b and c of the wires are immersed in an ice bath to form the cold junction and leads of material Z are connected to materials X and Y at points b and c , respectively, and these connections are inserted into a cold junction. These leads of material Z are then connected to a potentiometer or digital voltmeter (DVM) at d and e .

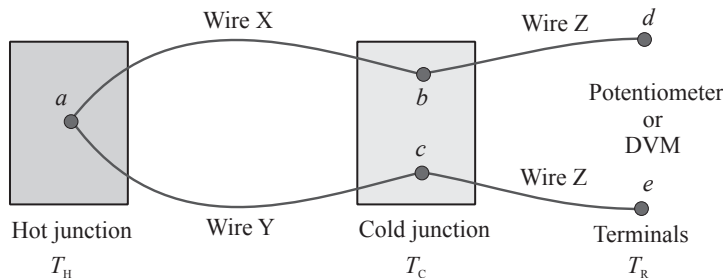


FIGURE 20.3

Schematic diagram of a thermocouple. DVM, digital voltmeter.

The voltage representing temperature T_H is obtained due to the thermoelectric effect in the leads when zero current flows, i.e. the potentiometer is balanced and $J_1 = 0$. At zero current, as previously discussed, the electromotive force (emf) at the potentiometer (or DVM) equals the thermal emf generated by the thermocouple.

From Eqn (20.48), the potential difference between each end of a wire of material M is related to the temperature difference between the points by the following equation.

$$d\varepsilon)_{J_1=0} = -S_M^* dT)_{J_1=0} \quad (20.50)$$

where S_M^* is the value of S^* for material M.

Equation (20.50) can be applied to each wire in the system shown above, to give the following

$$\text{Wire } ec \quad \varepsilon_c - \varepsilon_e = - \int_{T_R}^{T_C} S_Z^* dT$$

$$\text{Wire } ca \quad \varepsilon_a - \varepsilon_c = - \int_{T_C}^{T_H} S_Y^* dT$$

$$\text{Wire } ab \quad \varepsilon_b - \varepsilon_a = - \int_{T_H}^{T_C} S_X^* dT$$

$$\text{Wire } bd \quad \varepsilon_d - \varepsilon_b = - \int_{T_C}^{T_R} S_Z^* dT$$

Adding these equations to obtain the potential difference between points e and d gives the potential difference measured by the potentiometer or DVM

$$\begin{aligned} \varepsilon_d - \varepsilon_e &= - \int_{T_R}^{T_C} S_Z^* dT - \int_{T_C}^{T_H} S_Y^* dT - \int_{T_H}^{T_C} S_X^* dT - \int_{T_C}^{T_R} S_Z^* dT \\ &= - \int_{T_C}^{T_H} (S_Y^* - S_X^*) dT \end{aligned} \quad (20.51)$$

This can be written as

$$\varepsilon_{X,Y} = \varepsilon_d - \varepsilon_e = \int_{T_C}^{T_H} (S_X^* - S_Y^*) dT \quad (20.52)$$

Thus the emf of a thermocouple between any particular temperature T_H and the cold junction at $T_C = 0^\circ\text{C}$ is dependent only on the materials between the *hot* and *cold* junctions if the leads bd and ce

are both made of the same material. Since S^* is defined in terms of J_S and J_I it is independent of the length of the constituent wires, and hence the *emf generated is also independent of the length of the wires*.

Thermocouples are normally bought as pairs of wires which have been calibrated by experimental tests. For low temperatures (up to 150 °C) Cu-Ni thermocouples may be used, for high temperatures platinum–rhodium is used. The calibration of the thermocouple is dependent only on the wires used to make the junctions; the length of thermocouples is not a parameter in the calibration, see Eqns (20.50) and (20.52a).

20.6.4.1 Thermocouple with junctions at T_C and T_H and connections in one of the measuring wires

Figure 20.3 showed an idealised thermocouple in which the connections between the thermoelectric pair of wires and those connecting the thermocouple to the measuring device were maintained at the cold junction temperature. It might be inconvenient to set up the thermocouple in this way, and a more convenient arrangement is shown in Fig. 20.4.

It can be seen from Fig. 20.4 that there are now four junctions between dissimilar materials, and each of these has the capability of generating an emf. This system will be analysed to determine the potential difference at the DVM.

Applying $d\epsilon)_{J_I=0} = -S^*dT)_{J_I=0}$ to the system gives the following results.

$$\begin{aligned} \text{Wire } dc \quad \epsilon_c - \epsilon_d &= - \int_{T_R}^{T_{R'}} S_Z^* dT \\ \text{Wire } ca \quad \epsilon_a - \epsilon_c &= - \int_{T_{R'}}^{T_H} S_Y^* dT \end{aligned}$$

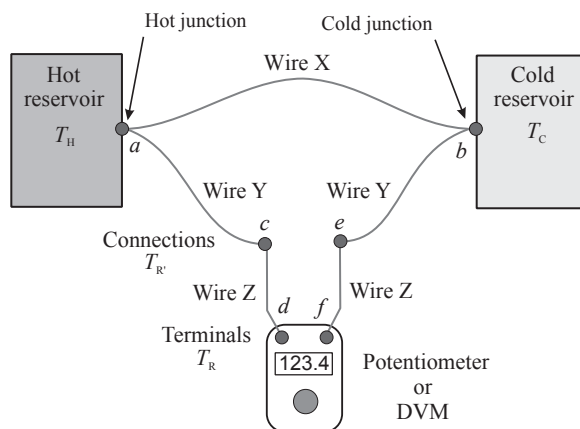


FIGURE 20.4

Conventional layout of thermocouple. DVM, digital voltmeter.

$$\text{Wire } ab \quad \varepsilon_b - \varepsilon_a = - \int_{T_H}^{T_C} S_X^* dT$$

$$\text{Wire } be \quad \varepsilon_e - \varepsilon_b = - \int_{T_C}^{T_{R'}} S_Y^* dT$$

$$\text{Wire } ef \quad \varepsilon_f - \varepsilon_e = - \int_{T_{R'}}^{T_R} S_Z^* dT$$

The emf at the potentiometer is given by

$$\begin{aligned} \varepsilon_f - \varepsilon_d &= - \int_{T_{R'}}^{T_R} S_Z^* dT - \int_{T_H}^{T_{R'}} S_Y^* dT - \int_{T_C}^{T_H} S_X^* dT - \int_{T_{R'}}^{T_C} S_Y^* dT - \int_{T_R}^{T_{R'}} S_Z^* dT. \\ &= - \int_{T_C}^{T_H} S_X^* dT - \int_{T_H}^{T_{R'}} S_Y^* dT - \int_{T_{R'}}^{T_C} S_Y^* dT \\ &= - \int_{T_C}^{T_H} S_X^* dT + \int_{T_C}^{T_H} S_Y^* dT = - \int_{T_C}^{T_H} (S_X^* - S_Y^*) dT \end{aligned} \quad (20.53)$$

This is the same result given before in Eqn (20.51). There is one important point which is apparent from this result and that is that the two junctions between wires Y and Z, points *c* and *e*, must be at the same temperature, i.e. $(T_{R'})_c = (T_{R'})_e$. If these junctions are not at the same temperature then each of them will act as another junction and generate an electrical potential. Hence, care must be taken when setting up a thermocouple wired in a manner similar to Fig. 20.4 to ensure that points *c* and *e* are close together and at the same temperature.

20.6.5 OTHER EFFECTS IN THERMOCOUPLES

20.6.5.1 Peltier effect or Peltier heating

As defined in Section (20.6.1), this effect occurs when the entire system is kept at uniform temperature and a current flows around the circuit. The temperature of the system tends to rise due to both Ohmic and Peltier heating. If the Ohmic heating is neglected initially then the Peltier coefficient, defined below in Eqn (20.54), can be evaluated.

$$J_{Q_{\text{Peltier}}} = \pi J_I \quad (20.54)$$

where

π = Peltier coefficient.

The Peltier heating effect at the junction in Fig. 20.5, is given by

$$J'_Q = (J_Q)_X - (J_Q)_Y \quad (20.55)$$

where J'_Q is the heat that must be transferred to a reservoir to maintain the temperature of the junction at T . From Eqn (20.54)

$$J'_Q = \pi_{X,Y} J_I \quad (20.56)$$

Hence, the heat transfer from the junction to maintain the temperature constant is

$$\pi_{X,Y} J_I = (J_Q)_X - (J_Q)_Y \quad (20.57)$$

This is the definition of the Peltier effect, and hence the Peltier coefficient is given by

$$\pi_{X,Y} = \left(\frac{J_Q}{J_I} \right)_X - \left(\frac{J_Q}{J_I} \right)_Y \quad (20.58)$$

The ratio $\left(\frac{J_Q}{J_I} \right)_{T=\text{constant}}$ was defined previously and given the name heat of transport, Q^* . It was shown (Eqn (20.47)) that $Q^* = TS^*$.

Thus

$$\pi_{X,Y} = TS_X^* - TS_Y^* = T(S_X^* - S_Y^*) \quad (20.59)$$

It is apparent from the form of Eqn (20.59) that the Peltier heating is reversible, i.e. if the current is reversed, the direction of heat flow will be reversed.

20.6.5.2 Thomson effect or Thomson heating

This was defined previously in Eqn (20.24). Rewriting this equation in the nomenclature now employed and applying it to the small element of wire, $\Delta\ell$, shown in Fig. 20.6

$$(J_Q)_{Th} = \sigma J_I \Delta T \quad (20.60)$$

Assume that initially there is no current flow, but that the heat flow gives rise to a temperature drop ΔT . Now if an electric current is switched on, it is found that a flow of heat is required to keep the wire at the same temperatures as previously; this is in addition to Joulean heating (see Section 20.6.1 (3)).

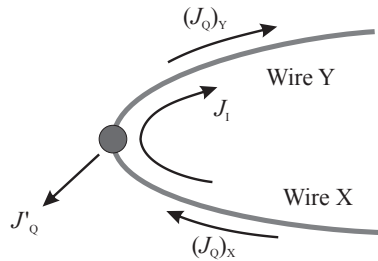
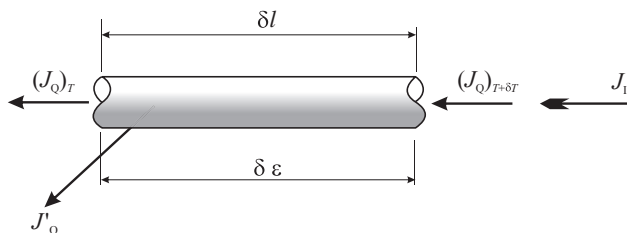


FIGURE 20.5

Peltier heating at a junction.

**FIGURE 20.6**

Small element of wire subject to current flow.

Let the required heat transfer, to a series of reservoirs, be J'_Q . Under these conditions, the heat flow due to heat conduction is the same as previously.

Then

$$J'_Q = \underbrace{(J_Q)_{T+\Delta T}}_{\text{Heat flow rate, } dQ/dt, \text{ at } T+\Delta T} - \underbrace{(J_Q)_T}_{\text{Heat flow rate, } dQ/dt, \text{ at } T} + \underbrace{J_I \Delta \epsilon}_{\text{Ohmic heating}} \quad (20.61)$$

At any given temperature, T , the heat of transport, Q^* , is (Eqn (20.47))

$$Q^* = \left(\frac{J_Q}{J_I} \right)_T = TS^*$$

and hence from Eqn (20.47)

$$(J_Q)_T = J_I TS^* \quad (20.62)$$

At a temperature, $T + \Delta T$

$$\begin{aligned} (J_Q)_{T+\Delta T} &= J_I(T + \Delta T) \left(S^* + \frac{dS^*}{dT} \Delta T \right) \\ &= J_I \left(TS^* + \frac{T dS^*}{dT} \Delta T + S^* \Delta T \right) \text{ if multiples of small terms are neglected} \end{aligned} \quad (20.63)$$

Now, for the element

$$\Delta \epsilon = - \frac{d\epsilon}{d\ell} \Delta \ell \quad (20.64)$$

and

$$\Delta T = - \frac{dT}{d\ell} \Delta \ell \quad (20.65)$$

Equation (20.38) can be rearranged to give

$$\frac{d\epsilon}{d\ell} = - \frac{J_I}{\lambda} - S^* \frac{dT}{d\ell} \quad (20.66)$$

Substituting the above relations into Eqn (20.61) gives

$$\begin{aligned}
 J'_Q &= J_I \left(TS^* + \frac{T dS^*}{dT} \Delta T + S^* \Delta T \right) - J_I TS^* + J_I \left(\frac{J_I}{\lambda} \Delta \ell - S^* \Delta T \right) \\
 &= \underbrace{J_I T \frac{dS^*}{dT} \Delta T}_{\text{Thomson heat extracted to maintain temperature}} + \underbrace{J_I^2 \frac{\Delta \ell}{\lambda}}_{\text{Ohmic heat generated}}
 \end{aligned} \tag{20.67}$$

Now the Thomson heat was defined in Eqn (20.60) as

$$J_Q = \sigma J_I \Delta T \tag{20.60a}$$

Thus

$$\sigma = -T \frac{dS^*}{dT} \tag{20.68}$$

For the thermocouple shown in Fig. 20.3, the difference in Thomson coefficients for the two wires is

$$\sigma_X - \sigma_Y = -T \frac{d}{dT} (S_X^* - S_Y^*) \tag{20.69}$$

20.6.6 SUMMARY

The equations for thermocouple phenomena for materials X and Y acting between temperature limits of T_H and T_C are as follows:

Seebeck Effect

$$\text{Seebeck coefficient} \quad \varepsilon_{X,Y} = \int_{T_C}^{T_H} (S_X^* - S_Y^*) dT \tag{20.52a}$$

Peltier Effect

$$\text{Peltier coefficient} \quad \pi_{X,Y} = T(S_X^* - S_Y^*) \tag{20.59a}$$

Thomson Effect

$$\text{Thomson coefficient} \quad \sigma_X - \sigma_Y = -T \frac{d}{dT} (S_X^* - S_Y^*) \tag{20.68}$$

20.7 DIFFUSION AND HEAT TRANSFER

20.7.1 BASIC PHENOMENA INVOLVED

The classical law of diffusion is due to Fick (1856). This states that the diffusion rate is proportional to the concentration gradient, and is the mass transfer analogy of the thermal conduction law. The constant of proportionality in Fick's law is called the diffusion coefficient. It was found from experimental evidence that the diffusion coefficient tended to vary with conditions and that better proportionality could be obtained if the rate of diffusion was related to the gradient of chemical potential; this law is due to Hartley. Figure 20.7 shows an adiabatic system made up of two parts connected by a porous membrane, or a pipe with a bore which is small compared to the mean free path of the molecules.

20.7.1.1 The Soret effect

This is a thermal diffusion effect. It is characterised by the setting up of a concentration gradient as a result of a temperature gradient.

20.7.1.2 The Dufour effect

This is the inverse phenomena to the Soret effect and is the nonuniformity of temperature encountered due to concentration gradients.

20.7.2 DEFINING THE FORCES AND FLUXES

To choose the forces and fluxes, it is necessary to consider the rate of entropy generation (see Section 20.4, and de Groot (1951)). Suppose that a system comprising two parts, I and II, connected by a hole, is enclosed in a reservoir. It will be assumed that both parts are the same volume, V , and when in thermostatic equilibrium the energy, U , and mass, m , in each part is equal, and there is an entropy, S , associated with each part of the system. (U and m were chosen as parameters because these obey conservation laws.)

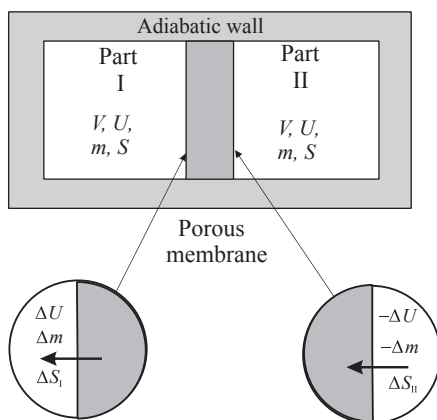


FIGURE 20.7

Schematic diagram of two containers connected by a porous membrane, or small bore pipe.

The system is isolated, hence variations ΔU and Δm in part I give rise to variations $-\Delta U$ and $-\Delta m$ in part II. The variation in entropy due to these changes may be found from Taylor's series.

$$\Delta S_I = \left(\frac{\partial S}{\partial U}\right)_m \Delta U + \left(\frac{\partial S}{\partial m}\right)_U \Delta m + \frac{1}{2} \left(\frac{\partial^2 S}{\partial U^2}\right) \Delta U^2 + \left(\frac{\partial^2 S}{\partial U \partial m}\right) \Delta U \Delta m + \frac{1}{2} \left(\frac{\partial^2 S}{\partial m^2}\right) \Delta m^2 \quad (20.70)$$

+higher order terms

ΔS_{II} may be found by a similar expansion, but the linear terms in ΔU and Δm are negative. Thus, the change of entropy of the universe is

$$\begin{aligned} \Delta S &= \Delta S_I + \Delta S_{II} \\ &= \left(\frac{\partial^2 S}{\partial U^2}\right)_m \Delta U^2 + 2 \frac{\partial^2 S}{\partial U \partial m} \Delta U \Delta m + \left(\frac{\partial^2 S}{\partial m^2}\right)_U \Delta m^2 + \text{higher order terms} \dots \end{aligned} \quad (20.71)$$

The time rate of change of ΔS , i.e. the rate of generation of entropy, is given by

$$\begin{aligned} \frac{d}{dt}(\Delta S) &= \left(\frac{\partial^2 S}{\partial U^2}\right) (2\Delta U) \Delta \dot{U} + 2 \left(\frac{\partial^2 S}{\partial U \partial m}\right) \Delta m \Delta \dot{U} + \left(\frac{\partial^2 S}{\partial U \partial m}\right) \Delta U \Delta \dot{m} + \left(\frac{\partial^2 S}{\partial m^2}\right) (2\Delta m) \Delta \dot{m} \\ &= 2\Delta \dot{U} \left\{ \left(\frac{\partial^2 S}{\partial U^2}\right) \Delta U + \left(\frac{\partial^2 S}{\partial U \partial m}\right) \Delta m \right\} + 2\Delta \dot{m} \left\{ \left(\frac{\partial^2 S}{\partial m^2}\right) \Delta m + \left(\frac{\partial^2 S}{\partial U \partial m}\right) \Delta U \right\} \\ &= 2\Delta \dot{U} \Delta \left(\frac{\partial S}{\partial U}\right)_m + 2\Delta \dot{m} \Delta \left(\frac{\partial S}{\partial m}\right)_U \end{aligned} \quad (20.72)$$

and the rate of generation of entropy per *unit volume* is

$$\frac{d}{dt}(\Delta S) = \frac{1}{2} \frac{d}{dt}(\Delta S) = \Delta \dot{U} \Delta \left(\frac{\partial S}{\partial U}\right)_m + \Delta \dot{m} \Delta \left(\frac{\partial S}{\partial m}\right)_U, \quad (20.73)$$

because the combined volume of systems I and II is $2V$, and the original terms were defined in relation to a single part of the system.

It was stated in [Eqn \(20.12\)](#), from Onsager's Relationship, that for a two-component system

$$T\theta = J_1 X_1 + J_2 X_2$$

which may be written, for this system, as

$$T\theta = \frac{d}{dt}(\Delta S) = J_U X_U + J_m X_m \quad (20.74)$$

Comparison of [Eqns \(20.73\) and \(20.74\)](#) enables the forces and fluxes to be defined, giving

$$\left. \begin{aligned} J_U &= \Delta \dot{U} & X_U &= \Delta \left(\frac{\partial S}{\partial U}\right)_m \\ J_m &= \Delta \dot{m} & X_m &= \Delta \left(\frac{\partial S}{\partial m}\right)_U \end{aligned} \right\} \quad (20.75)$$

From first and Second Laws, for a system at constant pressure

$$Tds = du + pdv - \mu dm \quad (20.76)$$

Hence

$$\Delta \left(\frac{\partial s}{\partial u} \right)_m = \Delta \left(\frac{\partial S}{\partial U} \right)_m = \Delta \left(\frac{1}{T} \right) = - \frac{\Delta T}{T^2} \quad (20.77)$$

$$\Delta \left(\frac{\partial S}{\partial m} \right)_U = - \Delta \left(\frac{\mu}{T} \right) = - \frac{T \Delta \mu - \mu \Delta T}{T^2} = - \frac{\Delta \mu}{T} + \mu \frac{\Delta T}{T^2} \quad (20.78)$$

Substituting for

$$\Delta \mu = v \Delta p - s \Delta T \quad (20.79)$$

and

$$h = \mu + Ts = u + pv \quad (20.80)$$

gives

$$\Delta \left(\frac{\partial S}{\partial m} \right)_U = -v \frac{\Delta p}{T} + s \frac{\Delta T}{T} + h \frac{\Delta T}{T^2} - Ts \frac{\Delta T}{T^2} = -v \frac{\Delta p}{T} + h \frac{\Delta T}{T^2} \quad (20.81)$$

Hence substituting these values in Eqn (20.8),

$$J_U = L_{11} X_U + L_{12} X_m$$

$$J_m = L_{21} X_U + L_{22} X_m$$

gives

$$\begin{aligned} J_U &= -L_{11} \frac{\Delta T}{T^2} + L_{12} \left(-v \frac{\Delta p}{T} + h \frac{\Delta T}{T^2} \right) \\ &= \left(\frac{hL_{12} - L_{11}}{T^2} \right) \Delta T - \frac{L_{12}}{T} v \Delta p \end{aligned} \quad (20.82)$$

and

$$\begin{aligned} J_m &= -\frac{L_{21} \Delta T}{T^2} + L_{22} \left(-v \frac{\Delta p}{T} + h \frac{\Delta T}{T^2} \right) \\ &= \left(\frac{hL_{22} - L_{21}}{T^2} \right) \Delta T - \frac{L_{22}}{T} v \Delta p. \end{aligned} \quad (20.83)$$

If the flow of internal energy which occurs due to the diffusion is defined as $\left(\frac{J_U}{J_m} \right)_{\Delta T=0} = U^*$ then

$$U^* = \left(\frac{J_U}{J_m} \right)_{\Delta T=0} = \frac{L_{12} v \Delta p}{T} \frac{T}{L_{22} v \Delta p} \quad (20.84)$$

i.e.

$$L_{12} = L_{22}U^* = L_{21} \quad (20.85)$$

In the stationary state, $J_m = 0$; i.e.

$$\frac{\Delta p}{\Delta T} = \left(\frac{hL_{22} - L_{21}}{T^2} \right) \frac{T}{L_{22}v} = \frac{h - \frac{L_{21}}{L_{22}}}{vT} = \frac{h - U^*}{vT} \quad (20.86)$$

Now, the term $h - U^*$ may be defined as $-Q^*$, and the significance of this is that it drives the system to generate a pressure gradient due to the temperature gradient. Hence, if two systems are connected together with a concentration (or more correctly, a chemical potential) gradient then a pressure difference will be established between the systems until $h = U^*$.

The pressure difference is defined as

$$\frac{\Delta p}{\Delta T} = -\frac{Q^*}{vT}. \quad (20.87)$$

The significance of this result will be returned to in [Section 20.7.3.3](#).

20.7.3 THE UNCOUPLED EQUATIONS OF DIFFUSION

It is also possible to derive the result in [Eqn \(20.87\)](#) in a more easily understandable manner, if the fluxes and forces defined above are simply accepted without proof.

20.7.3.1 Diffusion

For the uncoupled process of diffusion, it was shown in [Eqn \(20.78\)](#) that the thermodynamic force for component i , in one-dimensional diffusion, is

$$X_i = -T \frac{\partial(\mu_i/T)}{\partial x} \quad (20.88)$$

where

μ_i = chemical potential.

Evaluating the differential in [Eqn \(20.88\)](#) gives, as shown in [Eqn \(20.78\)](#)

$$\begin{aligned} X_i &= -T \left[\frac{T \frac{\partial \mu}{\partial x} - \mu \frac{\partial T}{\partial x}}{T^2} \right] \\ &= -\frac{\partial \mu}{\partial x} + \frac{\mu}{T} \frac{\partial T}{\partial x} \end{aligned} \quad (20.89)$$

[Equation \(20.89\)](#) applies for a single component only, but it is possible to derive the equations for multicomponent mixtures.

If Onsager's rule for entropy flux is applied to this situation, [Eqn \(20.12\)](#)

$$T\theta = \sum JX$$

Thus

$$T\theta = -J_m \frac{\partial \mu}{\partial x} + \frac{J_m}{T} \mu \frac{\partial T}{\partial x} \quad (20.90)$$

Hence the entropy production per unit volume, θ , is given as

$$\theta = \underbrace{-\frac{J_m}{T} \frac{\partial \mu}{\partial x}}_{\text{Due to isothermal diffusion}} + \underbrace{\frac{J_m}{T^2} \mu \frac{\partial T}{\partial x}}_{\text{Due to temperature gradient}}. \quad (20.91)$$

20.7.3.2 Coupled diffusion and heat processes

Such processes are also referred to as heat and mass transfer processes. Consider the system shown in Fig. 20.7. The equations governing the flow processes are the following:

Heat

$$J_Q = L_{11}X_1 + L_{12}X_2 \quad (20.92)$$

Diffusion (Mass Transfer)

$$J_m = L_{21}X_1 + L_{22}X_2 \quad (20.93)$$

The thermodynamic forces have been previously defined. For the heat transfer process $X_1 = -\frac{1}{T} \frac{dT}{dx}$ (see Section 20.6.2). For the mass transfer process $X_2 = -T \frac{\partial(\mu/T)}{\partial x}$ (see Section 20.7.2).

Thus, from Eqn (20.92)

$$J_Q = -\frac{L_{11}}{T} \frac{dT}{dx} - L_{12}T \frac{d(\mu/T)}{dx} \quad (20.94)$$

and, from Eqn (20.93)

$$J_m = -\frac{L_{21}}{T} \frac{dT}{dx} - L_{22}T \frac{d(\mu/T)}{dx} \quad (20.95)$$

Consider the steady state, i.e. when there is no flow between the two vessels and $J_m = 0$.

Consider the effect on J_Q , which can be calculated from Eqn (20.95)

$$-\frac{L_{21}}{T} \frac{dT}{dx} = L_{22}T \frac{d(\mu/T)}{dx} \quad (20.96)$$

or

$$d(\mu/T) = -\frac{L_{21}}{L_{22}} \frac{dT}{T^2} \quad (20.97)$$

Now $(\mu/T) = f(T, p) = (\mu/T)(T, p)$, and hence

$$d(\mu/T) = \left(\frac{\partial(\mu/T)}{\partial T} \right)_p dT + \left(\frac{\partial(\mu/T)}{\partial p} \right)_T dp. \quad (20.98)$$

The specific enthalpy, h , can be related to this parameter by

$$h = -T^2 \left(\frac{\partial(\mu/T)}{\partial T} \right). \quad (20.99)$$

Rearranging Eqn (20.99) gives

$$\left(\frac{\partial(\mu/T)}{\partial T} \right)_p = -\frac{h}{T^2}. \quad (20.100)$$

The term $\left(\frac{\partial(\mu/T)}{\partial p} \right)_T = \frac{1}{T} \left(\frac{\partial\mu}{\partial p} \right)_T$, because $T = \text{constant}$, and from the definition of chemical potential, μ , the term

$$d\mu = dg = vdp + sdT. \quad (20.101)$$

Thus

$$\left(\frac{\partial\mu}{\partial p} \right)_T = v. \quad (20.102)$$

Substituting for $\left(\frac{\partial(\mu/T)}{\partial T} \right)_p$ and $\left(\frac{\partial(\mu/T)}{\partial p} \right)_T$ in Eqn (20.98) gives

$$d(\mu/T) = -\frac{h}{T^2} dT + \frac{v}{T} dp. \quad (20.103)$$

Hence from Eqns (20.97) and (20.103)

$$-\frac{h}{T^2} dT + \frac{v}{T} dp = -\frac{L_{21}}{L_{22}} \frac{dT}{T^2} \quad (20.104)$$

giving

$$v dp = \left\{ h - \frac{L_{21}}{L_{22}} \right\} \frac{dT}{T} \quad (20.105)$$

If both vessels were at the same temperature then $\frac{dT}{dx} = 0$ and

$$J_Q|_T = -L_{12} T \frac{d(\mu/T)}{dx} \quad (20.106)$$

$$J_m|_T = -L_{22} T \frac{d(\mu/T)}{dx} \quad (20.107)$$

Thus, as shown in Eqn (20.84)

$$\left(\frac{J_Q}{J_m} \right)_T = \frac{L_{12}}{L_{22}} \quad (20.108)$$

The ratio $\left(\frac{J_Q}{J_m} \right)_T$ is the energy transported when there is *no* heat flow through thermal conduction.

Also from Onsager's reciprocal relation $\left(\frac{J_Q}{J_m} \right)_T = \frac{L_{21}}{L_{22}}$. If this ratio is denoted by the symbol U^* then Eqn (20.105) can be written, from Eqn (20.86)

$$\frac{dp}{dT} = \frac{(h - U^*)}{vT}.$$

Now the difference $h - U^*$ may be denoted $-Q^*$, which is called the *heat of transport*.

Using this definition Eqn (20.86) may be rewritten

$$\frac{dp}{dT} = -\frac{Q^*}{vT}$$

20.7.3.3 The significance of Q^*

Q^* is the heat transported from region I to region II by diffusion of the fluid. It is a measure of the difference in energy associated with the gradient of chemical potential. In a simple case, it is possible to evaluate Q^* . Weber showed by kinetic theory that when a gas passes from a vessel into a porous plate it has a decrease in the energy it carries. The energy carried by the gas molecule in molecular flow through the passages in the porous medium is smaller by $RT/2$ than it was when the motion was random.

Hence $Q^* = -RT/2$ for flow through a porous plug. The energy, Q^* , is liberated when the molecules enter the plug and the same amount is absorbed when the molecules emerge from the plug. When Q^* is dependent on temperature, as in the thermal effusion case, it would appear reasonable that if Q^* is liberated on entering the plug at temperature T then $Q^* + dQ^*$ would be absorbed on the molecule leaving the plug, when the general temperature is $T + dT$. This is erroneous and a qualitative explanation follows. Q^* is the amount by which the mean energy per unit mass of molecules which are in the process of transit through the plug exceeds the mean energy of the bulk of the fluid. Hence, if Q^* were not applicable to both sides of the plug then the principle of conservation of energy would be contravened. The difference of average values of the bulk fluid energy on either side of the plug has been taken into account by the different values of the enthalpy, h , on each side of the plug.

Now, if

$$Q^* = -RT/2, \quad (20.109)$$

and for a perfect gas

$$pv = RT \quad (20.110)$$

then

$$\frac{dp}{dT} = -\frac{Q^*}{vT} = \frac{RT}{2vT} = \frac{R}{2v} = \frac{p}{2T} \quad (20.111)$$

Integrating across plug from side I to side II.

$$\ln \frac{p_{II}}{p_I} = \frac{1}{2} \ln \frac{T_{II}}{T_I} \quad (20.112)$$

or

$$\frac{p_{II}}{p_I} = \sqrt{\frac{T_{II}}{T_I}}. \quad (20.113)$$

This is called the *Knudsen* equation for molecular flow. From Eqn (20.87) over an increment of distance, Δx

$$\Delta p = -\frac{Q^*}{vT}\Delta T. \quad (20.87a)$$

This means that if Q^* is negative, as in the thermal effusion case, the pressure increment is of the same sign as the temperature increment and molecules *flow* from the cold side to the hot side.

20.7.4 THERMAL TRANSPIRATION

It will be shown in this section without recourse to Onsager's relationship, that $L_{12} = L_{21}$. This derivation will be based on statistical mechanics, and this is the manner by which Onsager derived his relationship. The problem considered is similar to that discussed in Section 20.7.3, when flow through a porous plug was examined. In this case, the flow will be assumed to occur along a small bore pipe in which the cross-sectional area is small compared to the mean free path of the molecules: this is what happens when gas flows through the pores in a porous membrane.

It can be shown from statistical thermodynamics that the number of particles striking a unit area in unit time is

$$\frac{\dot{n}_c}{A} = \frac{p}{(2\pi kTm)^{1/2}}. \quad (20.114)$$

where

- $\dot{n}_c$ = number of particles striking wall;
- A = area of wall;
- p = 'pressure' of gas;
- k = Boltzmann's constant;
- T = temperature; and
- m = mass of 'particle'.

Consider a hole of area A , then $\dot{n}_c$ would be the number of particles passing through this hole. These particles would carry with them kinetic energy. The hole also makes a selection of the atoms which will pass through it and favours those of a higher energy because the frequency of higher velocity particles hitting the wall is higher. It can be shown that the energy passing through the hole is given by

$$\frac{\dot{E}}{A} = p \left(\frac{2kT}{\pi M} \right)^{1/2}. \quad (20.115)$$

Equations (20.114) and (20.115) may be written in the form

$$\frac{\dot{n}_c}{A} = \left(\frac{p}{\tilde{N}kT} \right) \left(\frac{kT}{2m} \right)^{1/2} \left(\frac{\tilde{N}m^{1/2}}{\pi^{1/2}} \right) \quad (20.116)$$

$$\frac{\dot{E}}{A} = \left(\frac{p}{\tilde{N}kT} \right) \left(\frac{kT}{2m} \right)^{1/2} \left(\frac{3}{2}kT \right) \left(\frac{4\tilde{N}}{3\pi^{1/2}} \right) \quad (20.117)$$

where

$\tilde{N}$ = Avogadro's number.

The groups of terms can be defined in the following way:

$$\left(\frac{p}{\tilde{N}kT}\right) \equiv \text{density}$$

$$\left(\frac{kT}{2m}\right)^{1/2} \equiv \text{velocity}$$

$$\frac{3}{2}kT \equiv \text{energy}.$$

$$\frac{\tilde{N}m^{1/2}}{\pi^{1/2}} \text{ and } \frac{4\tilde{N}}{3\pi^{1/2}} \text{ are weighting factors.}$$

Thus

$$\frac{\dot{n}_c}{A} = \text{density} \times \text{mean velocity}.$$

$$\frac{\dot{E}}{A} = \text{density} \times \text{mean velocity} \times \text{mean energy}$$

The weighting factors show that the particles passing through area A carry with them an unrepresentative sample of the energy of the system from which they come.

This example can be expanded into an apparatus which contains two systems separated by a porous wall. It will be assumed that the pores in the wall are much shorter than the mean free path of the molecules. The system is shown in Fig. 20.8. The gases on either side of the partition are the same, but one side of the system is heated and the other side is cooled.

From Eqn (20.114) the net flux of molecules passing through the wall is given by

$$\frac{\dot{n}'_c - \dot{n}_c}{A} = (2\pi km)^{-1/2} \left[\frac{p'}{\sqrt{T'}} - \frac{p}{\sqrt{T}} \right] \quad (20.118)$$

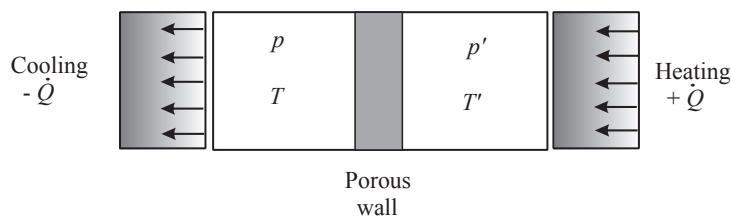


FIGURE 20.8

Arrangement for flow through a porous plug.

and the net energy passing through the wall is given from Eqn (20.115) as

$$\frac{\dot{E}' - \dot{E}}{A} = \left(\frac{2k}{\pi m}\right)^{1/2} [p'T'^{1/2} - pT^{1/2}] \quad (20.119)$$

It is possible to substitute for the pressure of a monatomic gas by the expression

$$p = e^{-\alpha} h^{-3} (2\pi m)^{3/2} \beta^{-5/2} \quad (20.120)$$

and the temperature by

$$T = 1/k\beta. \quad (20.121)$$

Then Eqns (20.118) and (20.119) become:

$$\frac{\dot{E}}{A} = (4\pi m h^{-3}) [e^{-\alpha} \beta^{-3} - e^{-\alpha'} \beta'^{-3}] \quad (20.122)$$

$$\frac{\dot{n}_c}{A} = (2\pi m h^{-3}) [e^{-\alpha} \beta^{-2} - e^{-\alpha'} \beta'^{-2}] \quad (20.123)$$

If the state denoted by the primed symbols is constant, then differentiating gives

$$d\left(\frac{\dot{E}}{A}\right) = (2\pi m h^{-3}) \beta^{-3} e^{-\alpha} [-6\beta^{-1} d\beta - 2 d\alpha] \quad (20.124)$$

$$d\left(\frac{\dot{n}_c}{A}\right) = (2\pi m h^{-3}) \beta^{-3} e^{-\alpha} [-2d\beta - \beta d\alpha] \quad (20.125)$$

Equations (20.124) and (20.125) may be written in the form

$$d\left(\frac{\dot{E}}{A}\right) = L_{\dot{E},\beta} d\beta + L_{\dot{E},\alpha} d\alpha \quad (20.126)$$

and

$$d\left(\frac{\dot{n}_c}{A}\right) = L_{\dot{n}_c,\beta} d\beta + L_{\dot{n}_c,\alpha} d\alpha \quad (20.127)$$

where

$$\left. \begin{aligned} L_{\dot{E},\beta} &= -12\pi m \beta^{-4} h^{-3} e^{-\alpha} \\ L_{\dot{E},\alpha} &= -4\pi m \beta^{-3} h^{-3} e^{-\alpha} \\ L_{\dot{n}_c,\beta} &= -4\pi m \beta^{-3} h^{-3} e^{-\alpha} \\ L_{\dot{n}_c,\alpha} &= -2\pi m \beta^{-2} h^{-3} e^{-\alpha}. \end{aligned} \right\}$$

Hence $L_{\dot{E},\alpha} = L_{\dot{n}_c,\beta}$, which is equivalent to the result given by Onsager, that $L_{12} = L_{21}$, and has been proved from statistical thermodynamics.

20.8 CONCLUDING REMARKS

This chapter has extended ‘thermodynamics’ into a truly dynamic arena. The processes involved are nonequilibrium ones which are in a steady, dynamic state. The concepts of entropy generation and coupled phenomena have been introduced, and Onsager’s reciprocal relationship has been used to enable the latter to be analysed.

Thermoelectric phenomena have been considered and the coupling between them has been described. The major thermoelectric effects have been defined in terms of the thermodynamics of the device. Coupled diffusion and heat transfer processes have been introduced and analysed using these techniques, and the conjugate forces and fluxes have been developed. Finally, statistical thermodynamics was used to demonstrate that Onsager’s reciprocal relation could be developed from molecular considerations.

20.9 PROBLEMS

P20.1 The emf of a copper–iron thermocouple caused by the Seebeck effect, with a cold junction at 0 °C, is given by

$$\varepsilon = \alpha_1 t + \frac{\alpha_2}{2} t^2 + \frac{\alpha_3}{3} t^3 \quad \text{V}$$

where

$$\begin{aligned}\alpha_1 &= -13.403 \times 10^{-6} \text{ V/}^\circ\text{C}; \\ \alpha_2 &= +0.0275 \times 10^{-6} \text{ V/}^\circ\text{C}^2; \\ \alpha_3 &= +0.00026 \times 10^{-6} \text{ V/}^\circ\text{C}^3; \text{ and} \\ t &= \text{temperature (}^\circ\text{C)}.\end{aligned}$$

If the hot junction is at $t = 100^\circ\text{C}$, calculate

- the Seebeck emf;
- the Peltier effect at the hot and cold junctions;
- the net Thomson emf;
- the difference between the entropy of transport of the copper and iron.

[1.116 mV; 3.66 mV; 3.00 mV; *, $-8.053 \times 10^{-6} \text{ V}$]

P20.2 The emf of a copper–iron thermocouple with its cold junction at 0 °C is given by

$$\varepsilon = -13.403t + 0.0138t^2 + 0.0001t^3 \quad \mu\text{V}$$

where $t = \text{temperature (}^\circ\text{C)}$.

Show that the difference in the Thomson coefficient for the two wires is

$$7.535 + 0.1914t + 0.0006t^2 \quad \mu\text{V/}^\circ\text{C}$$

P20.3 A fluid consisting of a single component is contained in two containers at different temperatures. Show that the difference in pressure between the two containers is given by

$$\frac{dp}{dT} = \frac{h - u^*}{vT},$$

where

h = specific enthalpy of the fluid at temperature T ;

u^* = the energy transported when there is no heat flow through thermal conduction;

v = specific volume; and

T = temperature.

- P20.4** A thermocouple is connected across a battery, and a current flows through it. The cold junction is connected to a reservoir at 0°C . When its hot junction is connected to a reservoir at 100°C the heat flux due to the Peltier effect is 2.68 mW/A , and when the hot junction is at 200°C the effect is 4.11 mW/A . If the emf of the thermocouple due to the Seebeck effect is given by $\varepsilon = at + bt^2$, calculate the values of the constants a and b . If the thermocouple is used to measure the temperature effect based on the Seebeck effect, i.e. there is no current flow, calculate the voltages at 100°C and 200°C .

[$5.679 \times 10^{-3}\text{ mV/K}$; $7.526 \times 10^{-3}\text{ mV/(K)}^2$; 0.6432 mV ; 1.437 mV]

- P20.5** A pure monatomic perfect gas with $c_p = 5R/2$ flows from one reservoir to another through a porous plug. The heat of transport of the gas through the plug is $-RT/2$. If the system is adiabatic, and the thermal conductivities of the gas and the plug are negligible, evaluate the temperature of the plug if the upstream temperature is 60°C .

[73°C]

- P20.6** A thermal conductor with constant thermal and electrical conductivities, k and λ respectively, connects two reservoirs at different temperatures and also carries an electrical current of density, J_1 . Show that the temperature distribution for one-dimensional flows is given by

$$\frac{d^2T}{dx^2} - \frac{J_1\sigma}{k} \frac{dT}{dx} + \frac{J_1^2}{\lambda} = 0$$

where σ is the Thomson coefficient of the wire.

- P20.7** A thermal conductor of constant cross-sectional area connects two reservoirs which are both maintained at the same temperature, T_0 . An electric current is passed through the conductor, and heats it due to Joulean heating and the Thomson effect. Show that if the thermal and electrical conductivities, k and λ , and the Thomson coefficient, σ , are constant the temperature in the conductor is given by

$$T - T_0 = \frac{J_1 k}{\lambda \sigma L} \left(\frac{x}{L} \right) - \frac{J_1 k}{\lambda \sigma L \left(e^{\frac{J_1 \sigma L}{k}} - 1 \right)} \left(e^{\frac{J_1 \sigma L}{k} \left(\frac{x}{L} \right)} - 1 \right).$$

Show that the maximum temperature is achieved at a distance

$$\left(\frac{x}{L} \right) = \frac{k}{J_1 \sigma L} \ln \left\{ \frac{k \left(e^{\frac{J_1 \sigma L}{k}} - 1 \right)}{J_1 \sigma L} \right\}.$$

Evaluate where the maximum temperature will occur if $\frac{J_1 \sigma L}{k} = 1$, and explain why it is not in the centre of the bar. Show that the maximum temperature achieved by Joulean heating alone is in the centre of the conductor.

[$x/L = 0.541$].

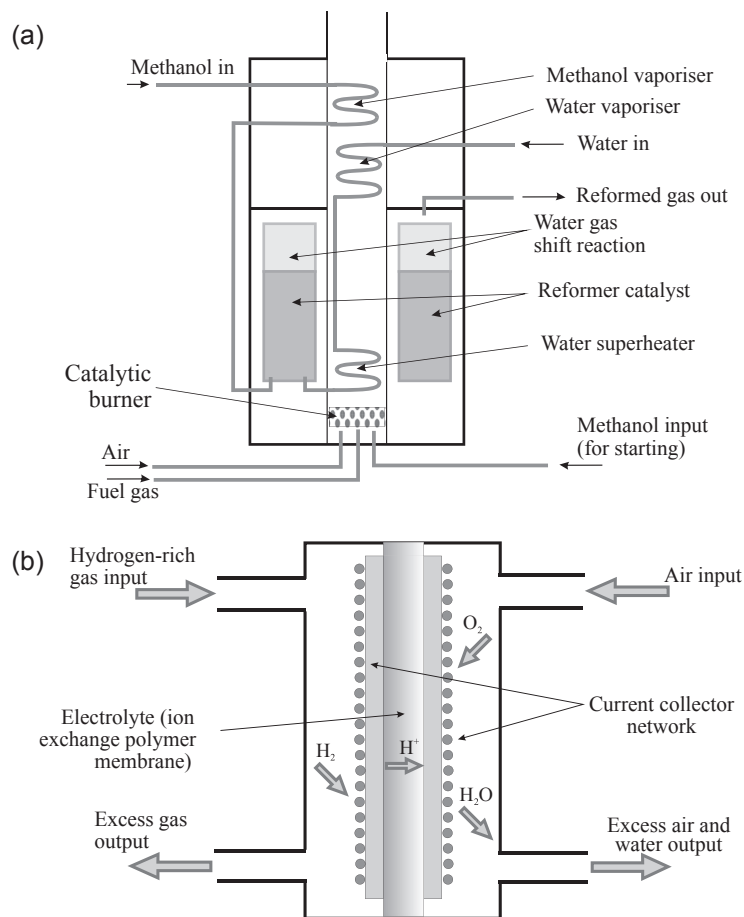
FUEL CELLS

21

Engineering thermodynamics concentrates on the production of work through cyclic devices, e.g. the power to drive a vehicle as produced by a reciprocating engine; the production of electricity by means of a steam turbine. As shown previously, these devices are all based on converting part of the Gibbs energy of the fuel to useful work, and if an engine is used, some energy must be thrown away: all engines are limited by the Carnot, or Second Law, efficiency.

However, there are some devices which are capable of converting the Gibbs energy of the fuel directly to electricity (a form of work): these are called *fuel cells*. The advantage of a fuel cell is that it is not a heat engine, and it is not limited by the Carnot efficiency. The thermodynamics of fuel cells will be developed below.

The concept of the fuel cell arises directly from the operating principle of the electric cell, e.g. the Daniell cell (see [Section 21.2](#)), and as early as 1880 Wilhelm Ostwald wrote “I do not know whether all of us realise fully what an imperfect thing is the most essential source of power which we are using in our highly developed engineering - the steam engine”. He realised that chemical processes could approach efficiencies of 100% in galvanic cells, and these were not limited by the Carnot efficiency. Conversion efficiencies as high as 60–80% have been achieved for fuel cells operating in hybrid systems, whereas the maximum practical limit even for sophisticated rotating machinery, as shown in earlier chapters, is not much above 50%. A further benefit of the fuel cell is that its efficiency is not reduced by part load operation, as is the case for all heat engines. Hence, if a fuel cell operating on hydrocarbon fuels can be developed, it will improve ‘thermal efficiency’ significantly and reduce pollution by CO_2 and NO_x . The current situation is that successful commercial fuel cells are still some way from general use but small ones have been used in specialist applications (e.g. space craft) and large ones are being developed (e.g. 1 MW by Tokyo Gas, Japan). Winterbone (2000) analyses the position of fuel cells relative to that of ‘heat engines’ and shows that there is significant potential for their development as power plant, but much work remains to be done. [Figure 21.1](#) shows a proposal for a fuel cell to power a motor vehicle using methanol (CH_3OH) as its primary fuel. In this case, the methanol is used to generate hydrogen for use in a hydrogen–oxygen fuel cell. [Figure 21.1\(a\)](#) shows the hydrogen generator which is based on the water-gas reaction, and [Fig. 21.1\(b\)](#) depicts the fuel cell itself. This arrangement has the advantage that the fuel can be carried in its liquid phase at atmospheric conditions, which is much more convenient than carrying hydrogen either in gas, liquid, or hydride form.

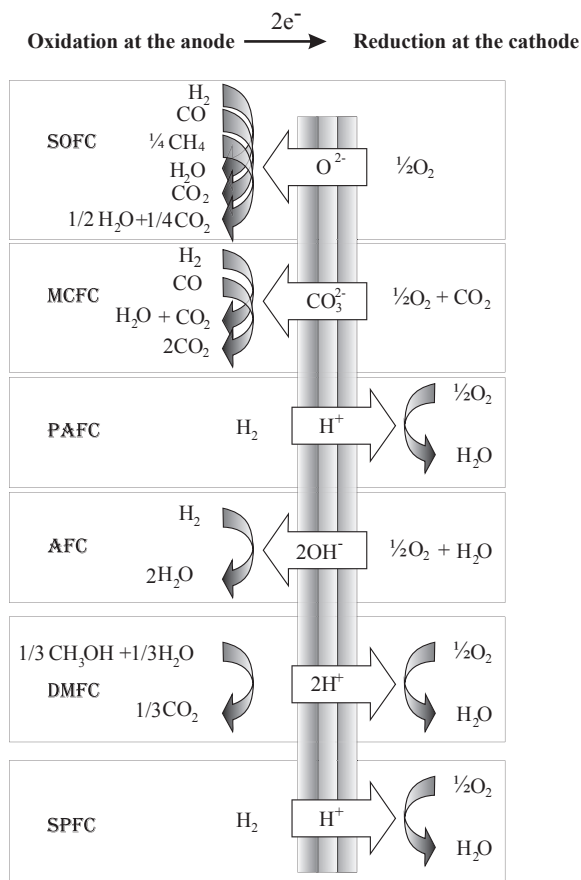
**FIGURE 21.1**

Proposed hydrogen fuel cell for vehicle applications.

The situation with respect to fuel cells in automotive applications is still very much under development. The major player in developing automotive fuel cells, Ballard (wiki (2014a)), pulled out of the hydrogen vehicle sector of its business in 2007: it sold it to Daimler AG (50.1%) and Ford Motor Company (49.9%). In 2013, they signed a three-way agreement with Nissan Motor Company to develop the world's first affordable, mass-market fuel cell electric vehicles as early as 2017 (wiki (2014b)).

21.1 TYPES OF FUEL CELLS

Fuel cells are an extremely active area of scientific and engineering research and many different types have been developed. Fig. 21.2 is a schematic showing most of the different types of cells available today. It can be seen that there is a wide range of devices, each using a different chemical process to produce electrical power output.

**FIGURE 21.2**

A cross-sectional view of a hypothetical “fuel cell” showing the different types of fuel cell, the ions that migrate, for the each type of fuel cell. At the square end of both the curved and straight arrows are the reactants, and at the pointed end are the products of the electrochemical reaction. On the left, the abbreviations of the fuel cell names: SOFC = Solid Oxide Fuel Cell, MCFC = Molten Carbonate Fuel Cell, PAFC = Phosphoric Acid Fuel Cell, AFC = Alkaline Fuel Cell, SPFC = Solid Polymer Fuel Cell, and DMFC = Direct Methanol Fuel Cell.

Fuel cells are described by their electrolyte:

- Alkaline – AFC
- Phosphoric acid – PAFC
- Solid polymer – SPFC (*also referred to as proton exchange membrane – PEMFC*)
- Molten carbonate – MCFC
- Solid oxide – SOFC.

The reactions shown in Fig. 21.2, with hydrogen ion (proton) transfer through the electrolyte, are only applicable to fuel cells with acid electrolytes and SPFC. Fig. 21.2 shows the reactions in each of the fuel cell types currently under development.

21.1.1 ALKALINE FUEL CELL

The AFC uses a liquid electrolyte of aqueous potassium hydroxide (KOH), which is a strong base. Alkali metal hydroxides quickly absorb CO_2 to form carbonates ($\text{KOH} \rightarrow \text{K}_2\text{CO}_3$), so for this reason the AFC cannot operate with reformed gases but requires pure hydrogen. The electrolyte, if in liquid form, can be circulated in a system to reduce concentration polarisation at the interface with the electrode when ions are depleted. An asbestos matrix can also be used to hold the electrolyte.

In the AFC, developed by Bacon between 1940 and 1946, an alkaline, or basic, electrolyte was chosen over an acidic medium to decrease the thermodynamic possibility of corrosion of the electrodes. The basic solution allowed the use of nickel, but to compensate for its lower catalytic activity, the operating temperature was raised to improve the reaction rate at the electrodes, and the operating pressure was raised to increase the voltage at chemical equilibrium. The fuel cells on the space shuttle operate at a lower temperature and have to resort to platinum electrodes for higher activity. Gold can be added to the surface of the catalyst to serve as a hydrophilic particle, forming a network of wettable surfaces that passively allows liquid transport.

Tomantschger and co-workers (1986) developed a low-cost version of the AFC that uses a carbon substrate (either cloth or paper), Polytetrafluoroethylene (PTFE) binder and hydrophobic material, carbon black (acetylene or furnace black) for catalyst support, and catalyst. Carbon itself is active as a catalyst for the oxygen electrode, but it is usually enhanced by the addition of silver, platinum, palladium (Kordes and Marko (1952) cited by Williams (1966, p.98)). The catalyst can be a noble metal or a base metal: palladium/rhodium (Pd/Rh) at a loading of 1 mg/cm^2 for the anode and 0.5 mg Pt/cm^2 on the cathode; a metal oxide that decomposes peroxide (an intermediate compound formed at the cathode) can be used on the cathode.

21.1.2 SOLID POLYMER FUEL CELL AND DIRECT METHANOL FUEL CELL

Grubb (1955) conceived the idea of using an *ion-exchange resin* (a solid polymer membrane) as the electrolyte for a fuel cell. The solid polymer used in present technology is a perfluorinated sulphonic acid membrane that conducts protons by the sulphonic acid groups held by the fluorinated polymer.

The electrodes of the Solid Polymer Fuel Cell (SPFC) are porous to allow the reactant gases, which are distributed on the electrode by the flow field plates, to diffuse to the catalyst and membrane. Platinum or a platinum-based catalyst is used for the anode, because platinum is the only catalyst that can withstand the corrosive environment at the cathode. The catalyst particles are supported on particles of carbon black to increase the dispersion and therefore the surface area for the electrochemical. The SPFC is able to reach its operating temperature ($\sim 80^\circ\text{C}$) relatively quickly from ambient conditions, and that characteristic makes it suitable for transportation applications. It also produces power at high densities, which allows it to satisfy the volume and mass restrictions in a vehicle: Ballard Power Systems have achieved power densities of 1000 W/l and 700 W/kg for fuel cell stacks operating on hydrogen and air at practical conditions for vehicles. A solid electrolyte is better suited for the manufacture of fuel cells in large quantities and also eliminates the difficulty of sealing.

The Direct Methanol Fuel Cell (DMFC) is a variation of the SPFC and shares similar components: carbon substrates, carbon-supported catalysts, and a solid polymer electrolyte. The anode catalyst oxidises methanol, which can be fed in either liquid or vapour form, and the protons migrate to the cathode as in an SPFC. The methanol fuel is diluted with water to a mixture of 3 wt.% methanol and 97 wt.% water. In the reaction, methanol diffuses through the membrane from the anode to the cathode, decreasing the performance of the cathode because of mixed potentials—additional reactions besides the oxygen reduction reaction that lower the total electrode potential. Development of membranes that reduce methanol cross-over is needed to improve the performance.

At Los Alamos National Laboratories (LANL), a DMFC operating near 100 °C produced 0.28 W/cm² peak power with a platinum catalyst loading of 2.6 mg/cm² (10 g Pt/W) (Ren et al., (1998, p.57)). The power density of the cell will have to reach at least 0.2 W/cm² for the technology to be applicable in the transportation industry. A fuel reformer is not required in this device (cf. Fig. 21.1) for operation because the anode uses methanol directly without reforming to hydrogen, so the power system is simplified. Also, in comparison to the SPFC, because of the space made available by the absence of the fuel processor, the DMFC can be competitive even with a lower power density and a larger size. Additionally, it may also achieve higher overall conversion efficiencies (based on voltage efficiency and fuel utilisation): the cell at LANL achieved 36% compared to the 30% reported for total systems (including air compressor losses) with a methanol fuel processor and SPFC (Ren et al., (1998, p.57)).

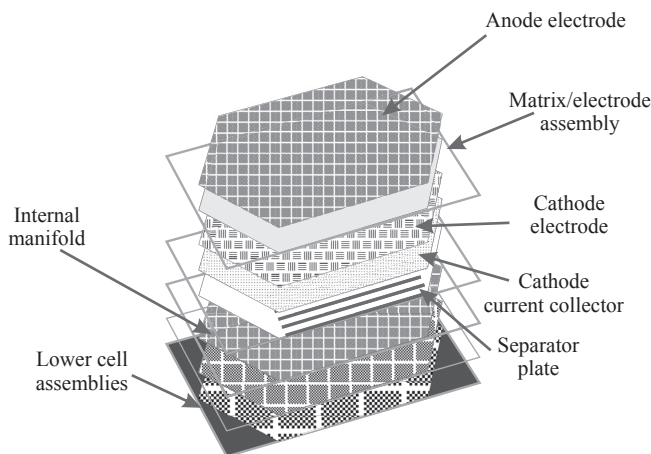
Platinum–ruthenium alloy catalysts are effective for methanol oxidation. The methanol dissociates into six protons and electrons and reacts with water to form carbon dioxide in the oxidation reaction. Currently, the catalyst loadings on the anode are too high at 2 mg/cm² and make the technology expensive.

21.1.3 PHOSPHORIC ACID FUEL CELL

The Phosphoric Acid Fuel Cell (PAFC) has a similar construction to that of the SPFC. The liquid phosphoric acid electrolyte (96 wt.%), H₃PO₄, is held in a matrix of silicon carbide powder (95–98 wt.%) and mixed with a PTFE binder. The anode catalyst is platinum or a platinum alloy (with ruthenium), and the cathode catalyst is platinum. At the anode, platinum is susceptible to *poisoning* from carbon monoxide, which is a by-product of the fuel reforming process; molecules of carbon monoxide adsorb onto the catalyst, block hydrogen from reaching the reaction sites, and lower the performance of the fuel cell. Only platinum can be used at the cathode because the electrolyte is very corrosive at the oxygen reduction potentials and the fuel cell operating temperature (180–200 °C).

To increase the surface area for the reactions, the catalysts are dispersed on carbon black (steam-treated Shawinigan acetylene black or graphitised Vulcan XC-72R), and the carbon-supported catalysts are bound to a substrate (tantalum screen, porous graphite, carbon paper) by PTFE.

The PAFC has been commercialised for stationary power generation after having been developed between 1967 and 1977 in a programme involving gas companies and the Pratt & Whitney Division of the United Aircraft Corporation (now United Technologies Corporation). In 1975, the Power Cell-11 (PC-11) underwent testing, producing 12.5 kW_e with internal steam reforming (SR) of natural gas, and in 1977, a 1 MW_e unit was developed. Today, the PC-25™ Model C, a 200 kW_e unit coupled to a steam reformer, is manufactured by ONSI Corporation ('On-site') as a joint venture between International Fuel Cells LLC (a subsidiary of United Technologies Corporation) and Toshiba Corporation, and is

**FIGURE 21.3**

Molten carbonate fuel cell electrodes designed by the Institute of Gas Research and used by M-C power corporation.

Figure is from the Website: www.mcpower.com/technology. IMHEX[®] Technology: Internally Manifoldd Heat Exchanger.

licensed to Ansaldo CLC for distribution in Europe. The operating temperature for the PAFC is 180–200 °C: in combined-heat-and-power mode, it can heat city water from 13 °C to 60 °C, or with the high-grade heat exchanger, 120 °C for 220 kW of thermal power.

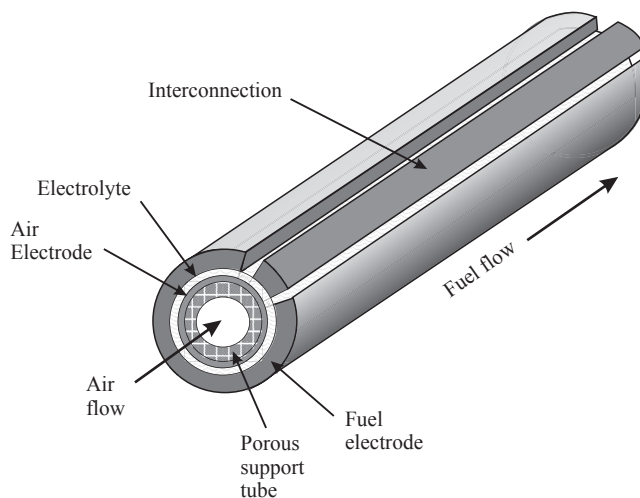
21.1.4 MOLTEN CARBONATE FUEL CELL

The electrolyte of the Molten Carbonate Fuel Cell (MCFC) see Fig. 21.3, is composed of alkali metal carbonates such as lithium carbonate (Li_2CO_3), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), or a mixture of carbonates, for example, 62% Li_2CO_3 and 38% K_2CO_3 . The electrolyte is coated over a porous ceramic matrix made of particles of lithium aluminate (LiAlO_2) or strontium titanate (SrTiO_3), and the matrix, which can measure 180- μm to 500- μm thick, improves the durability to thermal cycling (Iacovangelo & Browall, (1985)). Depending on the melting point of the carbonate composition, the temperatures can reach 500–700 °C. At these high temperatures, internal reforming of natural gas fuel is possible.

The anode electrode is made of strontium titanate and lithium aluminate ceramic particles, which can be plated with nickel, copper and alloys of these for internal reforming of the fuel. The cathode side uses lithium-containing nickel oxide (NiO).

21.1.5 SOLID OXIDE FUEL CELL

The electrolyte for the Solid Oxide Fuel Cell (SOFC) is zirconia stabilised by yttria (also referred to as yttria-stabilised zirconia, $\text{ZrO}_2(\text{Y}_2\text{O}_3)$, and abbreviated YSZ). The yttrium-oxide dopant stabilises the

**FIGURE 21.4**

Tubular solid oxide fuel cell manufactured by Siemens Westinghouse Power Corporation.

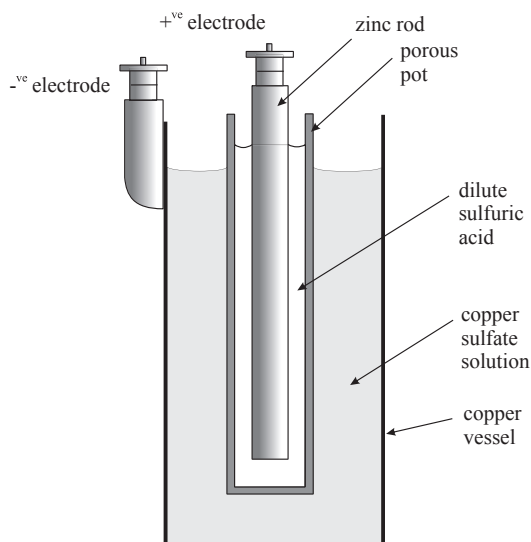
Figure is from the Website: stc.westinghouse.com.

zirconia in its cubic phase, which is the phase with the highest oxygen-ion conductivity. The electrolyte conducts oxygen ions because of oxygen vacancies created in the crystal lattice by the doping material. Oxygen ions jump between interstitial sites aided by the reduction in activation energy from the presence of the defects, and temperatures above 800 °C will give the thermal energy necessary for overcoming the activation energy of oxygen transport (Appleby & Foulkes, (1989, p.305)). At 1000 °C, the conductivity of the electrolyte reaches 1/10th of the molten carbonate electrolyte at 650 °C, so it is at this temperature that the SOFC should operate for competitive performance (Appleby & Foulkes, (1989, p.305)).

The configurations of the electrodes and membrane can be tubular, planar, or monolithic. The electrodes of the tubular SOFCs manufactured by Siemens Westinghouse Power Corporation have an advantage in that the gases are separated from each other by the electrodes, to prevent the mixing of reactants and avoiding the use of seals. The materials for the tubular electrodes are doped lanthanum manganite (doped with strontium, for example, $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$) for the air cathode and nickel-doped YSZ ($\text{Ni-ZrO}_2(\text{Y}_2\text{O}_3)$) for the anode. These electrodes are porous so the reactant gases can reach the interface between the electrodes and electrolyte. Chromium (as LaCrO_3) is used as a metallic *interconnect* that collects current from the anode and connects anodes of adjacent tubes to form an *array* (Singhal, (1999)) (Fig. 21.4).

21.2 THEORY OF FUEL CELLS

The theory of fuel cells can be developed from the previously derived thermodynamic principles, and it shows how equilibrium reversible thermodynamics can be interwoven with irreversible thermodynamics. Before developing the theory of the fuel cell itself, it is necessary to consider simpler electrical

**FIGURE 21.5**

Schematic diagram of Daniell cell.

cells. A good place to start is the Daniell cell which produces electricity through consuming one electrode into solution and depositing onto the other one.

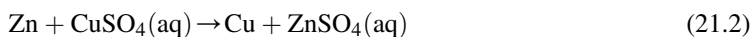
21.2.1 ELECTRIC CELLS

A schematic of a Daniell cell is shown in Fig. 21.5. This can be represented by the convention



where the | represents an interface, or phase boundary. The convention adopted in representing cells in this way is that the electrode at the right-hand side of Eqn (21.1) is positively charged relative to that on the left if the reaction takes place spontaneously.

To understand how the Daniell cell produces a potential and a current, it is necessary to consider the basic reaction involved, viz



which indicates that the zinc reacts with the copper sulphate solution to produce copper and zinc sulphate solution. The notation aq indicates an aqueous solution of the salt. If the reaction in Eqn (21.2) takes place in a constant volume container using 1 kmol Zn (45 kg Zn) then 214,852 kJ of heat must be transferred from the container to maintain the temperature of the system at 25 °C. This reaction is similar to a combustion reaction, and must obey the First Law of Thermodynamics

$$\delta Q = dU + \delta W \quad (21.3)$$

where $\delta W = 0$ in this case.

Hence

$$\delta Q_{oc} = -214852 \text{ kJ/kmol Zn} = u_{Cu} + u_{ZnSO_4(aq)} - u_{Zn} - u_{CuSO_4(aq)} \quad (21.4)$$

The reaction described above is basically an *open circuit reaction* for a Daniell cell, and δQ_{oc} represents the open circuit energy released. If, as is more usual, the reaction takes place while work is being taken from the cell then supposing a current I flows for time, t , then, from Faraday's laws of electrolysis, the ratio of the amount of substance (Zn) dissolved to the valency of the element, n/z , is proportional to the electric charge passed, i.e.

$$n/z \propto Q, \text{ i.e. } n/z = FQ \quad (21.5)$$

When $n/z = 1$ kmol, $Q = 96485$ kC (where kC denotes kilo-coulomb), and hence $F = 96485$ kC/kmol. This is known as the Faraday constant, and is the product of Avogadro's number and the charge on a proton. Now, if the potential between the electrodes is E_{oc} , then the work done is

$$\delta W = 2E_{oc}F \text{ volt.kC/kmol} = 2E_{oc}F \text{ kJ/kmol} \quad (21.6)$$

In a Daniell cell, the potential at zero current (i.e. on open circuit), which is called the electromotive force (*emf*), $E_{oc} = 1.107$ V at 25 °C. If it is assumed that the cell can maintain this potential at low currents, then

$$\delta W = 2 \times 1.107 \times 96485 = 213618 \text{ kJ/kmol.}$$

If the reaction described above takes place isothermally in a closed system, then it must obey the First Law which this time is applied to the *closed circuit* system and gives

$$\begin{aligned} dU &= \delta Q - \delta W \\ &= \delta Q_R - \delta W = \delta Q_R - 213618 \text{ kJ/kmol} \end{aligned} \quad (21.7)$$

Now the change in internal energy is simply due to the chemical changes taking place, and for an isothermal reaction must be equal to δQ_{oc} defined in Eqn (21.4), giving

$$\delta Q_R = -214852 + 213618 = -1234 \text{ kJ/kmol.} \quad (21.8)$$

This indicates that heat must be transferred *from* the cell to maintain the temperature constant. This heat transfer is a measure of the change of entropy contained in the bonds of the product ($ZnSO_4$) compared to the reactant ($CuSO_4$), and

$$\Delta S = -1230/298 = -4.141 \text{ kJ/K.} \quad (21.9)$$

In this approach, the Daniell cell has been treated as a thermodynamic system – a black box. It is possible to develop this approach further to evaluate the electrical performance of the cell. Suppose that an amount of substance of Zn, dn , enters the solution at the negative pole, then it will carry with it a charge of $zFdn$, where z is the valency (or charge number of the cell reaction) of the Zn, and is 2 in this case. The Coulombic forces in the cell are such that an equal and opposite charge has to be absorbed by the copper electrode, and this is achieved by the copper ions absorbing electrons which have flowed around the external circuit. The maximum work that can be done is achieved if the cell is reversible, and the potential is equal to the open circuit potential; thus

$$\delta W = zFEdn \quad (21.10)$$

However, the total work that could be obtained from a cell if it changed volume would be

$$\delta W = zFE dn + p dV \quad (21.11)$$

thus, applying the First Law, and assuming the processes are reversible gives

$$dU = \delta Q - \delta W = T dS - p dV - zFE dn \quad (21.12)$$

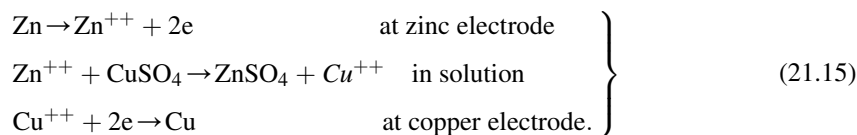
and hence the electrical work output is

$$-zFE dn = dU + p dV - T ds = dG = G_2 - G_1 \quad (21.13)$$

For a cell which is spontaneously discharging $G_2 < G_1$, and hence

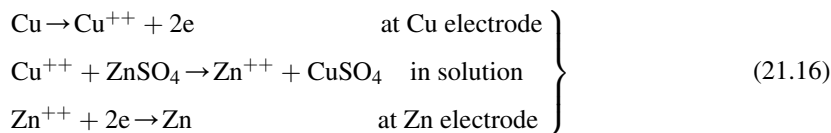
$$\delta W = -dG \quad (21.14)$$

The equations derived above define the operation of the Daniell cell from a macroscopic viewpoint. It is instructive to examine the processes which occur at the three interfaces shown in [Eqn \(21.1\)](#). Hence



This means that the zinc is ‘dissolved’ by the sulfuric acid at the zinc electrode and a zinc anion enters the solution. Meanwhile, two electrons are left on the zinc electrode (because the valency of zinc is 2) and these are free to travel around the circuit, but cause the zinc electrode to be at a negative potential, i.e. it is the cathode. The zinc anion reacts with the copper sulfate in solution to form zinc sulfate and releases a copper ion which migrates to the copper electrode, where it withdraws electrons from the electrode giving it a positive potential. Hence, the Daniell cell consists of electrons (negative charges) travelling around the outer circuit, from the cathode to the anode, while positive ions travel through the solution from cathode to anode. [Note: the convention for positive electric current is in the opposite direction to the electron flow; the current is said to flow from the anode to the cathode.] The net effect is to maintain the potential difference between the electrodes constant for any given current: this is a state of dynamic equilibrium. It can be seen that the electrochemical cell is a situation governed by thermodynamic equilibrium and steady state (irreversible) thermodynamics (see Chapter 20).

The reactions defined in [Eqn \(21.15\)](#) resulted in electrons flowing from the zinc to the copper (this would be defined as a current flowing from the copper (anode) to the zinc (cathode)), and the potential on the anode would be higher than the cathode. If the cell was connected to a potential source (e.g. a battery charger) such that the potential difference of the source was slightly higher than the cell emf then the current flow could be reversed and the reaction would become



Hence, the Daniell cell is *reversible*, if the current drawn from (or fed to) it is small. The Daniell cell can be used to ‘generate’ electricity, by consuming an electrode, or to store electricity.

Although the Daniell cell was one of the early examples of a device for generating electricity, it is relatively difficult to analyse thermodynamically because it has electrodes of different materials. A simpler device will be considered below to develop the equations defining the operation of such cells, but first it is necessary to introduce another property.

21.2.2 ELECTROCHEMICAL POTENTIAL

To be able to analyse the cell in more detail, it is necessary to introduce another parameter, the *electrochemical potential*, $\bar{\mu}$, of ions. This is related to the chemical potential by

$$\bar{\mu}_i = \mu_i + z_i \psi F, \quad (20.17)$$

Where

z_i = valency of (or charge on) the ion (+/–);

ψ = inner electric potential of the phase;

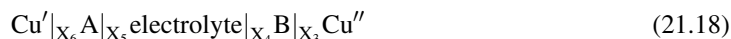
F = Faraday constant (96,485 kJ/kmol).

It was previously stated that the chemical potential was a ‘chemical pressure’ to bring about a change of composition to achieve a state of chemical equilibrium. In a similar manner, the electrochemical potential is an ‘electrical pressure’ that pushes the system towards electrical equilibrium. The electrochemical potential also contains a term for the change in capacity to do work through electrical processes, introduced to the system by the introduction of a unit of mass.

The value of ψ is the potential of the phase, and is obtained from electrostatic theory. It is the work done in bringing a unit positive charge from infinity to within the phase. Hence, $\bar{\mu}$ is the sum of the chemical potential, which has been based on the ‘chemistry’ of the material, and an electrical potential. It defines the energy that can be obtained from mechanical, chemical and electrical processes.

21.2.2.1 Thermodynamic origin of emf

Consider a simple galvanic cell, such as that shown in Fig. 21.6. This consists of two electrodes, A and B, made of different materials, an electrolyte, and two connecting wires of identical material. The cell can be represented as



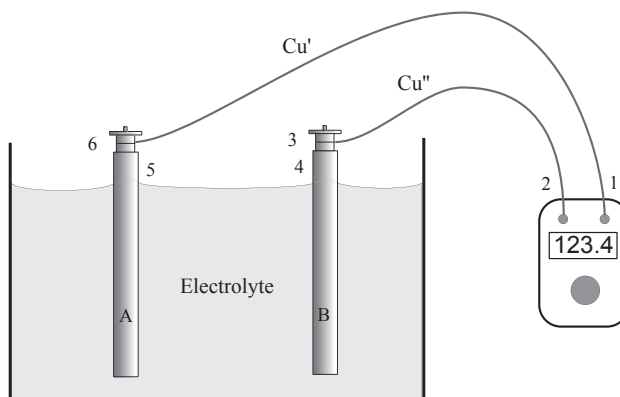
The junctions of interest here are X_5 and X_4 ; junctions X_6 and X_3 are potential thermocouples (because they are junctions of two dissimilar metals) but these effects will be neglected here.

Considering the electrochemical potential between points 1 and 2

$$\begin{aligned} \bar{\mu}_1 - \bar{\mu}_2 &= \bar{\mu}_1 - \bar{\mu}_6 - (\bar{\mu}_5 - \bar{\mu}_6) - (\bar{\mu}_4 - \bar{\mu}_5) - (\bar{\mu}_3 - \bar{\mu}_4) - (\bar{\mu}_2 - \bar{\mu}_3) \\ &= \bar{\mu}_{\text{Cu}'} - \bar{\mu}_A - (\bar{\mu}_{\text{elec}} - \bar{\mu}_A) - (\bar{\mu}_{\text{elec}} - \bar{\mu}_{\text{elec}}) - (\bar{\mu}_B - \bar{\mu}_{\text{elec}}) - (\bar{\mu}_{\text{Cu}''} - \bar{\mu}_B) \\ &= \bar{\mu}_{\text{Cu}'} - \bar{\mu}_{\text{Cu}''} \\ &= \mu_{\text{Cu}'} + z_{\text{Cu}'} \psi_{\text{Cu}'} F - (\mu_{\text{Cu}''} + z_{\text{Cu}''} \psi_{\text{Cu}''} F) \\ &= z_{\text{Cu}} F (\psi_{\text{Cu}'} - \psi_{\text{Cu}''}) \end{aligned} \quad (21.19)$$

FIGURE 21.6

Simple galvanic cell.



The difference in chemical potential of the two electrodes ($\mu_{\text{Cu}'} - \mu_{\text{Cu}''}$) is zero because both electrodes are of the same composition and are at the same temperature. Equation (21.19) defines the maximum work that can be obtained from the cell by a reversible process, i.e. a small flow of current. The difference, $\psi_{\text{Cu}'} - \psi_{\text{Cu}''}$, is equivalent to the open circuit potential, or emf, E_{oc} and hence

$$E_{\text{oc}} = \frac{\bar{\mu}_{\text{Cu}'} - \bar{\mu}_{\text{Cu}''}}{z_{\text{Cu}}F} = V_{\text{Cu}'} - V_{\text{Cu}''}. \quad (21.20)$$

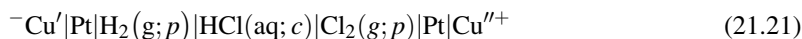
21.2.3 FUEL CELLS

The above sections have considered how electrical work can be obtained by the transfer of material from one electrode to another. In the Daniell cell, the Zn electrode is consumed, and ultimately the cell would cease to function. The situation in the Daniell cell can be reversed by recharging.

If it is desired to manufacture a cell which can operate without consuming the electrodes, then it is necessary to supply the fuel along an electrode: such a device is called a *fuel cell*, and a number of different types of fuel cell were introduced in Section 21.1.

A very simple example of a fuel cell is one which takes hydrogen (H_2) and combines it with chlorine (Cl_2) to form hydrochloric acid (HCl).

A practical cell similar to that in Fig. 21.6 can be constructed in the following way:



where

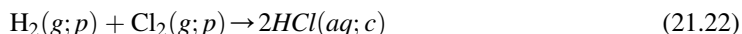
(g; p) denotes a gas at pressure, p

and (aq; c) denotes an aqueous solution with concentration, c

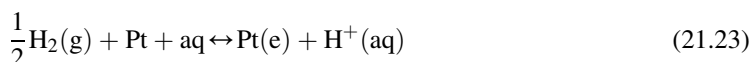
This is basically a cell using platinum electrodes (Pt) in an electrolyte of dilute hydrochloric acid (HCl). The platinum acts both as the electrodes and as the catalyst, and when it is dipped into the dilute hydrochloric acid, the system acts like an electric cell and hydrogen is evolved at the left-hand wire

and chlorine at the right-hand one: electricity flows around the circuit and the energy is derived by breaking the bonds in the HCl molecules.

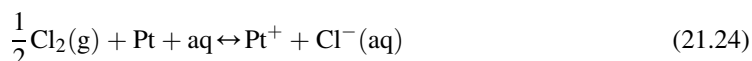
If the cell is to operate as a fuel cell then it will not break down the hydrochloric acid, as described above, but it will have hydrogen and chlorine delivered as fuels, which will be combined in the fuel cell to produce hydrochloric acid and electrical power. The operation is then defined by the reaction



where p is the pressure of the gases in the cell. The reactions at the interfaces are of interest because they produce the electrons and govern the potential. At the left-hand electrode, if the process is considered to be reversible,



This reaction indicates that for hydrogen gas (H_2) to be evolved at the electrode a hydrogen ion (H^+) must be released into the solution and an electron must be left on the electrode. Now, it is not obvious from Eqn (21.23) which direction the reaction will go: this is governed by considering the pair of processes occurring at the platinum electrodes. At the right-hand electrode



Equations (21.23) and (21.24) in combination show that for the reaction shown in Eqn (21.22) the electron current must flow from the Pt- H_2 electrode to the Pt- Cl_2 electrode. Hence, the Pt- H_2 is a cathode and the Pt- Cl_2 electrode is an anode. It is apparent that when the cell is operating open circuit it will build up a potential difference between the electrodes. However, once a current starts to flow that potential difference will be affected by the ability of the H^+ and Cl^- ions to undertake Reaction (21.22): this then introduces irreversible thermodynamics.

First, consider when the device is operating open circuit. It is in a state of equilibrium and $\Delta G)_{p,T} = 0$ for an infinitesimal process. If it is assumed that the equilibrium can be perturbed by an amount of substance $1/2 dn$ of hydrogen and chlorine being consumed at the electrodes, then these will generate $dn \text{ H}^+$ and Cl^- in the electrolyte and transfer dnF of charge from Cu' to Cu'' .

Thus



The reactions taking place in the cell can now be examined to give

$$\left. \begin{array}{l} (1) \text{ eqn (21.25)} \quad \Delta G_1 = \bar{\mu}_{\text{Pt}(\text{e})} - \bar{\mu}_{\text{Cu}''(\text{e})} \\ (2) \text{ eqn (21.24)} \quad \Delta G_2 = \bar{\mu}_{\text{Cl}^-(\text{aq})} - \bar{\mu}_{\text{Pt}(\text{e})} - \frac{1}{2}\mu_{\text{Cl}_2} - \mu_{\text{Pt}} \\ (3) \text{ eqn (21.23)} \quad \Delta G_3 = \bar{\mu}_{\text{H}^+(\text{aq})} + \bar{\mu}_{\text{Pt}(\text{e})} - \frac{1}{2}\mu_{\text{H}_2} - \mu_{\text{Pt}} \\ (4) \text{ eqn (21.26)} \quad \Delta G_4 = \bar{\mu}_{\text{Cu}'(\text{e})} - \bar{\mu}_{\text{Pt}(\text{e})} \end{array} \right\} \quad (21.27)$$

The change of molar Gibbs function across the cell is

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 \quad (21.28)$$

which gives

$$\Delta G = \bar{\mu}_{\text{H}^+_{\text{aq}}} + \bar{\mu}_{\text{Cl}^-_{\text{aq}}} - \frac{1}{2}\mu_{\text{H}_2} - \frac{1}{2}\mu_{\text{Cl}_2} + \bar{\mu}_{\text{Cu}'(\text{e})} - \bar{\mu}_{\text{Cu}''(\text{e})} \quad (21.29)$$

This equation consists of a mixture of chemical potential (μ) and electrochemical potential ($\bar{\mu}$) terms. Expanding the latter gives

$$\begin{aligned} \bar{\mu}_{\text{H}^+_{\text{aq}}} &= \mu_{\text{H}^+_{\text{aq}}} + F\psi_{\text{soln}} \\ \bar{\mu}_{\text{Cl}^-_{\text{aq}}} &= \mu_{\text{Cl}^-_{\text{aq}}} + F\psi_{\text{soln}} \\ \bar{\mu}_{\text{Cu}'(\text{e})} &= \mu_{\text{Cu}'} + F\psi_{\text{Cu}'} \\ \bar{\mu}_{\text{Cu}''(\text{e})} &= \mu_{\text{Cu}''} + F\psi_{\text{Cu}''} \end{aligned} \quad (21.30)$$

These terms may be substituted into Eqn (21.29) to give

$$\Delta G = \mu_{\text{H}^+_{\text{aq}}} + \mu_{\text{Cl}^-_{\text{aq}}} - \frac{1}{2}\mu_{\text{H}_2} - \frac{1}{2}\mu_{\text{Cl}_2} + F(\psi_{\text{Cu}'} - \psi_{\text{Cu}'}) \quad (21.31)$$

Now, at equilibrium $\Delta G)_{p,T} = 0$ and $F(\psi_{\text{Cu}'} - \psi_{\text{Cu}'}) = FE$, thus (introducing the valency, z , to maintain generality)

$$\begin{aligned} zFE &= -\left(\mu_{\text{H}^+_{\text{aq}}} + \mu_{\text{Cl}^-_{\text{aq}}} - \frac{1}{2}\mu_{\text{H}_2} - \frac{1}{2}\mu_{\text{Cl}_2}\right) \\ &= -\left(\mu_{\text{H}^+_{\text{aq}}}^0 + \mu_{\text{Cl}^-_{\text{aq}}}^0 - \frac{1}{2}\mu_{\text{H}_2}^0 - \frac{1}{2}\mu_{\text{Cl}_2}^0\right) - \Re T \ln\left(\frac{a_{\text{H}^+}a_{\text{Cl}^-}}{p_{\text{rH}_2}^{1/2}p_{\text{rCl}_2}^{1/2}}\right) \end{aligned} \quad (21.32)$$

where $p_{\text{r}} = p/p_0$ and a = the activity coefficient of the particular phase. The activity coefficient, a , can be defined in such a way that the chemical potential of a solution is

$$\mu_i = \mu_i^* + \Re T \ln a_i x_i \quad (21.33)$$

In Eqn (21.33), μ_i^* is a function of temperature and pressure alone, and a_i takes account of the interaction between the components in the solution. It can be shown that at low concentrations the activity coefficients are approximately equal to unity. If the standard chemical potential terms (μ^0) at temperature T are denoted ΔG_T^0 then

$$E = \frac{-\Delta G_T^0}{zF} - \frac{\Re T}{zF} \ln\left(\frac{a_{\text{H}^+}a_{\text{Cl}^-}}{p_{\text{rH}_2}^{1/2}p_{\text{rCl}_2}^{1/2}}\right) \quad (21.34)$$

where the term $-\Delta G_T^0/zF$ is called the standard emf of the cell, E^0 .

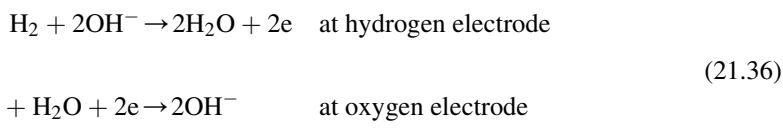
Equations (21.32) and (21.34) show quite distinctly that the processes taking place in the fuel cell are governed by similar equations to those describing combustion. The equations are similar to those for dissociation, which also obeys the Law of Mass Action. In the case of gaseous components the activity can be related to the partial pressures by $a_i = p_i/p_0$, where p_i = partial pressure of component i .

21.2.3.1 Example: a hydrogen–oxygen fuel cell

Consider a fuel cell in which the fuel is hydrogen and oxygen, and these gases are supplied down the electrodes. A suitable electrolyte for this cell is aqueous potassium hydroxide (KOH). The cell can be defined as



The basic reactions taking place at the electrodes are



and these can be combined to give the overall reaction



It can be seen that the KOH does not take part in the reaction, and simply acts as a medium through which the charges can flow. It is apparent from Eqn (21.36) that the valency (z_i) of hydrogen is 2. From Eqn (21.34), the cell open circuit potential, the standard emf, is given by

$$E^0 = -\frac{\Delta G_{298}^0}{z_{\text{H}_2}F} = -\frac{-[-30434.3 - 0.5 \times 52477.3 - (-239081.7 - 46370.1)]}{2 \times 96485} = 1.185 \text{ V} \quad (21.38)$$

The standard emf in Eqn (21.38) has been evaluated by assuming that the partial pressures of the gases are all 1 atm. In an actual cell at equilibrium they will be controlled by the chemical equation, and the actual emf achievable will be given by an equation similar to Eqn (21.34) which includes the partial pressures of the constituents, viz

$$E = \frac{-\Delta G_T^0}{z_i F} - \frac{\Re T}{z_i F} \ln \left(\frac{\prod_{\text{products}} p_r^v}{\prod_{\text{reactants}} p_r^v} \right) = E^0 - \frac{\Re T}{z_i F} \ln \left(\frac{\prod_{\text{products}} p_r^v}{\prod_{\text{reactants}} p_r^v} \right) \quad (21.39)$$

Equation (21.39) can be written in a shorter form as

$$E = \frac{-\Delta G_T^0}{z_i F} - \frac{\Re T}{z_i F} \ln \left(\prod p_r^v \right) = E^0 - \frac{\Re T}{z_i F} \ln \left(\prod p_r^v \right) \quad (21.39a)$$

where the stoichiometric coefficients, v , are defined as positive for products and negative for reactants.

Hence the emf of the hydrogen–oxygen fuel cell is

$$E = E^0 - \frac{\Re T}{z_i F} \ln \left(\frac{p_{\text{rH}_2\text{O}}}{p_{\text{rH}_2} p_{\text{rO}_2}^{1/2}} \right) \quad (21.40)$$

Considering again the term for E^0 , it is directly related to the equilibrium constant, K_{p_r} , by

$$E^0 = -\frac{\Delta G_T^0}{zF} = \frac{\Re T}{zF} \ln K_{p_r} \quad (21.41)$$

$$\text{giving } E = \frac{\Re T}{z_i F} \ln K_{p_r} - \frac{\Re T}{z_i F} \ln \left(\frac{p_{\text{rH}_2\text{O}}}{p_{\text{rH}_2} p_{\text{rO}_2}^{1/2}} \right) = \frac{\Re T}{z_i F} \left\{ \ln K_{p_r} - \ln \left(\frac{p_{\text{rH}_2\text{O}}}{p_{\text{rH}_2} p_{\text{rO}_2}^{1/2}} \right) \right\} \quad (21.42)$$

Examination of Eqn (21.42) shows that when the constituents of the cell are in equilibrium, which is defined by $K_{p_r} = \prod_{\text{products}} p_r^{\nu_r} / \prod_{\text{reactants}} p_r^{\nu_r}$, the potential output of the cell is zero. Hence, like a combustion process, the fuel cell only converts chemical bonds into another form of energy when it is transferring from one (metastable) equilibrium state to another (stable) one. A combustion process converts the bond energy of the reactants into thermal energy which can then be used to drive a power plant: the fuel cell converts the bond energy of the fuel *directly* into electrical energy, and the amount of electricity produced is not constrained by the Carnot efficiency. *The Second Law does limit the energy output but only defines the equilibrium condition.* A fuel cell is basically a direct conversion device which is constrained mainly by the First Law.

An interesting difference between the fuel cell and the combustion process is that many fuel cells attempt to release the *higher* enthalpy of reaction, whereas combustion usually releases the *lower* enthalpy (or internal energy) of reaction. In the case of the $\text{H}_2\text{--O}_2$ fuel cell the product (H_2O) is in the liquid phase and not the vapour phase as is usual after combustion. However, the potential to do work is not changed by the phase of the products (the chemical potential of H_2O at any particular temperature is the same in the liquid and vapour phases). This means that while fuel cells are controlled largely by the First Law, they have thermal efficiencies significantly below 100% based on the higher enthalpy of reaction: they have to transfer away the difference between the higher and lower enthalpy of reaction in the form of heat if they are going to operate isothermally.

21.2.4 EFFECT OF TEMPERATURE ON FUEL CELL OPERATION

The effect of the temperature of operation on the emf of the cell can be evaluated by differentiating Eqn (21.42) with respect to T , in this case keeping the pressure constant. This gives

$$\begin{aligned} \left. \frac{\partial E}{\partial T} \right|_p &= \frac{\partial}{\partial T} \left[\frac{\Re T}{z_i F} \left\{ \ln K_{p_r} - \ln \left(\prod p_r^{\nu_r} \right) \right\} \right] = \frac{\partial}{\partial T} \left[\frac{\Re T}{z_i F} \ln K_{p_r} - \frac{\Re T}{z_i F} \ln \left(\prod p_r^{\nu_r} \right) \right] \\ &= \frac{\Re}{z_i F} \ln K_{p_r} + \frac{\Re T}{z_i F} \frac{\partial}{\partial T} (\ln K_{p_r}) - \frac{\Re}{z_i F} \ln \left(\prod p_r^{\nu_r} \right) \\ &= \frac{\Re T}{z_i F} \frac{\partial}{\partial T} (\ln K_{p_r}) + \frac{E}{T} \end{aligned} \quad (21.43)$$

Now, from the Van't Hoff equation

$$\frac{d}{dT}(\ln K_p) = \frac{Q_p}{RT^2} \quad (21.44)$$

Substituting from Eqn (21.44) into Eqn (21.43) gives

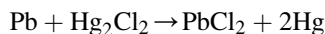
$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{RT}{z_i F} \frac{Q_p}{RT^2} + \frac{E}{T} = \frac{Q_p}{z_i FT} + \frac{E}{T} \quad (21.45)$$

Equation (21.45) shows that the change of emf is related to the heat of reaction, Q_p . Now, for exothermic reactions Q_p is negative, and this means that the emf of a cell based on an exothermic reaction decreases with temperature. This is in line with the effect of temperature on the degree of dissociation in a combustion process, as discussed in Chapter 12.

21.2.4.1 Examples

Example 1

A Pb–Hg fuel cell operates according to the following equation



and the heat of reaction, $Q_p = -95,200$ kJ/kmol Pb. The cell receives heat transfer of 8300 kJ/kmol Pb from the surroundings. Calculate the potential of the cell, and evaluate the electrical work produced per kilogram of reactants, assuming the following atomic weights: Pb – 207; Hg – 200; Cl – 35.

Solution

This problem can be solved by a macroscopic approach to the cell as a closed system. Applying the First Law gives

$$\begin{aligned} -zFE dn &= dU - \delta Q_{\text{trans}} + TdS - pdV \\ &= dG - \delta Q_{\text{trans}} \end{aligned}$$

Now this value of energy transfer has to be used in Eqn (21.34) in place of ΔG_T^0 , giving

$$E = -\frac{(\Delta G_T^0 - \delta Q_{\text{trans}})}{zF} = -\frac{-95200 - 8300}{2 \times 96487} = 0.5363 \text{ V}$$

The quantity of work obtained per kg of reactants is given in the following way. Assume the potential of the cell is not reduced by drawing a current, then the charge transferred through the cell per kmol Pb is $2F$ (because the valency of lead is 2). Hence the work done per kmol Pb is

$$\delta W = 2 \times 96485 \times 0.5363 = 103500 \text{ kJ/kmol Pb}$$

giving the work per unit mass of reactants as

$$\frac{\delta W}{m_{\text{react}}} = \frac{103500}{207 + 2 \times (200 + 35)} = 152.9 \text{ kJ/kg}$$

Example 2

A hydrogen–oxygen fuel cell operates at a constant temperature of 227 °C and the hydrogen and oxygen are fed to the cell at 40 bar, and the water is taken from it at the same pressure. Evaluate the emf at this condition, and the heat transfer from the cell.

Solution

This question requires the application of Eqn (21.42), giving

$$E = \frac{\Re T}{z_i F} \left\{ \ln K_{pr} - \ln \left(\frac{p_{\text{rH}_2\text{O}}}{p_{\text{rH}_2} p_{\text{rO}_2}^{1/2}} \right) \right\}$$

From tables at 500 K, $K_{pr} = 7.92127 \times 10^{22} \text{ bar}^{-1/2}$. Hence the open circuit potential is

$$\begin{aligned} E &= \frac{8.3143 \times 500}{2 \times 96487} \left\{ \ln(7.92127 \times 10^{22} \times 1^{1/2}) - \ln\left(\frac{40 \times 1^{1/2}}{40 \times 40^{1/2}}\right) \right\} \\ &= 1.176 \text{ V} \end{aligned}$$

The maximum work output from the fuel cell is based on Eqn (21.14) is

$$\begin{aligned} \dot{W} &= -\dot{m} \Delta G_T^0 = \dot{m} \{-239081.7 - 86346 - (0.5 \times [-95544] + [-58472])\} \\ &= \dot{m}(-219.18) \text{ MJ/kmol H}_2 \end{aligned}$$

Also, at 500 K the lower enthalpy of reaction of the process is 244.02 MJ/kmol, which gives a higher enthalpy of reaction of

$$Q_p = -(244.02 \times 10^3 + 18 \times 1831) = -277.0 \times 10^3 = -277.0 \text{ MJ/kmol H}_2$$

This is equal to the change of enthalpy of the working fluid as it passes through the cell, and hence applying the steady flow energy equation to the fuel cell gives

$$\dot{Q} - \dot{W} = \dot{m}(\Delta h)$$

giving $\dot{Q} = \dot{m}(\Delta h) + \dot{W} = -277.0 + 219.18 = -57.82 \text{ MJ/kmol H}_2$

Thus the efficiency of the fuel cell, based on the higher enthalpy of reaction, is

$$\eta = \frac{219.18}{277.0} = 0.7913$$

If it was evaluated from the lower enthalpy of reaction, which is usually used to calculate the efficiency of power plant, then the value would be

$$\eta = \frac{219.18}{244} = 0.8983.$$

Example 3

The operating pressure of the fuel cell in example 2 is changed to 80 bar. Calculate the change in emf.

Solution

If the pressure is raised to 80 bar, this only affects the pressure term because $K_{pr} = f(T)$, and hence

$$\begin{aligned} E_{80} - E_{40} &= \frac{\Re T}{z_i F} \left\{ \left[\ln K_{pr} - \ln \left(\frac{80 \times 1^{1/2}}{80 \times 80^{1/2}} \right) \right] - \left[\ln K_{pr} - \ln \left(\frac{40 \times 1^{1/2}}{40 \times 40^{1/2}} \right) \right] \right\} \\ &= \frac{\Re T}{z_i F} \ln(2^{1/2}) = 0.0075 \text{ V} \end{aligned}$$

giving $E_{80} = 1.176 + 0.0075 = 1.183 \text{ V}$.

This shows that the potential of the hydrogen–oxygen fuel cell increases with pressure. This is similar to the effect of pressure on the hydrogen–oxygen combustion reaction, when dissociation decreased from 0.0673 to 0.0221 as the pressure was increased from 1 bar to 100 bar for the stoichiometric combustion of methane in Chapter 11. Hence, if the number of moles of reactants is not equal to the number of moles of products then the emf of the cell will be a function of the pressure of operation.

21.3 EFFICIENCY OF A FUEL CELL

The fuel cell is not 100% efficient, and it is possible to define its efficiency by the following equation

$$\eta = \frac{\text{Maximum useful work output}}{\text{Heat of reaction}} = \frac{w_{\text{use}}}{Q_p} \quad (21.46)$$

Now the maximum useful work output obtainable is defined by the change of Gibbs energy, i.e.

$$\begin{aligned} w_{\text{use}} &= \Delta G = G_{\text{products}} - G_{\text{reactants}} \\ &= \sum_{\text{products}} H_f^0 - \sum_{\text{reactants}} H_f^0 - T \left(\sum_{\text{products}} S_f^0 - \sum_{\text{reactants}} S_f^0 \right) \end{aligned} \quad (21.47)$$

and
$$Q_p = \sum_{\text{products}} H_f^0 - \sum_{\text{reactants}} H_f^0 \quad (21.48)$$

Thus, the efficiency is

$$\eta = 1 + \frac{T \left(\sum_{\text{products}} S_f^0 - \sum_{\text{reactants}} S_f^0 \right)}{\sum_{\text{products}} H_f^0 - \sum_{\text{reactants}} H_f^0} = 1 - \frac{T\Delta S}{Q_p} = 1 + \frac{T\Delta S}{Q'_p} \quad (21.49)$$

The last expression in Eqn (21.49) has been written in terms of the calorific value of the fuel because this is usually positive, and hence the efficiency is defined by the sign of the change of entropy. If the entropy change is positive then the efficiency is greater than unity; if it is negative then it is less than unity. Consider now the hydrogen–oxygen reaction described above. If the fuel cell is maintained at the standard temperature of 25 °C, and the processes are assumed to be isothermal then

$$\begin{aligned} \Delta G &= (h_f^0)_{\text{H}_2\text{O}} - T(s_{\text{H}_2\text{O}} - s_{\text{H}_2} - 0.5s_{\text{O}_2}) \\ &= -241820 - 298(188.71 - 130.57 - 0.5 \times 205.04) \\ &= -228594.8 \text{ kJ/kmol} \end{aligned} \quad (21.50)$$

and $Q_p = -241820 \text{ kJ/kmol}$. Hence the efficiency is

$$\eta = \frac{228594.8}{241820} = 0.945 \quad (21.51)$$

This efficiency can be evaluated using Eqn (21.49) to give

$$\eta = 1 + \frac{T\Delta S}{Q'_p} = 1 + \frac{298(188.71 - 130.57 - 0.5 \times 205.04)}{241820} = 1 - 0.0547 = 0.945. \quad (21.52)$$

This is exactly the same value as was obtained in Chapter 3 on exergy and availability. The rational efficiency of this, and any, fuel cell would be 100%. The efficiency of this cell is less than 100% because the change of entropy as the reactants change to products is negative. Hence, if the value of $T\Delta S < 0$ then the cell will be less than 100% efficient, and this is because ‘heat’ equivalent to $T\Delta S$ must be transferred with the surroundings, i.e. to the surroundings. If $T\Delta S > 0$ then the efficiency can be greater than 100%, and this comes about because energy has to be transferred to the fuel cell from the surroundings to make the process isothermal.

21.4 THERMODYNAMICS OF CELLS WORKING IN STEADY STATE

The previous theory did not relate to a cell in which current was being continually drawn from it. Under such circumstances, concentration gradients might be set up in the cell, and it will be governed by the theories of irreversible thermodynamics (Chapter 20). It can be shown for a fuel cell that a possible force term is the gradient of electrochemical potential, which is similar to the use of the chemical potential gradient when considering diffusion processes [note that when considering thermal and mass diffusion in combination the gradient of the ratio of chemical potential and temperature (μ/T) was used]. Hence, the force term is

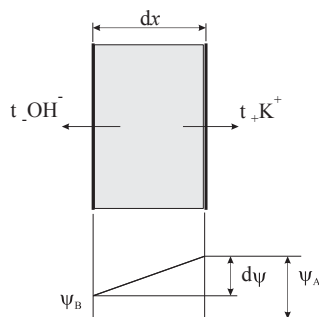
$$\frac{d}{dx} \bar{\mu}_i = \frac{d}{dx} (\mu_i + F\psi) = \frac{d\mu_i}{dx} + F \frac{d\psi}{dx} \quad (21.53)$$

In this analysis, the flux term is taken to be the movement of charge per unit area through the cell. Since the charge is carried on the ions travelling through the cell, it can be directly related to the transfer of the ions from one electrode to the other, and this is equivalent to current density (e.g. amp/m²). Hence, the current in the cell is

$$J = \left(\sum_{\text{all ions}} J_i \right) F \quad (21.54)$$

If the hydrogen–oxygen cell is taken as an example, it is apparent that the charge is carried across the cell by OH[−] ions being absorbed on the hydrogen electrode, and being produced on the oxygen electrode. These OH[−] ions are produced in the electrolyte (KOH) as the KOH molecule spontaneously dissociates into K⁺ and OH[−] ions (in weak aqueous solutions), so while the negative ions travel in one direction, the positive ones go in the opposite direction. This can be considered schematically as in Fig. 21.7, which represents a thin element of the electrolyte. Ions are flowing through the electrolyte, and t_+ represents the transport number of the cations, while t_- represents that of the anions. If the electrochemical potentials of the two ions on side A of the element are

$$\begin{aligned} \bar{\mu}_{K^+} &= \mu_{K^+} + F\psi_A \\ \bar{\mu}_{OH^-} &= \mu_{OH^-} - F\psi_A \end{aligned} \quad (21.55)$$

**FIGURE 21.7**

Ions in cell.

then it is possible to evaluate the change in Gibbs energy, dG , when an infinitesimal number of ions move through the element, giving

$$-dG = t_{+}d\bar{\mu}_{\text{K}^{+}} - t_{-}d\bar{\mu}_{\text{OH}^{-}} \quad (21.56)$$

Now when the system is in the steady state dG must be zero, and hence, substituting from Eqn (21.55)

$$-t_{+}d\mu_{\text{K}^{+}} - t_{+}Fd\psi + t_{-}d\mu_{\text{OH}^{-}} - t_{-}Fd\psi = 0 \quad (21.57)$$

Since $t_{+} + t_{-} = 1$ then

$$Fd\psi = -t_{+}d\mu_{\text{K}^{+}} + t_{-}d\mu_{\text{OH}^{-}} \quad (21.58)$$

Applying Onsager's relationship, $J_i = \sum_{k=1}^k L_{ik}X_k$, gives

$$\left. \begin{aligned} J_{\text{K}^{+}} &= -L_{11}d\mu_{+} - L_{12}d\mu_{-} - L_{13}d\psi \\ J_{\text{OH}^{-}} &= -L_{21}d\mu_{+} - L_{22}d\mu_{-} - L_{23}d\psi \\ J &= -L_{31}d\mu_{+} - L_{32}d\mu_{-} - L_{33}d\psi \end{aligned} \right\} \quad (21.59)$$

The term L_{33} is equivalent to the conductance of the electrolyte, k , and by the reciprocal relationship

$$\begin{aligned} L_{32} &= L_{23} = -\frac{t_{-}k}{F}, \\ L_{31} &= L_{13} = +\frac{t_{+}k}{F} \end{aligned} \quad (21.60)$$

Hence, the current, J , is given by

$$J = -\frac{t_{+}k}{F}d\mu_{+} + \frac{t_{+}k}{F}d\mu_{-} - kd\psi \quad (21.61)$$

If the circuit connecting the electrodes is open then no current flows and $J = 0$, giving the result obtained in Eqn (21.58). In the case where a current flows, $J > 0$, then there will be a reduction in the

potential available at the electrodes because some of the ‘force’ that can be generated in the cell has to be used to propel the ions through the concentration gradients that exist.

A more comprehensive analysis of the irreversible thermodynamics of the cell would take into account the temperature gradients that might be set up in operating the cell, and another group of equations for thermal conduction would have to be added to the equations in the matrix of Eqn (21.59).

21.5 LOSSES IN FUEL CELLS

The analyses performed above were all based on fundamental thermodynamic consideration of the processes in the fuel cell. This section will describe the more practical aspects of fuel cell operation.

The losses that can occur in fuel cells are the following:

- overvoltage or overpotential, polarisation, irreversibility, losses, voltage drop
- There are four principal causes of these voltage drops:
 - activation losses,
 - fuel crossover and internal currents,
 - Ohmic losses, and
 - mass transport or concentration losses.

21.5.1 ACTIVATION LOSSES

Activation losses are caused by the slowness of the reactions taking place on the surface of electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons to or from the electrode.

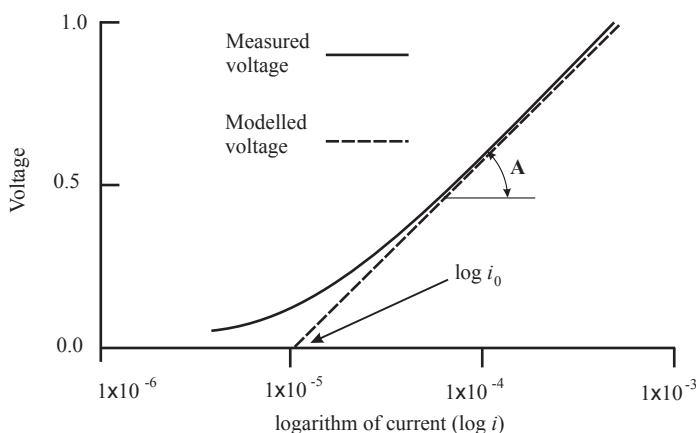
In 1905, Tafel (see Bard and Faulkner (2001)) experimentally found that the voltage loss at an electrode followed a similar mathematical model for many electrochemical reactions. He developed plots known as Tafel plots (Fig. 21.8) which are a plot of voltage *loss* against *log* current. Tafel noted these curves could be modelled by the following equation:

$$V = A \ln \left(\frac{i}{i_0} \right) \quad (21.62)$$

The constant **A** can be found from the gradient of the measured voltage and i_0 the intersect with the *x*-axis.

This equation is valid when the current flowing (*i*) is greater than i_0 . The constant of a Tafel plot **A** is typically around 0.06 V for an SPFC, and is dependent on the speed of the reaction, with **A** being higher for a slow reaction.

The more significant Tafel variable is known as the exchange current i_0 . This factor is linked to the reversibility of the electrode reactions. If no current is flowing, then it might be assumed that the reaction at the hydrogen electrode is not to be taking place: however, in reality the reaction is occurring reversibly in both directions at an equilibrium rate. If this equilibrium current flow is occurring at a high rate then it will be easier to shift the reaction to one side to allow a current to flow. If the equilibrium reaction is occurring at a low rate, then it is harder to shift the equilibrium rate: this means it is desirable for i_0 to be as large as possible. This increase in i_0 is achieved by changing the material of the electrode, see Table 21.1; the surface area of an electrode also plays a large part.

**FIGURE 21.8**

Sample Tafel plot.

Table 21.1 Table of i_0 for the Hydrogen Electrode

Metal	i_0 (A cm ⁻²)
Silver (Ag)	4.0×10^{-7}
Nickel (Ni)	6.0×10^{-6}
Platinum (Pt)	5.0×10^{-4}

Bloom and Cutman [1981].

For a low temperature hydrogen-fed fuel cell running on air at ambient pressure, a typical value for i_0 would be about 0.1 mA/cm² at the cathode and about 200 mA/cm² at the anode.

If this voltage loss is taken into account, the theoretical voltage–current graph is given by the theoretical voltage (E) minus the activation loss, referred to as the Tafel equation:

$$V = E - A \ln \left(\frac{i}{i_0} \right). \quad (21.63)$$

21.5.2 FUEL CROSSOVER AND INTERNAL CURRENTS

The electrolyte in a fuel cell is designed to only allow the mobile ion species to conduct across; in the case of an SPFC, the polymer exchange membrane (PEM) allows the H⁺ ions to conduct through. The PEM is never ideal and will allow some of the hydrogen fuel and also electrons to conduct across. These two leaks have a noticeable effect on the current–voltage curve. Fig. 21.9 shows how an electron conducting through the electrolyte bypasses the external circuit and does no electrical work. Similarly

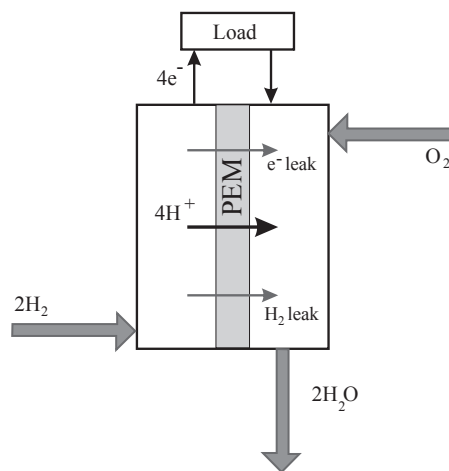
**FIGURE 21.9**

Diagram showing fuel crossover and internal current losses in a solid polymer fuel cell. PEM, polymer exchange membrane.

if a hydrogen molecule passes across the electrolyte it will either react to form water or disperse in the oxidant flow, wasting two electrons.

With low-temperature fuel cells, such as the SPFC, the open-circuit voltage is smaller than the theoretical value of 1.2 V. This open-circuit voltage drop is caused by the fuel and electron leakage. This leakage acts as a current flowing even when the cell is open circuit so the current flow is not zero but around 2 mA/cm². This current flow leads to an activation loss of 0.23 V:

$$A = 0.06 \text{ V} \quad i_o = 0.04 \text{ mA} \quad V_{\text{activation loss}} = 0.06 \ln\left(\frac{2}{0.04}\right) = 0.23 \text{ V}$$

This loss leads to a lower open-circuit voltage of around 0.97 V. This loss can be modelled mathematically by adding an extra current term (i_n) into the activation loss equation (and any other loss equation containing i), giving a theoretical voltage equation of:

$$V = E - A \ln\left(\frac{i + i_n}{i_o}\right) \quad (21.64)$$

Using different membrane materials and designing them to resist fuel leakage and electron conduction can reduce this loss. When there is a large activation loss (as with SPFC), then a small change in leakage has a large effect on the open-circuit voltage.

21.5.3 OHMIC LOSSES

This Ohmic voltage loss occurs due to resistance in the fuel cell, the electrodes, electrolyte and cell connections and simply follows Ohm's law (viz $V_{\text{loss}} = i \cdot r_{\text{cell}}$). This loss has the effect of

causing the theoretical voltage to fall linearly as current increases. It can be measured using a current interrupt test, and can be reduced by lowering the resistance of the cell components.

21.5.4 MASS TRANSFER LOSSES

These mass transfer losses occur mainly when mixed fuels or oxidants are used, for example: air to provide oxygen as the oxidant, or a hydrogen–carbon dioxide fuel mixture. Here there are gas species that do not take an active part in the fuel cell reaction. At the surface of the PEM, the hydrogen and oxygen are used up in the production of water. This reduces the concentration of the fuel and oxidant gases at the active membrane surface. These depleted regions of hydrogen and oxygen are replenished by diffusion of the reactant gases through the inactive species. The depleted regions cause a reduction in the partial pressures of the hydrogen and oxygen. It can be shown, by considering the Nernst equation, that pressure has an effect on the fuel cell voltage so mass transfer or concentration losses can be modelled by the following equation (which takes negative values):

$$\text{Voltage drop due to mass transfer, } \Delta V_{\text{mass}} = -B \ln \left(1 - \frac{i}{i_l} \right) \quad (21.65)$$

The effect of mass transfer losses is that at high current drains, the voltage suddenly reaches a cut-off point where the current drawn cannot increase and the voltage collapses as shown in Fig. 21.10.

This effect also occurs with pure gases due to pressure drops in the fuel cell system because there is a maximum flow rate to the membrane surface. If the current drawn demands a greater flow rate than this, then the voltage will drop off, as the required gas flow rate cannot be supplied.

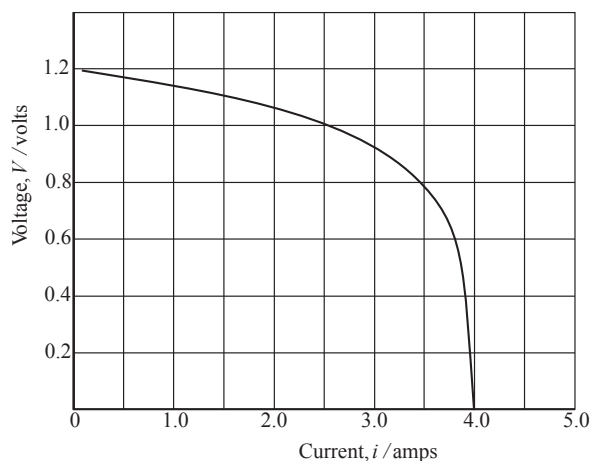


FIGURE 21.10

Theoretical current-voltage plot showing mass transfer losses. [$E = 1.2$ V, $B = 0.2$ V, $i_l = 4$ A].

21.5.5 OVERALL RESPONSE

The overall response is derived using a combination of these loss terms, giving:

$$V = E - (i + i_n)r - A \ln \left(\frac{i + i_n}{i_0} \right) + B \ln \left(1 - \frac{i + i_n}{i_l} \right) \quad (21.66)$$

The high capital cost and bulk of fuel cells mean that they are frequently operated at the maximum power density, giving a cell voltage of about 0.6 V for both SPFCs and SOFCs. The reasons for the voltage losses are quite different for the two types of cell. The SOFC has a high Ohmic loss, but a low activation loss, while for the SPFC it is the other way around. Acres and Hards [1996] show a typical fuel cell performance (Fig. 21.11), and Fig. 21.12 highlights the areas where these losses take effect in an SPFC cell. Table 21.2 shows how typical parameters for SPFC and SOFC fuel cells vary between the devices.

Figures 21.11 and 21.12 show why considerable research and development is being focused on improving the cell voltage efficiency (η_E) via improved electrocatalysis. Further extensive development is being made to improve the system efficiency (η_s) by improved design of the stack and the ancillary systems. Overall thermal efficiencies of about 50% can be achieved at current densities of 0.7 A/cm² with state of the art SPFC stacks. The heat produced by an operating fuel cell stack can be estimated from the difference between the change in enthalpy (corrected for operating conditions) and the electricity produced by the cell.

One major advantage of fuel cells is the lower sensitivity of efficiency to scale than is achievable with thermal power systems, which means that fuel cells in the kilowatt range have very similar overall system efficiencies as those in the megawatt range. A further benefit is the relatively flat efficiency versus load curve compared to internal combustion engines.

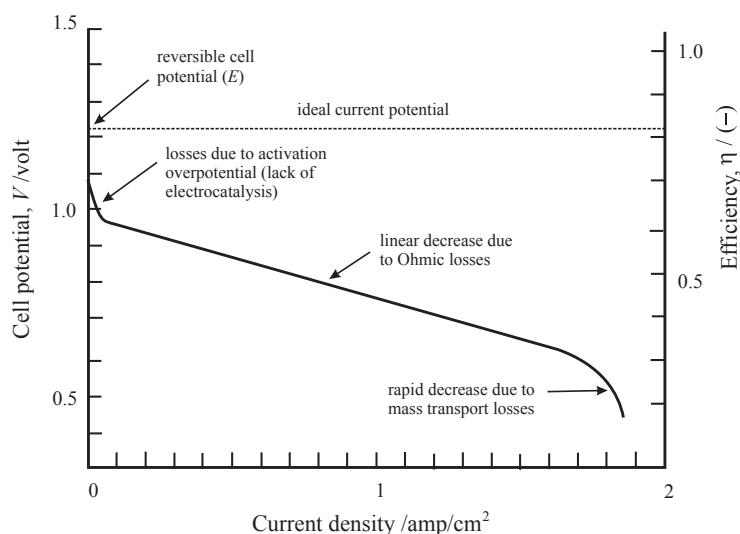
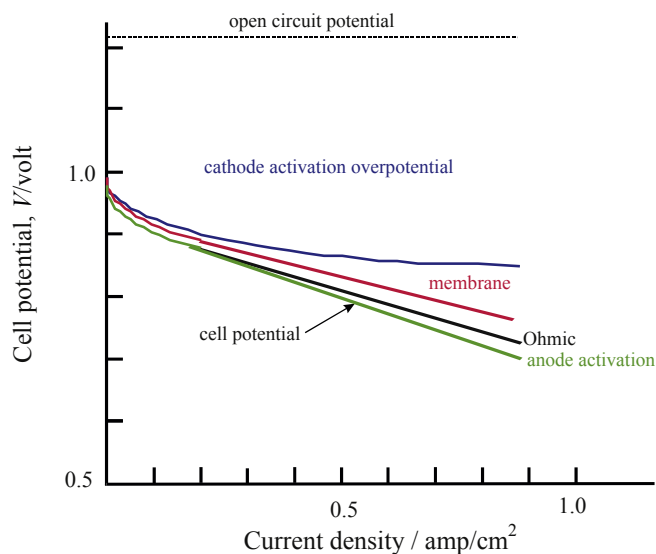


FIGURE 21.11

Potential vs current relationship for a typical hydrogen-oxygen cell.

From Acres & Hards (1996).

**FIGURE 21.12**

Characteristics of a specific SPFC: the contribution of cathode activation overpotential; membrane; Ohmic electrode and anode activation losses.

From Acres & Hards (1996).

Table 21.2 Coefficients to Define the Losses in Fuel Cells		
Constant	SPFC	SOFC
E/volts	1.2	1.0
$i_n/\text{mA}/\text{cm}^2$	2	2
$r/\text{k}\Omega/\text{cm}^2$	30×10^{-6}	300×10^{-6}
$i_o/\text{mA}/\text{cm}^2$	0.067	300
A/volts	0.06	0.03
B/volts	0.05	0.08
$I_l/\text{mA}/\text{cm}^2$	900	900

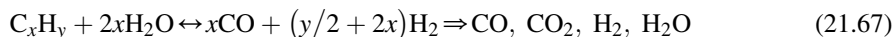
*SPFC, Solid polymer fuel cell; SOFC, Solid oxide fuel cell.
Larminie & Dicks (2003).*

21.6 SOURCES OF HYDROGEN FOR FUEL CELLS

Hydrogen can be produced by electrolysis, and while this should be reversible, in practice it only has an efficiency of about 80%. The losses are for the same reasons as there are losses in fuel cells. A more practical source, and one that has better energy utilisation is fuel reforming, of which there are three systems: SR, partial oxidation (POX) reforming, and autothermal reforming (AR). Each of these will be discussed in turn.

21.6.1 STEAM REFORMING

Widely used throughout the petrochemical industry, SR combines a vaporised hydrocarbon with steam over a catalyst (often nickel supported on alumina) at high temperatures (700–1000 °C).



During SR, the water-gas shift reaction also takes place, thereby converting the hydrogen in water directly to hydrogen gas.



The most common design of SR for industrial use is the tubular reformer, a furnace containing several tubes filled with catalysts through which the reactants pass. The reaction inside the tubes obtains heat from a flame external to the tubes. Tubular reformers present one main drawback for small PEM systems: they are not easily miniaturised.

21.6.2 POX REFORMING

In a POX reaction, the hydrocarbon is reacted with an amount of oxygen below the stoichiometric amount:



During POX, a small fraction of steam is added both to prevent carbon deposition on reformer surfaces and to reduce carbon monoxide production.



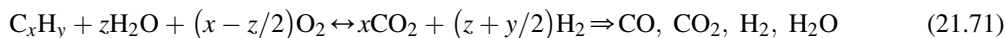
The primary disadvantage of the POX reaction is that it may waste a significant portion of the energy in the fuel as heat if this heat is not recovered. Its primary advantages are that

1. it is exothermic and therefore self-sustaining, and
2. it can be used on fuels with a variety of chemical components because catalysts are not required.

A POX reaction may be either noncatalytic or catalytic.

21.6.3 AUTOTHERMAL REFORMING

AR combines the processes of SR and POX. By combining the hydrocarbon with a mixture of oxygen and steam, the reformer uses the exothermic reaction of the hydrocarbon and oxygen to provide heat for the endothermic reaction of the hydrocarbon and steam.



For methane, the change in enthalpy for the above reaction is zero when y is equal to 1.115. The primary benefits of the AR are:

1. its high thermal efficiency (as a result of combining reactions),
2. its compactness (as a result of avoiding a separate combustion stream to provide heat as with a steam reformer), and
3. its rapid start up and quick load following (as a result of combining reactions).

The primary disadvantage is its lower hydrogen yield, only 42–48% hydrogen content in the output gas stream (dry basis), as compared with SR which produces 75–80% hydrogen (dry basis). The low hydrogen yield results from the intake of nitrogen, which dilutes the output gas.

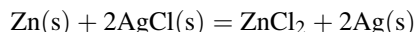
21.7 CONCLUDING REMARKS

This chapter has described some of the various types of fuel cell under development. Some of the practical losses and problems that occur in fuel cells have been discussed. The thermodynamic equations for the processes that occur in fuel cells have been developed, and a new property, electrochemical potential, has been introduced. While some analysis of fuel cell parameters can be made using equilibrium thermodynamics, the theory has been developed to consider the irreversible thermodynamics that occurs when the fuel cell is delivering a power output.

21.8 PROBLEMS

Assume the value of the Faraday constant, $F = 96,487 \text{ kC/kmol}$

P21.1 An electric cell has the following chemical reaction



and produces an emf of 1.005 V at 25 °C and 1.015 V at 0 °C, at a pressure of 1 bar. Estimate the following parameters at 25 °C and 1 bar:

1. change in enthalpy during the reaction,
2. amount of heat absorbed by the cell, per unit amount of zinc, to maintain the temperature constant during reversible operation.

[−216,937 kJ/kmol Zn; −23,002 kJ/kmol Zn]

P21.2 An electric cell is based on the reaction $\text{Pb} + \text{Hg}_2\text{Cl}_2 \rightarrow \text{PbCl}_2 + 2\text{Hg}$. If the enthalpy of reaction for this reaction, Q_p , at 25 °C is −95,200 kJ/kg Pb, calculate the emf, and rate of change of emf with temperature at constant pressure if the heat transfer to the cell is 8300 kJ/kg Pb.

[0.5363 V; $1.44 \times 10^{-4} \text{ V/K}$]

P21.3 Calculate the emf of a hydrogen–oxygen fuel cell operating reversibly if the overall reduction in Gibbs energy is 238 MJ/kg H_2 . If the cell operates at 75% of the reversible emf

due to internal irreversibilities calculate the magnitude and direction of the heat transfer with the surroundings, assuming that the enthalpy of reaction at the same conditions is -286 MJ/kmol H_2 .

[1.233 V; $-53,750 \text{ kJ/kg H}_2$]

- P21.4** An ideal, isothermal, reversible fuel cell with reactants of oxygen and hydrogen, and a product of water operates at a temperature of 400 K and a pressure of 1 bar. If the operating temperature increases to 410 K what must be the new pressure if the open circuit voltage is maintained constant? The values of K_{p_r} are

$$K_{p_r} = 1.8134 \times 10^{29} \text{ bar}^{-1/2} \text{ at } 400 \text{ K and } 2.4621 \times 10^{28} \text{ bar}^{-1/2} \text{ at } 410 \text{ K.}$$

[2.029 bar]

- P21.5** A hydrogen–oxygen fuel cell is required to produce a constant voltage and operate over a pressure range of 0.125–10 bars. The datum voltage is 1.16 V at a temperature of 350 K. If all the streams are at the same pressure evaluate the range of temperature required to maintain the voltage at this level, and show how the operating temperature must vary with pressure.

Assume that the enthalpy of reaction of the cell, $Q_p = -286,000 \text{ kJ/kmol H}_2$, and that this remains constant over the full temperature range. The valency, $z_i = 2$.

[317.4 K]

- P21.6** A hydrogen–oxygen fuel cell operates at a temperature of 450 K and the reactants and products are all at a pressure of 3 bar. Due to internal resistances the emf of the cell is only 70% of the ideal value. Calculate the ‘fuel consumption’ of the ideal cell and the actual one in g/kW h.

An alternative method of producing electrical power from the hydrogen is to burn it in an internal combustion engine connected to an electrical generator. If the engine has a thermal efficiency of 30% and the generator is 85% efficient, calculate the fuel consumption in this case and compare it with that of the fuel cell. Explain why one is higher than the other.

Table of values of enthalpy and Gibbs energy at $T = 450 \text{ K}$

Species	Enthalpy, h/(kJ/kmol)	Gibbs energy, g/(kJ/kmol)
Oxygen, O ₂	13,125	-84,603
Hydrogen, H ₂	12,791	-51,330
Water, H ₂ O	-223,672	-314,796

[32.25 g/kW h; 46 g/kW h; 116.2 g/kW h]

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This bibliography lists many of the texts that have been used in preparing the book, and on which some of the ideas were based. In general it is simply a bibliography and not a set of specific references, although some information has been drawn from the material in this list; where that is the case a specific reference is made in the text. There is not a bibliography for all chapters because the information is subsumed into the books relating to adjacent chapters.

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CHAPTER 8: EQUATIONS OF STATE

This subject is covered in most of the general texts on engineering thermodynamics. The reader is referred to these to obtain additional information or to see different approaches.

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