

Modern Thermodynamics

Modern Thermodynamics

From Heat Engines to Dissipative Structures

Second Edition

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*To all who contributed to our knowledge of Dissipative Structures
and
to Shelley and Maryna*

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Preface to the Second Edition

The first edition of this book was published in 1998 and we were pleased that it was well received. It has been used in over 25 countries as a text for courses in physics, chemistry and engineering, and it has been translated into French, Italian, Japanese, Portuguese and Russian. Thermodynamics as formulated in the twentieth century, what we chose to call ‘Modern Thermodynamics’ is a *theory of irreversible processes* in contrast to nineteenth century thermodynamics, which is a *theory of states*. In the latter, thermodynamics is confined to initial and final states, the processes that transform a state are not central to the theory; they are treated as another subject, ‘kinetics’. In Modern Thermodynamics, however, entropy-increasing irreversible processes are central to the theory. In it, we find additional tools, such as the rate of entropy production, to characterize and analyze nonequilibrium systems, and new results, such as the Onsager reciprocal relations, that are applicable to the thermoelectric effect, thermal diffusion and other cross-effects.

The context in which thermodynamics is being taught is rapidly changing. Therefore we have added new sections to chapters, which show more applications of the subject. The following is a partial list. In Chapter 2 we have included ‘energy flows’ in turbines and jet engines, and basics of renewable energies such as solar and wind energy. We have also included a description of the hurricane as a heat engine in Chapter 3. Chapter 11 now has sections on nonequilibrium electromagnetic radiation. In Chapter 19, we have included rates of entropy production in dissipative structures. In response to suggestions by users of this text, we have included a chapter on Statistical Thermodynamics, which makes this text self-contained by the inclusion of derivations of heat capacities of solids and Planck’s law of blackbody radiation. Several other changes have been made to improve the presentation of the concepts.

Entropy and entropy-producing irreversible processes are generally thought of as agents of disorder. A central message of this book is that, under far-from-equilibrium conditions, irreversible processes are, in fact, the drivers of self-organization and order we see all around us in Nature. These emergent structures, called *dissipative structures*, are distinct from machines and are a good thermodynamic basis on which we may begin to build a theory of biological organisms. It is an important direction for future developments in thermodynamics. We have included a section on this topic in the final chapter.

Preface to the First Edition

Why Thermodynamics?

I

Since half a century ago, our view of Nature has changed drastically. Classical science emphasized equilibrium and stability. Now we see fluctuations, instability, evolutionary processes on all levels from chemistry and biology to cosmology. Everywhere we observe irreversible processes in which time symmetry is broken. The distinction between reversible and irreversible processes was first introduced in thermodynamics through the concept of ‘entropy’, the arrow of time, as Arthur Eddington called it. Therefore our new view of Nature leads to an increased interest in thermodynamics. Unfortunately, most introductory texts are limited to the study of equilibrium states, restricting thermodynamics to idealized, infinitely slow reversible processes. The student does not see the relationship between irreversible processes that naturally occur, such as chemical reactions and heat conduction, and the rate of increase of entropy. In this text, we present a modern formulation of thermodynamics in which the relation between the rate of increase of entropy and irreversible processes is made clear from the very outset. Equilibrium remains an interesting field of inquiry but in the present state of science, it appears essential to include irreversible processes as well.

It is the aim of this book to give a readable introduction to present-day thermodynamics, starting with its historical roots as associated with heat engines but including also the thermodynamic description of far-from-equilibrium situations. As is well known today, far-from-equilibrium situations lead to new space–time structures. For this reason the restriction to equilibrium situations hides, in our opinion, some essential features of the behavior of matter and energy. An example is the role of fluctuations. The atomic structure of matter leads to fluctuations. However, at equilibrium or near equilibrium, these fluctuations are inconsequential.

Indeed a characteristic feature of equilibrium thermodynamics is the existence of extremum principles. For isolated systems entropy increases and is therefore maximum at equilibrium. In other situations (such as constant temperature) there exist functions called thermodynamic potentials which are also extrema (that is maximum or minimum) at equilibrium. This has important consequences. A fluctuation that leads to a temporal deviation from equilibrium is followed by a response that brings back the system to the extremum of the thermodynamic potential. The equilibrium world is also a stable world. This is no longer so in far-from-equilibrium situations. Here fluctuations may be amplified by irreversible dissipative processes and lead to new space–time structures which one of us (I. Prigogine) has called ‘dissipative structures’ to distinguish them from ‘equilibrium’ structures such as crystals. Therefore distance from equilibrium becomes a parameter somewhat similar to temperature. When we lower the temperature, we go from the gaseous state to a liquid and then a solid. As we shall see, here the variety is even greater. Take the example of chemical reactions. Increasing the distance from equilibrium we may obtain in succession oscillatory reactions, new spatial periodic structures and chaotic situations in which the time behavior becomes so irregular that initially close trajectories diverge exponentially.

One aspect is common to all these nonequilibrium situations, the appearance of long-range coherence. Macroscopically distinct parts become correlated. This is in contrast to equilibrium situations where the range of correlations is determined by short-range intermolecular forces. As a result, situations that are impossible to

realize at equilibrium become possible in far-from-equilibrium situations. This leads to important applications in a variety of fields. We can produce new materials in nonequilibrium situations where we escape from the restrictions imposed by the phase rule. Also, nonequilibrium structures appear at all levels in biology. We give some simple examples in Chapters 19 and the postface. It is now generally admitted that biological evolution is the combined result of Darwin's natural selection as well as of self-organization, which results from irreversible processes.

Since Ludwig Boltzmann (1844–1906) introduced a statistical definition of entropy in 1872, entropy is associated with disorder. The increase of entropy is then described as an increase of disorder, as the destruction of any coherence that may be present in the initial state. This has unfortunately led to the view that the consequences of the Second Law are self-evident, are trivial. This is, however, not true even for equilibrium thermodynamics, which leads to highly nontrivial predictions. Anyway, equilibrium thermodynamics covers only a small fraction of our everyday experience. We now understand that we cannot describe Nature around us without an appeal to nonequilibrium situations. The biosphere is maintained in nonequilibrium through the flow of energy coming from the Sun and this flow is itself the result of the nonequilibrium situation of our present state of the universe.

It is true that the information obtained from thermodynamics both for equilibrium and nonequilibrium situations is limited to a few general statements. We have to supplement them by the equation of state at equilibrium or the rate laws, such as chemical reaction rates. Still the information we obtain from thermodynamics is quite valuable precisely because of its generality.

II

Our book is subdivided into five parts. The first, Chapters 1 to 4, deals with the basic principles. The systems considered in thermodynamics are large systems (the number of particles N is a typical Avogadro number). Such systems are described by two types of variables, variables such as pressure or temperature, which are independent of the size of the system and are called 'intensive' variables, and variables such as the total energy, which are proportional to the number of particles ('extensive variables'). Historically thermodynamics started with empirical observations concerning the relation between these variables (e.g. the relation between pressure and volume). This is the main subject of Chapter 1. However, the two conceptual innovations of thermodynamics are the formulation of the 'First Law' expressing conservation of energy (Chapter 2) and of the 'Second Law' introducing entropy (Chapter 3).

Ignis mutat res. Fire transforms matter; fire leads to chemical reactions, to processes such as melting and evaporation. Fire makes fuel burn and release heat. Out of all this common knowledge, nineteenth century science concentrated on the single fact that combustion produces heat and that heat may lead to an increase in volume; as a result, combustion produces work. Fire leads, therefore, to a new kind of machine, the heat engine, the technological innovation on which industrial society has been founded.

What is then the link between 'heat' and 'work'? This question was at the origin of the formulation of the principle of energy conservation. Heat is of the same nature as energy. In the heat engine, heat is transferred into work but energy is conserved.

However, there was more. In 1811 Baron Jean-Joseph Fourier, the Prefect of Isère, won the prize of the French Academy of Sciences for his mathematical description of the propagation of heat in solids. The result stated by Fourier was surprisingly simple and elegant: heat flow is proportional to the gradient of temperature. It is remarkable that this simple law applies to matter, whether its state is solid, liquid or gaseous. Moreover, it remains valid whatever the chemical composition of the body, whether it is iron or gold. It is only the coefficient of proportionality between the heat flow and the gradient of temperature that is specific to each substance.

Fourier's law was the first example describing an irreversible process. There is a privileged direction of time as heat flows according to Fourier's law, from higher to lower temperature. This is in contrast with the laws of Newtonian dynamics in which the past and future play the same role (time enters only in Newton's law through a second derivative, so Newton's law is invariant in respect to time inversion). As already mentioned, it is the Second Law of thermodynamics that expresses the difference between 'reversible' and irreversible processes through the introduction of entropy. Irreversible processes produce entropy.

The history of the two principles of thermodynamics is a most curious one. Born in the middle of technological questions, they acquired rapidly a cosmological status. Let us indeed state the two principles as formulated by Rudolph Clausius (1822–1888) in the year 1865:

The energy of the universe is constant.

The entropy of the universe approaches a maximum.

It was the first evolutionary formulation of cosmology. This was a revolutionary statement as the existence of irreversible processes (and therefore of entropy) conflicts with the time-reversible view of dynamics. Of course, classical dynamics has been superseded by quantum theory and relativity. However, this conflict remains because, in both quantum theory and relativity, the basic dynamical laws are time-reversible.

The traditional answer to this question is to emphasize that the systems considered in thermodynamics are so complex (they contain a large number of interacting particles) that we are obliged to introduce approximations. The Second Law of thermodynamics would have its roots in these approximations! Some authors go so far as to state that entropy is only the expression of our ignorance!

Here again the recent extension of thermodynamics to situations far-from-equilibrium is essential. As we mentioned already, irreversible processes lead then to new space–time structures. They therefore play a basic constructive role. No life would be possible without irreversible processes (see Chapter 19). It seems absurd to suggest that life would be the result of our approximations! We can therefore not deny the reality of entropy, the very essence of an arrow of time in nature. We are the children of evolution and not its progenitors.

Questions regarding the relation between entropy and dynamics have received great attention recently but they are far from simple. Not all dynamical processes require the concept of entropy. The motion of the Earth around the Sun is an example in which irreversibility (such as friction due to tides) can be ignored and the motion described by time symmetric equations. However, recent developments in nonlinear dynamics have shown that such systems are exceptions. Most systems exhibit chaos and irreversible behavior. We begin to be able to characterize the dynamical systems for which irreversibility is an essential feature leading to an increase in entropy.

Let us go back to our book. In our presentation a central role is played by entropy production. As we show in Chapter 15, entropy production can be expressed in terms of thermodynamic flows J_i and thermodynamic forces X_i . An example is heat conduction where J_i is the flow of heat and X_i the gradient of temperature. We can now distinguish three stages. At equilibrium both the flows and the forces vanish. This is the domain of traditional thermodynamics. It is covered in Chapters 5 to 11. The reader will find many results familiar from all textbooks on thermodynamics. However, some subjects neglected in most textbooks are treated here. An example is thermodynamic stability theory, which plays an important role both at equilibrium and out from equilibrium. This forms the second part of the book.

Thermodynamic theory of stability and fluctuation, which originated in the work of Gibbs, is the subject of Chapters 12 to 14. Here, first we go through the classical theory of stability, as Gibbs formulated it, which depends on thermodynamic potentials. We then discuss the theory of stability in terms of the modern theory of entropy production, which is more general than the classical theory. This gives us the foundation for the study of stability of nonequilibrium systems discussed in the later part of the book. We then turn to the thermodynamic theory of fluctuations, which has its origin in Einstein's famous formula that relates the

probability of a fluctuation to a decrease in entropy. This theory also gives us the basic results that will later lead us to Onsager's reciprocal relations, discussed in Chapter 16.

The fourth part, Chapters 15 to 17, is devoted to the neighborhood of equilibrium, which is defined by linear relations between flows and forces (such as realized in Fourier's law). This is a well-explored field dominated by Onsager's reciprocity relations. Indeed in 1931, Lars Onsager discovered the first general relations in nonequilibrium thermodynamics for the linear, near-equilibrium region. These are the famous 'reciprocal relations'. In qualitative terms, they state that if a force, say 'one' (corresponding, for example, to a temperature gradient), may influence a flux 'two' (for example a diffusion process), then force 'two' (a concentration gradient) will also influence the flux 'one' (the heat flow).

The general nature of Onsager's relations has to be emphasized. It is immaterial, for instance, whether the irreversible processes take place in a gaseous, liquid or solid medium. The reciprocity expressions are valid independently of any microscopic assumptions.

Reciprocal relations have been the first results in the thermodynamics of irreversible processes to indicate that this was not some ill-defined no-man's-land but a worthwhile subject of study whose fertility could be compared with that of equilibrium thermodynamics. Equilibrium thermodynamics was an achievement of the nineteenth century, nonequilibrium thermodynamics was developed in the twentieth century and Onsager's relations mark a crucial point in the shift of interest away from equilibrium toward nonequilibrium.

It is interesting to notice that now the flow of entropy, even close to equilibrium, irreversibility can no longer be identified with the tendency to disorder. We shall give numerous examples in the text, but let us already illustrate this conclusion in a simple situation corresponding to thermal diffusion. We take two boxes connected by a cylinder, we heat one box and cool the other. Inside the box there is a mixture of two gases, say hydrogen and nitrogen. We then observe that, at the steady state, the concentration of hydrogen is higher in one box, of nitrogen in the other. Irreversible processes here cause the flow of heat to produce both disorder ('thermal motion') and order (separation of the two components). We see that a nonequilibrium system may evolve spontaneously to a state of increased complexity. This constructive role of irreversibility becomes ever more striking in far-from-equilibrium situations to which we now turn.

The main novelty is that in far-from-equilibrium situations, which correspond to the third stages of thermodynamics, there is in general no longer any extremum principle (Chapters 18 and 19). As a result, fluctuations are no longer necessarily damped. Stability is no longer the consequence of the general laws of physics. Fluctuations may grow and invade the whole system. As mentioned, we have called 'dissipative structures' these new spatiotemporal organizations, which may emerge in far-from-equilibrium situations. These dissipative structures correspond to a form of supramolecular coherence involving an immense number of molecules. In far-from-equilibrium situations we begin to observe new properties of matter that are hidden at equilibrium.

We already mentioned the constructive role of irreversibility and the appearance of long-range correlations in far-from-equilibrium systems. Let us add also 'unpredictability' because the new nonequilibrium states of matter appear at so-called bifurcation points where the system may in general 'choose' between various states. We are far from the classical description of nature as an automaton.

One often speaks of 'self-organization'. Indeed, as there are generally a multitude of dissipative structures available, molecular fluctuations determine which one will be chosen. We begin to understand the enormous variety of structures we observe in the natural world. Today the notion of dissipative structures and of self-organization appear in a wide range of fields from astrophysics up to human sciences and the economy. We want to quote a recent report to the European Communities due to C.K. Biebracher, G. Nicolis and P. Schuster:

The maintenance of the organization in nature is not – and cannot be – achieved by central management; order can only be maintained by self-organization. Self-organizing systems allow adaptation to the prevailing environment, i.e., they react to changes in the environment with a thermodynamic response which

makes the systems extraordinarily flexible and robust against perturbations of the outer conditions. We want to point out the superiority of self-organizing systems over conventional human technology which carefully avoids complexity and hierarchically manages nearly all technical processes. For instance, in synthetic chemistry, different reaction steps are usually carefully separated from each other and contributions from the diffusion of the reactants are avoided by stirring reactors. An entirely new technology will have to be developed to tap the high guidance and regulation potential of self-organizing systems for technical processes. The superiority of self-organizing systems is illustrated by biological systems where complex products can be formed with unsurpassed accuracy, efficiency and speed.

(From C.F. Biebricher, G. Nicolis and P. Schuster, *Self-Organization in the Physico-Chemical and Life Sciences*, 1994, Report on Review Studies, PSS 0396, Commission of the European Communities, Director General for Science, Research and Development)

III

This book is aimed to be an introductory text. No previous familiarity with thermodynamics is assumed. Interested readers are invited to consult more specialized texts. For this reason we have excluded a number of interesting problems often associated with ‘extended thermodynamics’. These are the questions that deal with strong gradients or with very long time scales when memory effects have to be included. Every theory is based on idealizations, which have a limited domain of validity. In our presentation the assumption is that at least local quantities such as temperature and pressure take well-defined values. More precisely this is called the ‘local equilibrium assumption’, which is a reasonable approximation for the phenomena studied in this book.

Science has no final form and is moving away from a static geometrical picture towards a description in which evolution and history plays an essential role. For this new description of nature, thermodynamics is basic. This is the message our book wants to transmit to the reader.

Acknowledgments

This book is the outcome of decades of work. The senior author was a student of Theophile de Donder (1870–1957), the founder of the Brussels School of Thermodynamics. Contrary to the opinion prevalent at that time, de Donder considered that thermodynamics should not be limited to equilibrium situations. He created an active school in Belgium. However, his approach remained isolated. Today the situation has drastically changed. There is a major effort going on in the study of nonequilibrium processes, be it in hydrodynamics, chemistry, optics or biology. The need for an extension of thermodynamics is now universally accepted.

This book is intended to present an introductory text that covers both the traditional aspects of thermodynamics as well as its more recent developments. In the literature there are many texts devoted to classical thermodynamics and others, generally more advanced, specialized in nonequilibrium processes. We believe, however, that from the start the student has to be familiar with both aspects in order to grasp the contrasting behavior of matter at equilibrium and far from equilibrium.



*De Donder (seated at the center) with his colleagues on the occasion of his 70th birthday.
First row (seated) L to R: Henri Vanderlinden, Frans van den Dungen, Georgette Schouls, Théophile De Donder,
Yvonne De Keghel-Dupont, Georges Lemaître, Théophile Lepage; Second row (standing) L to R: Pierrs
Boudoux, Frans van Bergen, Jacques Vorobeitchik, Raymond Defay, Marcel Pourbaix, Robert Debeyer, Raymond
Couurtez, Jean Bosquet, Ilya Prigogine, Jacques Van Mieghem, R. Deladrière, Maurice Nuyens, Jean Pelseneer,
Georges Homés, Jules Géhéniau*

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This book could not have been realized without the continuous support of many institutions. We especially want to thank the Belgian Communauté Française, the International Solvay Institutes in Brussels, the Department of Energy (DOE) of the United States, The Welch Foundation of Texas and the University of Texas at Austin. We would also like to thank Wake Forest University for granting Reynolds Leave for one of us (D.K.) to facilitate the writing of this second edition of the book.

We believe that we are today at a decisive moment in the history of science. At all levels of observation, we see an evolutionary universe, we see fluctuations and instabilities. Thermodynamics is the first science that brought an evolutionary view of Nature. This is in contrast with classical or even quantum mechanics, which presents us with the picture of time reversible and deterministic laws. While there is also no arrow of time and no place for instabilities in equilibrium thermodynamics, this is no more so in nonequilibrium thermodynamics where fluctuations and instabilities play an essential role. Therefore it is important that students already at an early stage become familiar with the role of nonequilibrium processes and learn how thermodynamics describes the transition between the idealized static world of classical physics and the evolving, fluctuating world in which we live.

^{*}P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Stability and Fluctuations*, John Wiley & Sons, Inc., New York, London, 1971.

[†]I. Prigogine and I. Stengers, *Order Out of Chaos*, Bantam Books, New York, 1980; see also *The End of Certitudes*, Free Press, New York, 1997.

Notes for Instructors

The first 11 chapters and Chapter 20 (statistical thermodynamics) are intended for a one-semester introductory undergraduate course on modern thermodynamics for students in physics, chemistry and engineering. Not all chapters are meant to be for all the three branches; the instructor may drop a few chapters to emphasize others. Exercises in each chapter are chosen to illustrate applications of the subject in many areas. In the current research environment, interdisciplinary research is becoming increasingly important. It is therefore important to make the students aware of a wide variety of applications of thermodynamics at an early stage.

Chapters 12 to 19 are meant for an advanced undergraduate or a graduate course in thermodynamics. For these chapters a good knowledge of vector calculus is assumed. These chapters do not include worked examples. The exercises are designed to give the student a deeper understanding of the topics and practical applications.

Throughout the text, the reader is encouraged to use *Mathematica** or *Maple*[†] to do tedious calculations or look at complex physicochemical situations. Appendix 1.2 in the first chapter introduces the reader to the use of *Mathematica*.

[Supplementary Online Material]

Full solutions to exercises, PowerPoint slides of all figures, Data Tables and Answers to Exercises, are available for instructors as PDF files at:

<http://sites.google.com/site/modernthermodynamics/>

These supplementary website files are password protected. Instructors can obtain the password by sending a request to Professor Kondepudi at dilip@wfu.edu. The above website also contains other useful thermodynamic information related to the book.

**Mathematica* is the registered trademark of Wolfram Research Inc.

[†]*Maple* is the registered trademark of Waterloo Maple Inc.

List of Variables

Variables

a	van der Waals constant	H^\ddagger	transition-state enthalpy
a_k	activity of k	I	electric current
A	affinity	J_k	thermodynamic flow
A_k	affinity of reaction k	k	rate constant
b	van der Waals constant	k_B	Boltzmann constant
$c_x, [x]$	concentration of x (mol L ⁻¹)	$K(T)$	equilibrium constant at temperature T
c^0	standard state concentration	K_i	Henry's constant of i
C	heat capacity	m_k	molality, concentration (in moles of solute/kilogram of solvent)
C_m	molar heat capacity	m^0	standard state molality
C_{mp}	molar heat capacity at constant pressure	M_k	molar mass of component k
C_{mV}	molar heat capacity at constant volume	n_k	concentration (mol m ⁻³)
e	electron charge	N	molar amount of substance
E_a	activation energy	\tilde{N}	number of molecules
f	fugacity	N_k	total molar amount of k
F	Faraday constant	N_A	Avogadro constant
F	Helmholtz energy	p^0	standard state pressure
F_m	molar Helmholtz energy	p	total pressure
g	acceleration due to gravity	p_c	critical pressure
G	Gibbs free energy	p_k	partial pressure of k
G_m	molar Gibbs (free) energy	q	molecular partition function
ΔG_f	Gibbs (free) energy of formation	Q	total partition function
ΔG_f^0	standard Gibbs energy of formation	R_{kf}	forward rate of reaction k
ΔG_r	Gibbs (free) energy of a reaction	R_{kr}	reverse rate of reaction k
ΔG_{fus}	enthalpy of fusion	$s(x)$	entropy density at x
ΔG_{vap}	enthalpy of vaporization	S	total entropy
G^\ddagger	transition-state Gibbs energy	S_m	molar entropy
$h_{T,p}$	heat of reaction per unit ξ	S^\ddagger	transition-state entropy
h	enthalpy density	T	temperature
H	enthalpy	T_b	boiling point
H_m	molar enthalpy	T_c	critical temperature
H_{mk}	partial molar enthalpy of k	T_m	melting point
ΔH_f	enthalpy of formation	u	energy density
ΔH_f^0	standard enthalpy of formation	U	total internal energy
ΔH_r	enthalpy of a reaction	U_m	total molar energy
ΔH_{fus}	enthalpy of fusion	v (dξ/dt)	velocity of reaction or rate of conversion
ΔH_{vap}	enthalpy of vaporization	V	total volume

V	voltage or potential difference	$[x], c_x$	concentration of x (mol L ⁻¹)
V_m	molar volume	x_k	mole fraction of k
V_{mc}	critical molar volume	z_k	ion-number of k
V_{mk}	partial molar volume of k	Z	compressibility factor

Greek letters

α	isothermal compressibility
β	Stefan–Boltzmann constant
ϕ	electrical potential
ϕ_k	osmotic coefficient of k
γ	ratio of molar heat capacities
γ_k	surface tension
Γ_k	activity coefficient of
μ_k	general mobility k in a field
μ_k^0	chemical potential of k
μ_\pm	standard chemical potential of k
	mean activity coefficient

v_{jk}	stoichiometric coefficients of reaction k
Π	osmotic pressure
ρ	density
Σ	interfacial area
ξ	extent of reaction
$d\xi/dt (v)$	velocity of reaction or rate of conversion
ξ_k	extent of reaction of reaction k
$d\xi_k/dt (v_k)$	velocity of reaction k or rate of conversion k
$\tau_k \psi$	interaction energy per mole of k due to potential ψ

Part I

Historical Roots: From Heat Engines to Cosmology

1

Basic Concepts and the Laws of Gases

Introduction

Adam Smith's *Wealth of Nations* was published in the year 1776, seven years after James Watt (1736–1819) had obtained a patent for his version of the steam engine. Both men worked at the University of Glasgow. Yet, in Adam Smith's great work the only use for coal was in providing heat for workers [1]. The machines of the eighteenth century were driven by wind, water and animals. Nearly 2000 years had passed since Hero of Alexandria made a sphere spin with the force of steam, but still the power of fire to generate motion and drive machines remained hidden. Adam Smith (1723–1790) did not see in coal a buried wealth of nations.

The steam engine revealed a new possibility. While wind, water and animals converted one form of motion to another, the steam engine was fundamentally different: it converted heat to mechanical motion. Its enormous impact on civilization not only heralded the industrial revolution but also gave birth to a new science: *thermodynamics*. Unlike the science of Newtonian mechanics, which had its origins in theories of motion of heavenly bodies, thermodynamics was born out of a more practical interest: generating motion from heat.

Initially, thermodynamics was the study of heat and its potential to generate motion; then it merged with the larger subject of energy and its interconversion from one form to another. With time, thermodynamics evolved into a theory that describes transformations of states of matter in general, motion generated by heat being a consequence of particular transformations. It is founded on essentially two fundamental laws, one concerning *energy* and the other *entropy*. A precise definition of energy and entropy, as measurable physical quantities, will be presented in Chapters 2 and 3 respectively. In these chapters, we will also touch upon the remarkable story behind the formulation of these two concepts. In the following two sections we will give an overview of thermodynamics and familiarize the reader with the terminology and concepts that will be developed in the rest of the book.

Every system is associated with an energy and an entropy. When matter undergoes transformation from one state to another, the total amount of energy in the system and its exterior is conserved; total entropy, however, can only increase or, in idealized cases, remain unchanged. These two simple-sounding statements have far-reaching consequences. Max Planck (1858–1947) was deeply influenced by the breadth of the conclusions that can be drawn from them and devoted much of his time to the study of thermodynamics. In reading this

book, I hope the reader will come to appreciate the significance of the following often-quoted opinion of Albert Einstein (1879–1955):

A theory is more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.

The thermodynamics of the nineteenth century, which so impressed Planck and Einstein, described static systems that were in thermodynamic equilibrium. It was formulated to calculate the initial and final entropies when a system evolved from one equilibrium state to another. In this ‘Classical Thermodynamics’ there was no direct relationship between natural processes, such as chemical reactions and conduction of heat, and the rate at which entropy changed. During the twentieth century, Lars Onsager (1903–1976), Ilya Prigogine (1917–2003) and others extended the formalism of classical thermodynamics to relate the *rate* of entropy change to *rates* of processes, such as chemical reactions and heat conduction. From the outset, we will take the approach of this ‘Modern Thermodynamics’ in which thermodynamics is a theory of irreversible processes, not merely a theory of equilibrium states. Equipped with a formalism to calculate the rate of entropy changes, Modern Thermodynamics gives us new insight into the role of irreversible processes in Nature.

1.1 Thermodynamic Systems

A thermodynamic description of natural processes usually begins by dividing the world into a ‘system’ and its ‘exterior’, which is the rest of the world. This cannot be done, of course, when one is considering the thermodynamic nature of the entire universe; however, although there is no ‘exterior’, thermodynamics can be applied to the entire universe. The definition of a thermodynamic system depends on the existence of ‘boundaries’, boundaries that separate the system from its exterior and determine the way the system interacts with its exterior. In understanding the thermodynamic behavior of a system, the manner in which it exchanges energy and matter with its exterior is important. Therefore, thermodynamic systems are classified into three types: isolated, closed and open systems (Figure 1.1) according to the way they interact with the exterior.

Isolated systems do not exchange energy or matter with the exterior. Such systems are generally considered for pedagogical reasons, while systems with an extremely slow exchange of energy and matter can be realized in a laboratory. Except for the universe as a whole, truly isolated systems do not exist in Nature.

Closed systems exchange energy but not matter with their exterior. It is obvious that such systems can easily be realized in a laboratory. A closed flask of reacting chemicals that is maintained at a fixed temperature is a closed system. The Earth, on a time-scale of years, during which it exchanges negligible amounts of matter with its exterior, may be considered a closed system; the Earth only absorbs solar energy and emits it back into space.

Open systems exchange both energy and matter with their exterior. All living and ecological systems are open systems. The complex organization in open systems is a result of exchange of matter and energy and the entropy generating irreversible processes that occur within.

In thermodynamics, the **state** of a system is specified in terms of macroscopic **state variables**, such as volume, V , pressure, p , temperature, T , and moles, N_k , of chemical constituent k , which are self-evident. These variables are adequate for the description of equilibrium systems. When a system is not in thermodynamic

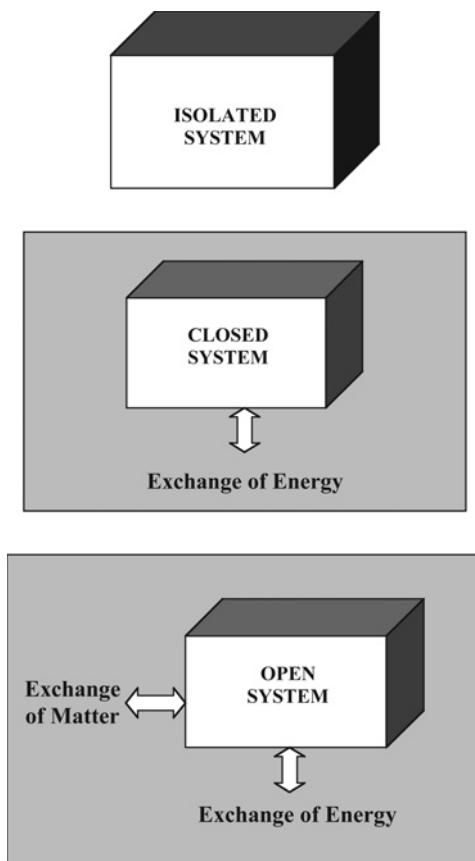


Figure 1.1 Isolated, closed and open systems. Isolated systems exchange neither energy nor matter with the exterior. Closed systems exchange heat and mechanical energy but not matter with the exterior. Open systems exchange both energy and matter with the exterior.

equilibrium, more variables, such as the rate of convective flow or of metabolism, may be needed to describe it. The two laws of thermodynamics are founded on the concepts of energy, U , and entropy, S , which, as we shall see, are **functions of state variables**.

Since the fundamental quantities in thermodynamics are functions of many variables, thermodynamics makes extensive use of multivariable calculus. Functions of state variables, such as U and S , are multivariable functions and are called **state functions**. A brief summary of some basic properties of functions of many variables is given in Appendix A1.1 (at the end of this chapter).

It is convenient to classify thermodynamic variables into two categories. Variables such as volume V and amount of a substance N_k (moles), which indicate the size of the system, are called **extensive variables**. Variables such as temperature T and pressure p , which specify a local property and do not indicate the system's size, are called **intensive variables**.

If the temperature is not uniform, then heat will flow until the entire system reaches a state of uniform temperature. Such a state is the state of **thermal equilibrium**. The state of thermal equilibrium is a special

state towards which all isolated systems will inexorably evolve. A precise description of this state will be given later in this book. In the state of thermal equilibrium, the values of total internal energy U and entropy S are completely specified by the temperature T , the volume V and the amounts of the system's chemical constituents N_k (moles):

$$U = U(T, V, N_k) \quad \text{or} \quad S = S(T, V, N_k) \quad (1.1.1)$$

The values of an extensive variable, such as total internal energy U or entropy S , can also be specified by other extensive variables:

$$U = U(S, V, N_k) \quad \text{or} \quad S = S(U, V, N_k) \quad (1.1.2)$$

As we shall see in the following chapters, intensive variables can be expressed as derivatives of one extensive variable with respect to another. For example, we shall see that the temperature $T = (\partial U / \partial S)_{V, N_k}$. The laws of thermodynamics and the calculus of multivariable functions give us a rich understanding of many phenomena we observe in Nature.

1.2 Equilibrium and Nonequilibrium Systems

It is our experience that if a physical system is isolated, its state – specified by macroscopic variables such as pressure, temperature and chemical composition – evolves *irreversibly* towards a time-invariant state in which we see no further physical or chemical change. This is the state of **thermodynamic equilibrium**. It is characterized by a uniform temperature throughout the system. The state of equilibrium is also characterized by several other physical features that we will describe in the following chapters.

The evolution of a system towards the state of equilibrium is due to **irreversible processes**, such as heat conduction and chemical reactions, which act in a specific direction but not its reverse. For example, heat always flows from a higher to a lower temperature, never in the reverse direction; similarly, chemical reactions cause compositional changes in a specific direction, not its reverse (which, as we shall see in Chapter 4, is described using the concept of ‘chemical potential’, a quantity similar to temperature, and ‘affinity’, a thermodynamic force that drives chemical reactions). At equilibrium, these processes vanish. Thus, a nonequilibrium state can be characterized as one in which irreversible processes are taking place, driving the system towards the equilibrium state. In some situations, especially during chemical transformations, the rates at which the state is transforming irreversibly may be extremely small, and an isolated system might appear as if it is time invariant and has reached its state of equilibrium. Nevertheless, with appropriate specification of the chemical reactions, the nonequilibrium nature of the state can be identified.

Two or more systems that interact and exchange energy and/or matter will eventually reach the state of thermal equilibrium in which the temperature within each system is spatially uniform and the temperature of all the systems are the same. If a system A is in thermal equilibrium with system B and if B is in thermal equilibrium with system C, then it follows that A is in thermal equilibrium with C. This ‘transitivity’ of the state of equilibrium is sometimes called the **zeroth law**. Thus, equilibrium systems have a well-defined, spatially uniform temperature; for such systems, the energy and entropy are functions of state as expressed in Equation (1.1.1).

Uniformity of temperature, however, is not a requirement for the entropy or energy of a system to be well defined. For **nonequilibrium systems**, in which the temperature is not uniform but is well defined locally

at every point x , we can define densities of thermodynamic quantities such as energy and entropy. Thus, the energy density, u , at the location x ,

$$u[T(x), n_k(x)] = \text{internal energy per unit volume} \quad (1.2.1)$$

can be defined in terms of the local temperature $T(x)$ and the concentrations

$$n_k(x) = \text{moles of constituent } k \text{ per unit volume} \quad (1.2.2)$$

Similarly, an entropy density $s(T, n_k)$ can be defined. (We use a lower case letter for the densities of thermodynamic quantities). The atmosphere of the Earth, shown in Box 1.1, is an example of a nonequilibrium system in which both n_k and T are functions of position. The total energy U , the total entropy S and the total amount of the substance N_k are

$$S = \int_V s[T(x), n_k(x)]dV \quad (1.2.3)$$

$$U = \int_V u[T(x), n_k(x)]dV \quad (1.2.4)$$

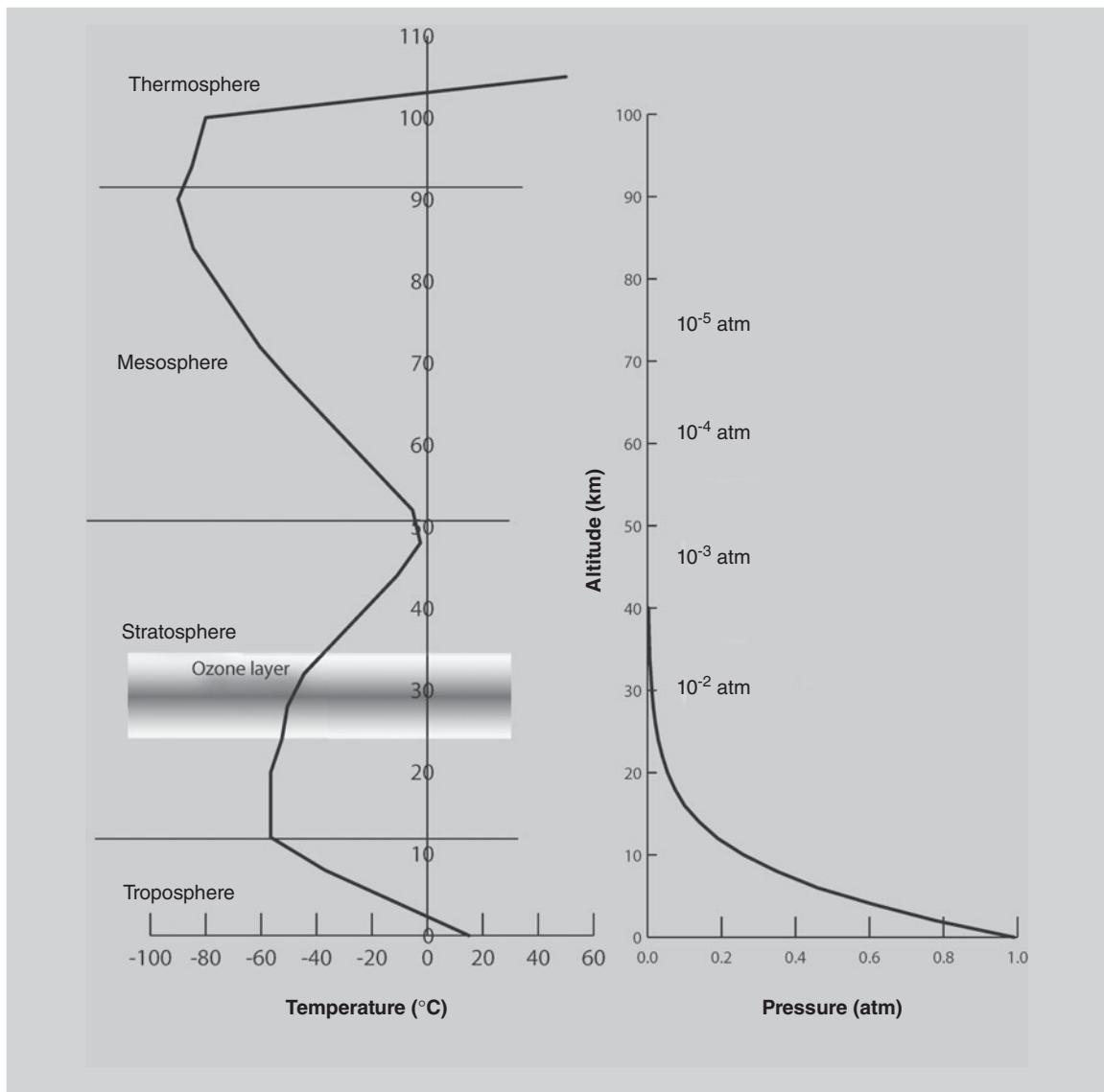
$$N_k = \int_V n_k(x)dV \quad (1.2.5)$$

In nonequilibrium (nonuniform) systems, the total energy U is no longer a function of other extensive variables such as S , V and N_k , as in Equation (1.1.2), and obviously one cannot define a single temperature for the entire system because it may not be uniform. In general, each of the variables, the total energy U , entropy S , the amount of substance N_k and the volume V , is no longer a function of the other three variables, as in Equation (1.1.2). However, this does not restrict in any way our ability to determine the entropy or energy of a system that is not in thermodynamic equilibrium; we can determine them using the expressions above, as long as the temperature is locally well defined.

In texts on classical thermodynamics, it is sometimes stated that entropy of a nonequilibrium system is not defined; it only means that S is not a function of the variables U , V and N_k . If the temperature of the system is locally well defined, then indeed the entropy of a nonequilibrium system can be defined in terms of an entropy density, as in Equation (1.2.3).

Box 1.1 The atmosphere of the Earth

Blaise Pascal (1623–1662) explained the nature of atmospheric pressure. The pressure at any point in the atmosphere is due to the column of air above it. The atmosphere of the Earth is not in thermodynamic equilibrium: its temperature is not uniform and the amounts of its chemical constituents (N_2 , O_2 , Ar, CO_2 , etc.) are maintained at a nonequilibrium value through cycles of production and consumption.



1.3 Biological and Other Open Systems

Open systems are particularly interesting because in them we see spontaneous self-organization. The most spectacular example of self-organization in open systems is life. Every living cell is an open system that exchanges matter and energy with its exterior. The cells of a leaf absorb energy from the sun and exchange matter by absorbing CO_2 , H_2O and other nutrients and releasing O_2 into the atmosphere. A biological open system can be defined more generally: it could be a single cell, an organ, an organism or an ecosystem. Other examples of open systems can be found in industry; in chemical reactors, for example, raw materials and energy are the inputs and the desired and waste products are the outputs.

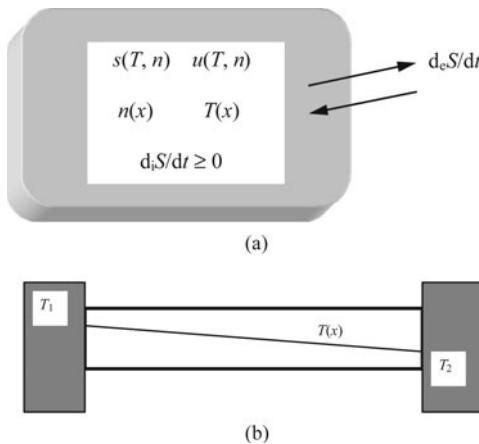


Figure 1.2 (a) In a nonequilibrium system, the temperature $T(x)$ and molar density $n_k(x)$ may vary with position. The entropy and energy of such a system may be described by an entropy density $s(T, n_k)$ and an energy density $u(T, n_k)$. The total entropy $S = \int_V s[T(x), n_k(x)]dV$, the total energy $U = \int_V u[T(x), n_k(x)]dV$ and the total molar amount $N_k = \int_V n_k(x)dV$. For such a nonequilibrium system, the total entropy S is not a function of U , N_k and the total volume V . The term $d_i S/dt$ is the rate of change of entropy due to chemical reactions, diffusion, heat conduction and other such irreversible processes; according to the Second Law, $d_i S/dt$ can only be positive. In an open system, entropy can also change due to the exchange of energy and matter; this is indicated by the term $d_e S/dt$, which can be either positive or negative. (b) A system in contact with thermal reservoirs of unequal temperatures is a simple example of a nonequilibrium system. The temperature is not uniform and there is a flow of heat due to the temperature gradient. The term $d_e S/dt$ is related to the exchange of heat at the boundaries in contact with the heat reservoirs, whereas $d_i S/dt$ is due to the irreversible flow of heat within the system.

As noted in the previous section, when a system is not in equilibrium, processes such as chemical reactions, conduction of heat and transport of matter take place so as to drive the system towards equilibrium. All of these processes generate entropy in accordance with the Second Law (see Figure 1.2). However, this does not mean that the entropy of the system must always increase: the exchange of energy and matter may also result in the net output of entropy in such a way that the entropy of a system is maintained at a low value.

One of the most remarkable aspects of nonequilibrium systems that came to light in the twentieth century is the phenomenon of self-organization. Under certain nonequilibrium conditions, systems can spontaneously undergo transitions to organized states, which, in general, are states with lower entropy. For example, nonequilibrium chemical systems can make a transition to a state in which the concentrations of reacting compounds vary periodically, thus becoming a ‘chemical clock’. The reacting chemicals can also spatially organize into patterns with great symmetry. In fact, it can be argued that most of the ‘organized’ behavior we see in Nature is created by irreversible processes that dissipate energy and generate entropy. For these reasons, these structures are called **dissipative structures** [1]. Chapter 19 is devoted to this important topic, an active field of current research. In an open system, these organized states could be maintained indefinitely, but only at the expense of exchange of energy and matter and increase of entropy outside the system.

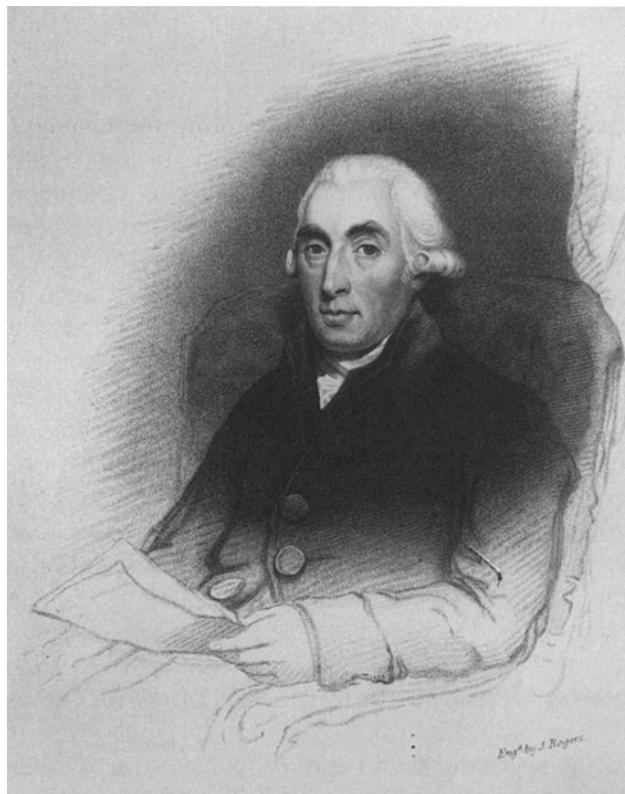
1.4 Temperature, Heat and Quantitative Laws of Gases

During the seventeenth and eighteenth centuries, a fundamental change occurred in our conception of Nature. Nature slowly but surely ceased to be solely a vehicle of God’s will, comprehensible only through theology.

The new ‘scientific’ conception of Nature based on rationalism and experimentation gave us a different world view, a view that liberated the human mind from the confines of religious doctrine. In the new view, Nature obeyed simple and universal laws, laws that humans can know and express in the precise language of mathematics. Right and wrong were decided through experiments and observation. It was a new dialogue with Nature. Our questions became experiments, and Nature’s answers were consistent and unambiguous.

It was during this time of great conceptual change that a scientific study of the nature of heat began. This was primarily due to the development of the thermometer, which was constructed and used in scientific investigations since the time of Galileo Galilei (1564–1642) [2, 3]. The impact of this simple instrument was considerable. In the words of Sir Humphry Davy (1778–1829), ‘Nothing tends to the advancement of knowledge as the application of a new instrument.’

The most insightful use of the thermometer was made by Joseph Black (1728–1799), a professor of medicine and chemistry at Glasgow. Black drew a clear distinction between temperature, or degree of hotness, and the quantity of heat (in terms of current terminology, temperature is an intensive quantity whereas heat is an extensive quantity). His experiments using the newly developed thermometers established the fundamental fact that *the temperatures of all the substances in contact with each other will eventually reach the same value, i.e. systems that can exchange heat will reach a state of thermal equilibrium.* This idea was not easily



Joseph Black (1728–1799).

(Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library.)

accepted by his contemporaries because it seems to contradict the ordinary experience of touch, in which a piece of metal felt colder than a piece of wood even after they had been in contact for a very long time. However, the thermometer proved this point beyond doubt. With the thermometer, Black discovered **specific heat**, laying to rest the general belief of his time that the amount of heat required to increase the temperature of a substance by a given amount depended solely on its mass, not specific to its makeup. He also discovered latent heats of fusion and evaporation of water – the latter with the enthusiastic help from his pupil James Watt (1736–1819) [4].

Though the work of Joseph Black and others clearly established the distinction between heat and temperature, the nature of heat remained an enigma for a long time. Whether heat was an indestructible substance without mass, called the ‘caloric’, that moved from substance to substance or whether it was a form of microscopic motion was still under debate as late as the nineteenth century. After considerable debate and experimentation it became clear that heat was a form of energy that could be transformed to other forms, and so the caloric theory was abandoned – though we still measure the amount of heat in ‘calories’, in addition to using the SI units of joules.

Temperature can be measured by noting the change of a physical property, such as the volume of a fluid (such as mercury), the pressure of a gas or the electrical resistance of a wire, with degree of hotness. This is an *empirical* definition of temperature. In this case, the uniformity of the unit of temperature depends on the uniformity with which the measured property changes as the substance gets hotter. The familiar Celsius scale, which was introduced in the eighteenth century by Anders Celsius (1701–1744), has largely replaced the Fahrenheit scale, which was also introduced in the eighteenth century by Gabriel Fahrenheit (1686–1736). As we shall see in the following chapters, the development of the Second Law of thermodynamics during the middle of the nineteenth century gave rise to the concept of an *absolute scale of temperature* that is independent of material properties. Thermodynamics is formulated in terms of the absolute temperature. We shall denote this absolute temperature by T .

1.4.1 The Laws of Gases

In the rest of this section we will present an overview of the laws of gases without going into much detail. We assume the reader is familiar with the laws of ideal gases and some basic definitions are given in Box 1.2.

Box 1.2 Basic definitions

Pressure is defined as the force per unit area. The pascal is the SI unit of pressure:

$$\text{pascal (Pa)} = 1 \text{ N m}^{-2}$$

The pressure due to a column of fluid of uniform density ρ and height h equals $h\rho g$, where g is the acceleration due to gravity (9.806 m s^{-2}). The pressure due to the Earth’s atmosphere changes with location and time, but it is often close to 10^5 Pa at sea level. For this reason, a unit called the **bar** is defined as

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa}$$

The atmospheric pressure at the Earth's surface is also nearly equal to the pressure due to a 760 mm column of mercury. For this reason, the following units are defined:

torr = pressure due to 1.00 mm column of mercury

$$\mathbf{1\ atmosphere\ (atm)} = \mathbf{760\ torr} = \mathbf{101.325\ kPa}$$

1 atm equals approximately 10 N cm^{-2} (1 kg weight cm^{-2} or 15 lb inch^{-2}). The atmospheric pressure decreases exponentially with altitude (see Box 1.1).

Temperature is usually measured in kelvin (K), Celsius ($^{\circ}\text{C}$) or Fahrenheit ($^{\circ}\text{F}$). The Celsius and Fahrenheit scales are empirical, whereas (as we shall see in Chapter 3) the kelvin scale is an absolute scale based on the Second Law of thermodynamics: 0 K is the absolute zero, the lowest possible temperature. Temperatures measured in these scales are related as follows:

$$T\text{ }(^{\circ}\text{C}) = (5/9)[T\text{ }(^{\circ}\text{F}) - 32], \quad T(K) = T(^{\circ}\text{C}) + 273.15$$

On the Earth, the highest recorded temperature is $57.8\text{ }^{\circ}\text{C}$, or $136\text{ }^{\circ}\text{F}$; it was recorded in El Azizia, Libya, in 1922. The lowest recorded temperature is $-88.3\text{ }^{\circ}\text{C}$, or $-129\text{ }^{\circ}\text{F}$; it was recorded in Vostok, Antarctica. In the laboratory, sodium gas has been cooled to temperatures as low as 10^{-9} K , and temperatures as high as 10^8 K have been reached in nuclear fusion reactors.

Heat was initially thought to be an indestructible substance called the **caloric**. According to this view, caloric, a fluid without mass, passed from one body to another, causing changes in temperature. However, in the nineteenth century it was established that heat was not an indestructible caloric but a form of energy that can convert to other forms of energy (see Chapter 2). Hence, heat is measured in the units of energy. In this text we shall mostly use the SI units in which heat is measured in **joules**, though the calorie is an often-used unit of heat. A calorie was originally defined as the amount of heat required to increase the temperature of 1 g of water from $14.5\text{ }^{\circ}\text{C}$ to $15.5\text{ }^{\circ}\text{C}$. The current practice is to *define* a thermochemical calorie as 4.184 J.

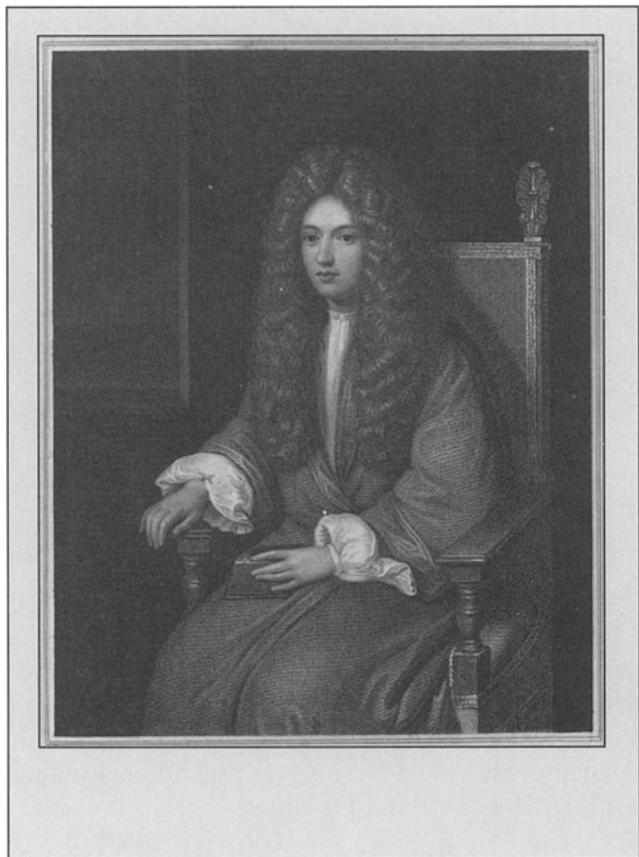
The **gas constant** R appears in the ideal gas law, $pV = NRT$. Its numerical values are:

$$\begin{aligned} R &= 8.314\text{ J K mol}^{-1} \text{ (or Pa m}^3\text{ K}^{-1}\text{ mol}^{-1}) = 0.08314\text{ bar L K}^{-1}\text{ mol}^{-1} \\ &= 0.0821\text{ atm L K}^{-1}\text{ mol}^{-1} \end{aligned}$$

The **Avogadro number** $N_A = 6.023 \times 10^{23}\text{ mol}^{-1}$. The **Boltzmann constant** $k_B = R/N_A = 1.3807 \times 10^{-23}\text{ J K}^{-1}$.

One of the earliest quantitative laws describing the behavior of gases was due to Robert Boyle (1627–1691), an Englishman and a contemporary of Isaac Newton (1642–1727). The same law was also discovered by Edmé Mariotte (1620(?)–1684) in France. In 1660, Boyle published his conclusion in his *New Experiments Physico-mechanical, Touching the Spring of the Air and Its Effects*: at a fixed temperature T , the volume V of a gas was inversely proportional to the pressure p , i.e.:

$$V = \frac{f_1(T)}{p} \text{ in which } f_1(T) \text{ is some function of the temperature } T \quad (1.4.1)$$



Robert Boyle (1627–1691).

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(Though the temperature that Boyle knew and used was the empirical temperature, as we shall see in Chapter 3, it is appropriate to use the absolute temperature T (in kelvin) in the formulation of the law of ideal gases. To avoid excessive notation we shall use T whenever it is appropriate.) Boyle also advocated the view that heat was not an indestructible substance (caloric) that passed from one object to another but was ‘... intense commotion of the parts ...’ [5].

At constant pressure, the variation of volume with temperature was studied by Jacques Charles (1746–1823), who established that

$$\frac{V}{T} = f_2(p) \text{, in which } f_2(p) \text{ is a function of } p \quad (1.4.2)$$

In 1811, Amedeo Avogadro (1776–1856) announced his hypothesis that, under conditions of the same temperature and pressure, equal volumes of all gases contained equal numbers of molecules. This hypothesis greatly helped in explaining the changes in pressure due to chemical reactions in which the reactants and products were gases. It implied that, at constant pressure and temperature, the volume of a gas is proportional

to the amount of the gas (number of molecules). Hence, in accordance with Boyle's law (1.4.1), for N moles of a gas:

$$V = N \frac{f_1(T)}{p}, \text{ in which } f_1(T) \text{ is a function of } T \quad (1.4.3)$$



Jacques Charles (1746–1823).

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A comparison of Equations (1.4.1), (1.4.2) and (1.4.3) leads to the conclusion that $f_1(T)$ is proportional to T and to the well-known **law of ideal gases**:

$$pV = NRT \quad (1.4.4)$$

in which R is the gas constant. Note that $R = 8.314\ 41\ \text{J K}^{-1}\ \text{mol}^{-1}$ (or $\text{Pa m}^3\ \text{K}^{-1}\ \text{mol}^{-1}$) = $0.083\ 14\ \text{bar L K}^{-1}\ \text{mol}^{-1}$ = $0.0821\ \text{atm L K}^{-1}\ \text{mol}^{-1}$.

As more gases were identified and isolated by the chemists during the eighteenth and nineteenth centuries, their properties were studied. It was found that many obeyed Boyle's law approximately. For most gases, this law describes the experimentally observed behavior fairly well for pressures to about 10 atm. As we shall see in the next section, the behavior of gases under a wider range of pressures can be described by modifications of the ideal gas law that take into consideration the molecular size and intermolecular forces.

For a *mixture* of ideal gases, we have **Dalton's law of partial pressures**, according to which the pressure exerted by each component of the mixture is independent of the other components of the mixture and each component obeys the ideal gas equation. Thus, if p_k is the partial pressure due to component k , we have

$$p_k V = N_k RT \quad (1.4.5)$$

Joseph-Louis Gay-Lussac (1778–1850), who made important contributions to the laws of gases, discovered that a dilute gas expanding into a vacuum did so without a change in temperature. James Prescott Joule (1818–1889) also verified this fact in his series of experiments that established the equivalence between mechanical energy and heat. In Chapter 2 we will discuss Joule's work and the law of conservation of energy in detail. When the concept of energy and its conservation was established, the implication of this observation became

clear. Since a gas expanding into vacuum does not do any work during the processes of expansion, its energy does not change. The fact that the temperature does not change during expansion into a vacuum, while the volume and pressure do change, implies that the energy of a given amount of ideal gas depends only on its temperature T , not on its volume or pressure. Also, a change in the ideal gas temperature occurs only when its energy is changed through exchange of heat or mechanical work. These observations lead to the conclusion that the energy of a given amount of ideal gas is a function only of its temperature T . Since the amount of energy (heat) needed to increase the temperature of an ideal gas is proportional to the amount of the gas, the energy is proportional to N , the amount of gas in moles. Thus, the energy of the ideal gas, $U(T, N)$, is a function only of the temperature T and the amount of gas N . It can be written as

$$U(T, N) = N U_m(T) \quad (1.4.6)$$

in which U_m is the total internal energy per mole, or **molar energy**. For a mixture of gases the total energy is the sum of the energies of the components:



Joseph-Louis Gay-Lussac (1778–1850).

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$$U(T, N) = \sum_k U_k(T, N_k) = \sum_k N_k U_{mk}(T) \quad (1.4.7)$$

in which the components are indexed by k . Later developments established that

$$U_m = cRT + U_0 \quad (1.4.8)$$

to a good approximation, in which U_0 is a constant. For monatomic gases, such as He and Ar, $c = 3/2$; for diatomic gases, such as N_2 and O_2 , $c = 5/2$. The factor c can be deduced from the kinetic theory of gases, which relates the energy U to the motion of a gas molecules.

The experiments of Gay-Lussac also showed that, at constant pressure, the relative change in volume $\delta V/V$ due to an increase in temperature had nearly the same value for all dilute gases; it was equal to $1/273 \text{ } ^\circ\text{C}^{-1}$.

Thus, a gas thermometer in which the volume of a gas at constant pressure was the indicator of temperature t had the quantitative relation

$$V = V_0(1 + \alpha t) \quad (1.4.9)$$

in which $\alpha = 1/273$ is the coefficient of expansion at constant pressure. In Chapter 3 we will establish the relation between the temperature t , measured by the gas thermometer, and the absolute temperature T .

The above empirical laws of gases played an important part in the development of thermodynamics. They are the testing ground for any general principle and are often used to illustrate these principles. They were also important for developments in the atomic theory of matter and chemistry.

For most gases, such as CO_2 , N_2 and O_2 , the ideal gas law was found to be an excellent description of the experimentally observed relation between p , V and T only for pressures up to about 20 atm. Significant improvements in the laws of gases did not come until the molecular nature of gases was understood. In 1873, more than 200 years after Boyle published his famous results, Johannes Diderik van der Waals (1837–1923) proposed an equation in which he incorporated the effects of attractive forces between molecules and molecular size on the pressure and volume of a gas. We shall study van der Waals' equation in detail in the next section, but here we would like to familiarize the reader with its basic form so that it can be compared with the ideal gas equation. According to van der Waals, p , V , N and T are related by

$$\left(p + a \frac{N^2}{V^2} \right) (V - Nb) = NRT \quad (1.4.10)$$

In this equation, the constant a is a measure of the attractive forces between molecules and b is proportional to the size of the molecules. For example, the values of a and b for helium are smaller than the corresponding values for a gas such as CO_2 . The values of the constants a and b for some of the common gases are given in Table 1.1. Unlike the ideal gas equation, this equation explicitly contains molecular parameters and it tells us

Table 1.1 Van der Waals constants a and b and critical constants T_c , p_c and V_{mc} for selected gases.

Gas	A (bar $\text{L}^2 \text{ mol}^{-2}$)	B (L mol^{-1})	T_c (K)	p_c (bar)	V_{mc} (L mol^{-1})
Acetylene (C_2H_2)	4.516	0.0522	308.3	61.39	0.113
Ammonia (NH_3)	4.225	0.0371	405.5	113.5	0.072
Argon (Ar)	1.355	0.0320	150.9	49.55	0.075
Carbon dioxide (CO_2)	3.658	0.0429	304.1	73.75	0.094
Carbon monoxide (CO)	1.472	0.0395	132.9	34.99	0.093
Chlorine (Cl_2)	6.343	0.0542	416.9	79.91	0.123
Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	12.56	0.0871	513.9	61.32	0.167
Helium (He)	0.0346	0.0238	5.19	2.22	0.057
Hydrogen (H_2)	0.245	0.0265	32.97	12.93	0.065
Hydrogen chloride (HCl)	3.700	0.0406	324.7	83.1	0.081
Methane (CH_4)	2.300	0.0430	190.5	46.04	0.099
Nitric oxide (NO)	1.46	0.0289	180	64.8	0.058
Nitrogen (N_2)	1.370	0.0387	126.2	33.9	0.090
Oxygen (O_2)	1.382	0.0319	154.59	50.43	0.073
Propane (C_3H_8)	9.385	0.0904	369.82	42.50	0.203
Sulfur dioxide (SO_2)	6.865	0.0568	430.8	78.84	0.122
Sulfur hexafluoride (SF_6)	7.857	0.0879	318.69	37.7	0.199
Water (H_2O)	5.537	0.0305	647.14	220.6	0.056

Source: An extensive listing of van der Waals constants can be found in D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 75th edition, 1994, CRC Press: Ann Arbor, MI.

how the ideal gas pressure and volume are to be ‘corrected’ because of the molecular size and intermolecular forces. We shall see how van der Waals arrived at this equation in the next section. At this point, students are encouraged to pause and to try and derive this equation on their own before proceeding to the next section.

As one might expect, the energy of the gas is also altered due to forces between molecules. In Chapter 6 we will see that the energy U_{vw} of a van der Waals gas can be written as

$$U_{\text{vw}} = U_{\text{ideal}} - a \left(\frac{N}{V} \right)^2 V \quad (1.4.11)$$

The van der Waals equation was a great improvement over the ideal gas law, in that it described the observed liquefaction of gases and the fact that, above a certain temperature, called the critical temperature, gases could not be liquefied regardless of the pressure, as we will see in the following section. However, it was found that the van der Waals equation failed at very high pressures (Exercise 1.13). Various improvements suggested by Clausius, Berthelot and others are discussed in Chapter 6.

1.5 States of Matter and the van der Waals Equation

The simplest transformations of matter caused by heat is the melting of solids and the vaporization of liquids. In thermodynamics, the various states of matter (solid, liquid, gas) are often referred to as **phases**. Every compound has a definite temperature T_m at which it melts and a definite temperature T_b at which it boils. In fact, this property can be used to identify a compound or separate the constituents of a mixture. With the development of the thermometer, these properties could be studied with precision. As noted earlier, Joseph Black and James Watt discovered another interesting phenomenon associated with the changes of phase: at the melting or the boiling temperature, the heat supplied to a system does not result in an increase in temperature; it only has the effect of converting the substance from one phase to another. This heat that lays ‘latent’ or hidden without increasing the temperature was called the **latent heat**. When a liquid solidifies, for example, this heat is given out to the surroundings. This phenomenon is summarized in Figure 1.3.

Clearly, the ideal gas equation, good as it is in describing many properties of gases, does not help us to understand why gases convert to liquids when compressed. An ideal gas remains a gas at all temperatures and its volume can be compressed without limit. In 1822, Gay-Lussac’s friend Cagniard de la Tour (1777–1859) discovered that a gas does not liquefy when compressed unless its temperature is below a critical value, called the **critical temperature**. This behavior of gases was studied in detail by Thomas Andrews (1813–1885), who published his work in 1869. During this time, atomic theory was gaining more and more ground, while Maxwell, Clausius and others advanced the idea that heat was related to molecular motion and began to find an explanation of the properties of gases, such as pressure and viscosity, in the random motion of molecules. It was in this context that Johannes Diderik van der Waals (1837–1923) sought a single equation of state for the liquid and gas phases of a substance. In 1873, van der Waals presented his doctoral thesis titled *On the Continuity of the Gas and Liquid State*, in which he brilliantly explained the conversion of a gas to a liquid and the existence of critical temperature as the consequence of forces between molecules and molecular volume.

Van der Waals realized that two main factors modify the ideal gas equation: the effect of molecular volume and the effect of intermolecular forces. Since molecules have a nonzero volume, the volume of a gas cannot be reduced to an arbitrarily small value by increasing p . The corresponding modification of the ideal gas equation would be $(V - bN) = NRT/p$, in which the constant b is the limiting volume of 1 mol of the gas as $p \rightarrow \infty$. The constant b is sometimes called the ‘excluded volume’. The effect of intermolecular forces, van der Waals noted, is to decrease the pressure, as illustrated in Figure 1.4. Hence, the above ‘volume-corrected’ equation is further modified to

$$p = \frac{NRT}{V - bN} - \delta p$$

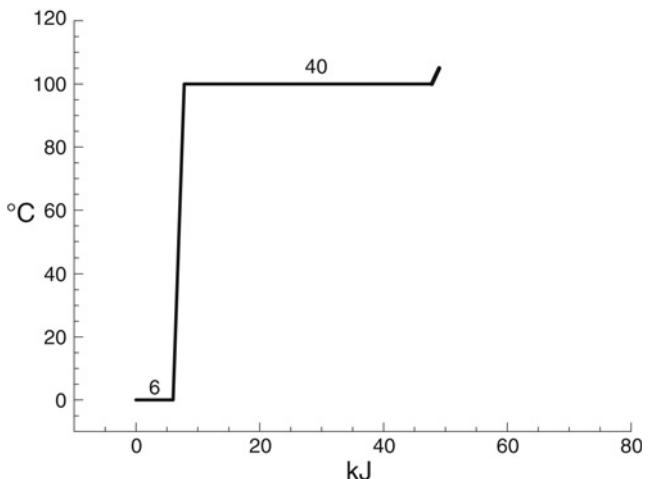


Figure 1.3 The change in temperature of 1 mol of H_2O versus the amount of heat, at a pressure of 1 atm. At the melting point, absorption of heat does not increase the temperature until all the ice melts. It takes about 6 kJ to melt 1 mol of ice, the 'latent heat' discovered by Joseph Black. Then the temperature increases until the boiling point is reached, at which point it remains constant until all the water turns to steam. It takes about 40 kJ to convert 1 mol of water to steam.

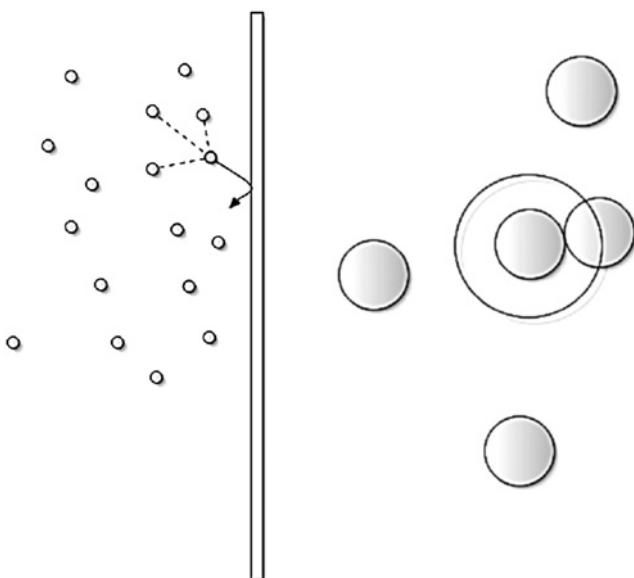
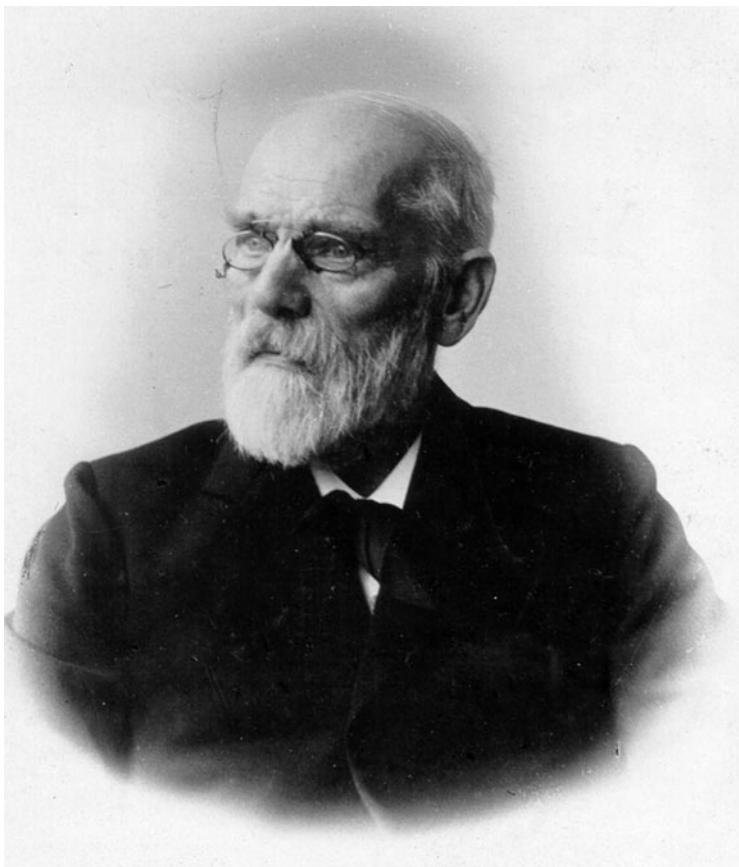


Figure 1.4 Van der Waals considered molecular interaction and molecular size to improve the ideal gas equation. As shown on the left, the pressure of a real gas is less than the ideal gas pressure because intermolecular attraction decreases the speed of the molecules approaching the wall. Therefore, $p = p_{\text{ideal}} - \delta p$. As shown on the right, since the molecules of a gas have a nonzero size, the volume available to molecules is less than the volume of the container. Each molecule has a volume around it that is not accessible to other molecules because the distance between the centers of the molecules cannot be less than the sum of the molecular radii. As a result, the volume of the gas cannot decrease below this 'excluded volume'. Thus, V in the ideal gas equation is replaced with $(V - bN)$ so that as $p \rightarrow \infty$, $V \rightarrow bN$.



Johannes van der Waals (1837–1923).

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Next, van der Waals related the factor δp to the molar density N/V using the kinetic theory of gases, which showed how molecular collisions with container walls cause pressure. Pressure depends on the number of molecules that collide with the walls per unit area, per unit time; therefore, it is proportional to the molar density N/V (as can be seen from the ideal gas equation). In addition, each molecule that is close to a container wall and moving towards it experiences the retarding attractive forces of molecules behind it (see Figure 1.4). This force would also be proportional to molar density N/V ; hence, δp should be proportional to two factors of N/V , so that one may write $\delta p = a(N/V)^2$, in which the constant a is a measure of the intermolecular forces. The expression for pressure that van der Waals proposed is

$$p = \frac{NRT}{V - bN} - a \frac{N^2}{V^2}$$

or, as it is usually written:

$$\left(p + a \frac{N^2}{V^2} \right) (V - Nb) = NRT \quad (1.5.1)$$

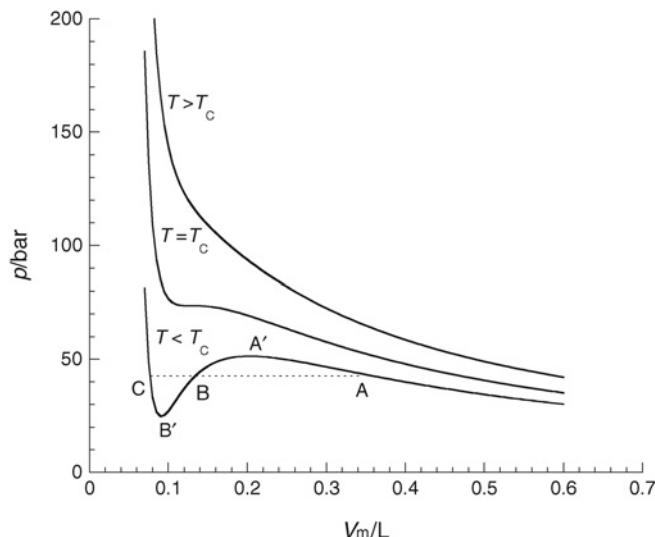


Figure 1.5 The van der Waals isotherms for CO_2 ($T_c = 304.14 \text{ K}$). When $T < T_c$, there is a region $AA'BB'C$ in which, for a given value of p , the van der Waals equation does not specify a unique volume V ; in this region, the gas transforms to a liquid. The segment $A'BB'$ is an unstable region; states corresponding to points on this segment are not experimentally realizable. Experimentally realizable states are on the dotted line ABC . The observed state follows the path ABC . A detailed description of this region is discussed in Chapter 7.

This turns out to be an equation of state for both the liquid and the gas phase. Van der Waals' insight revealed that the two phases, which were considered distinct, can, in fact, be described by a single equation. Let us see how.

For a given T , a p - V curve, called the **p - V isotherm**, can be plotted. Such isotherms for the van der Waals equation (1.5.1) are shown in Figure 1.5. They show an important feature: the **critical temperature** T_c studied by Thomas Andrews. If the temperature T is greater than T_c then the p - V curve is always single valued, much like the ideal gas isotherm, indicating that there is no transition to the liquid state. However, for lower temperatures, $T < T_c$, the isotherm has a maximum and a minimum. There are two extrema because the van der Waals equation is cubic in V . This region represents a state in which the liquid and the gas phases coexist in thermal equilibrium. When $T < T_c$, on the p - V curve shown in Figure 1.5, the gas begins to condense into a liquid at point A ; the conversion of gas to liquid continues until point C , at which all the gas has been converted to liquid. Between A and C , the actual state of the gas does not follow the path $AA'BB'C$ along the p - V curve because this curve represents an unstable supersaturated state in which the gas condenses to a liquid. The actual state of the gas follows the straight line ABC , which represents states in which the liquid and gas states coexist. In fact, when $T < T_c$, the pressure on the van der Waals curve can be negative (Exercise 1.16), but such states are not physically realized; the physically realized states are on the line ABC . This line, called the **coexistence line**, is such that the area enclosed by the van der Waals curve above it ($AA'B$) equals the area enclosed below it ($BB'C$). The coexistence line will be discussed in more detail in Chapter 7.

As T increases, the two extrema move closer and finally coalesce at $T = T_c$. For one mole of a gas, the point (p, V) at which the two extrema coincide is defined as the **critical pressure** p_c and **critical molar volume** V_{mc} . For T higher than T_c , there is no **phase transition** from a gas to a liquid; the distinction between gas and liquid disappears. (This does not happen for a transition between a solid and a liquid because a solid is more

ordered than a liquid; the two states are always distinct.) Experimentally, the **critical constants** p_c , V_{mc} and T_c can be measured and they are tabulated (Table 1.1 lists some examples).

We can relate the critical parameters to the van der Waals parameters a and b by the following means. We note that if we regard $p(V, T)$ as a function of V , then, for $T < T_c$, the derivative $(\partial p / \partial V)_T = 0$ at the two extrema, but the second derivatives have opposite signs. As T increases, at the point where the two extrema coincide the second derivative is therefore zero. Hence, at the critical point $T = T_c$, $p = p_c$ and $V = V_{mc}$, we have an *inflection point* at which the second derivatives of a function vanish. Since the first derivative is also zero at the critical point:

$$\left(\frac{\partial p}{\partial V} \right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0 \quad (1.5.2)$$

Using these equations, one can obtain the following relations between the critical constants and the constants a and b (Exercise 1.17):

$$a = \frac{9}{8}RT_cV_{mc}, \quad b = \frac{V_{mc}}{3} \quad (1.5.3)$$

in which V_{mc} is the molar critical volume. Conversely, we can write the critical constants in terms of the van der Waals constants a and b (Exercise 1.17):

$$T_c = \frac{8a}{27Rb}, \quad p_c = \frac{a}{27b^2}, \quad V_{mc} = 3b \quad (1.5.4)$$

Table 1.1 contains the values of a and b and critical constants for some gases.

1.5.1 The Law of Corresponding States

Every gas has a characteristic temperature T_c , pressure p_c , and volume V_{mc} , which depend on the molecular size and intermolecular forces. In view of this, one can introduce dimensionless **reduced variables** defined by

$$T_r = \frac{T}{T_c}, \quad V_r = \frac{V_m}{V_{mc}}, \quad p_r = \frac{p}{p_c} \quad (1.5.5)$$

Van der Waals showed that, if his equation is rewritten in terms of these reduced variables, one obtains the following ‘universal equation’ (Exercise 1.18), which is independent of the constants a and b :

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \quad (1.5.6)$$

This is a remarkable equation because it implies that gases have corresponding states: *at a given value of reduced volume and reduced temperature, all gases have the same reduced pressure*. This statement is called the **law of corresponding states** or **principle of corresponding states**, which van der Waals enunciated in an 1880 publication. Noting that the reduced variables are defined wholly in terms of the experimentally measured critical constants, p_c , V_{mc} and T_c , he conjectured that the principle has a general validity, independent of his equation of state. According to the principle of corresponding states, at a given T_r and V_{mr} the reduced pressures p_r of all gases should be the same (which is not necessarily the value given by Equation (1.5.6)).

The deviation from ideal gas behavior is usually expressed by defining a **compressibility factor**:

$$Z = \frac{V_m}{V_{m,ideal}} = \frac{pV_m}{RT}$$

which is the ratio between the actual volume of a gas and that of the ideal gas at a given T and p . Ideal gas behavior corresponds to $Z = 1$. For real gases, at low pressures and temperatures, it is found that $Z < 1$, but for higher pressures and temperatures, $Z > 1$. It is also found that there is a particular temperature, called the Boyle temperature, at which Z is nearly 1 and the relationship between p and V is close to that of an ideal gas (Exercise 1.11). One way to verify the law of corresponding states experimentally is to plot Z as a function of reduced pressure p_r at a given reduced temperature T_r . The compressibility factor Z can be written in terms of the reduced variables: $Z = (p_c V_{mc}/RT_c)(p_r V_{mr}/T_r) = Z_c(p_r V_{mr}/T_r)$ in which $(p_c V_{mc}/RT_c) = Z_c$. The value of Z_c may not vary much from one gas to another. For example, for the van der Waals gas, $Z_c = (p_c V_{mc}/RT_c) = 3/8$ (Exercise 1.18). If we assume Z_c is constant, then Z is a function of the reduced variables.

Experimentally, for a given p_r and T_r , the value of V_{mr} , and hence Z , can be obtained. Experimental values of Z for different gases could be plotted as a function of p_r for a fixed T_r . If the law of corresponding states is valid, then at a given value of T_r and p_r the value of Z must be the same for all gases. The plot shown in Figure 1.6 indicates that the validity of the law of corresponding states is fairly general. Note that this experimental verification of the law of corresponding states is not based on the validity of a particular equation of state.

The van der Waals equation and the law of corresponding states, however, have their limitations, which van der Waals himself noted in his 1910 Nobel Lecture:

But closer examination showed me that matters were not so simple. To my surprise I realized that the amount by which the volume must be reduced is variable, that in extremely dilute state this amount, which I notated b , is fourfold the molecular volume¹ – but that this amount decreases with decreasing external volume and gradually falls to about half. But the law governing this decrease has still not been found.

Van der Waals also noted that the experimental value of $Z_c = (p_c V_{mc}/RT_c)$ for most gases was not $3/8 = 0.375$, as predicted by his equation, but was around 0.25 (0.23 for water and 0.29 for Ar). Furthermore, it became evident that the van der Waals constant a depended on the temperature – Rudolf Clausius even suggested that a was inversely proportional to T . Thus, the parameters a and b might themselves be functions of gas density and temperature. As a result, a number of alternative equations have been proposed for the description of real gases. For example, engineers and geologists often use the following equation, known as the **Redlich–Kwong equation**:

$$p = \frac{NRT}{V - Nb} - \frac{a}{\sqrt{T}} \frac{N^2}{V(V + Nb)} = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)} \quad (1.5.7)$$

The constants a and b in this equation differ from those in the van der Waals equation; they can be related to the critical constants and they are tabulated in the same way as the van der Waals a and b . We will discuss other similar equations used to describe real gases in Chapter 6.

The limitation of van der Waals-type equations and the principle of corresponding states lies in the fact that molecular forces and volume are quantified with just two parameters, a and b . As explained below, two parameters can characterize the forces between small molecules fairly well, but larger molecules require more parameters.

¹Molecular volume is the actual volume of the molecules ($N_A 4\pi r^3/3$ for a mole of spherical molecules of radius r).

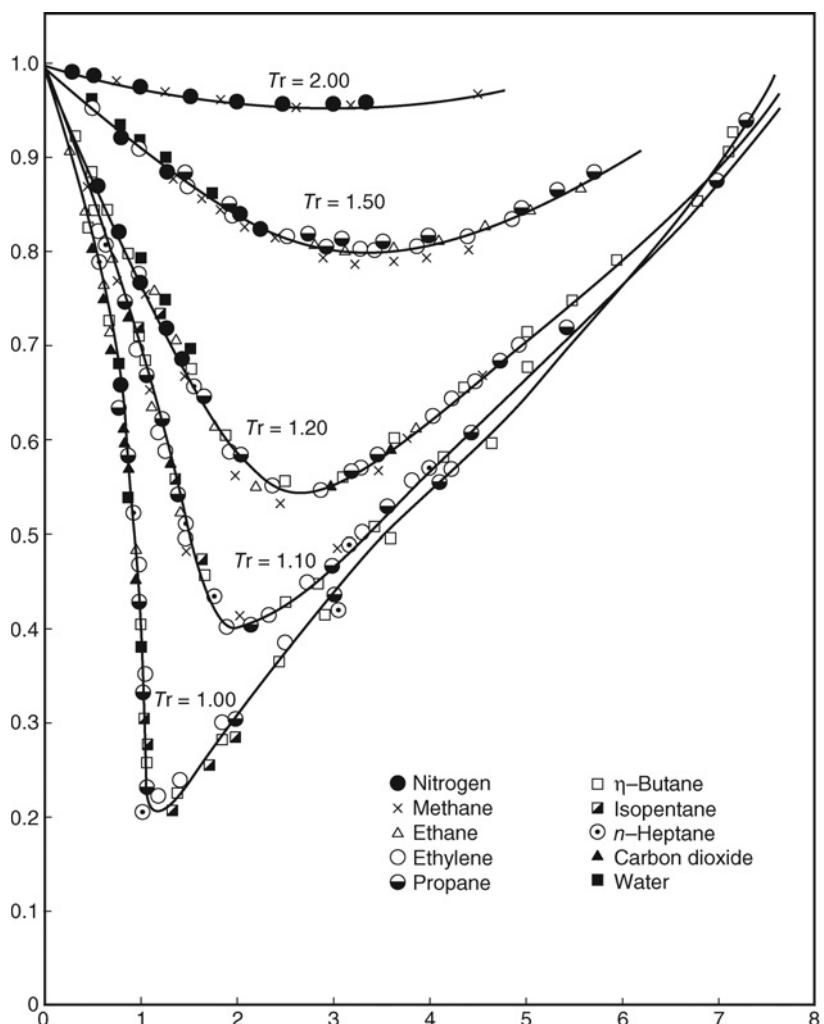


Figure 1.6 Isotherms of compressibility factor Z (y-axis) as a function of reduced pressure p_r (x-axis) for various gases showing the validity of the law of corresponding states. At very low pressures, the compressibility factor approaches the ideal gas value $Z = 1$. (Reproduced with permission from Goug-Jen Su, Industrial and Engineering Chemistry, **38** (1946), 803. Copyright 1946, American Chemical Society).

1.5.2 Molecular Forces and the Law of Corresponding States

From a molecular point of view, the van der Waals equation has two parameters, a and b , that describe molecular forces, often called the **van der Waals forces**. These forces are attractive when the molecules are far apart but are repulsive when they come into contact, thus making the condensed state (liquid or solid) hard to compress. It is the repulsive core that gives the molecule a nonzero volume. The typical potential energy between two molecules is expressed by the so-called Lennard–Jones energy:

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (1.5.8)$$

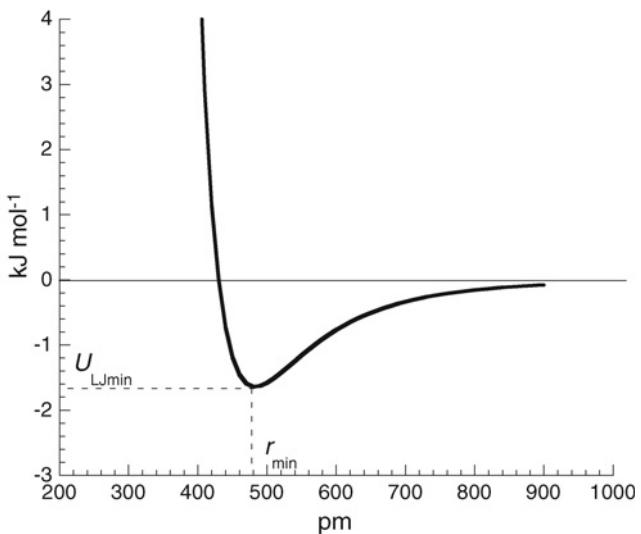


Figure 1.7 Lennard–Jones ‘6–12’ potential energy between two molecules as a function of the distance between their centers. It is common to specify ϵ in units of kelvin using the ratio ϵ/k_B , in which k_B is the Boltzmann constant. The assumed Lennard–Jones parameter values for the above curve are $\epsilon/k_B = 197 \text{ K}$ (which corresponds to $\epsilon N_A = 1.638 \text{ kJ mol}^{-1}$) and $\sigma = 430 \text{ pm}$. These values represent the approximate interaction energy between CO_2 molecules.

Figure 1.7 shows a plot of this potential energy as a function of the distance r between the centers of the molecules. As the distance between the molecules decreases, U_{LJ} decreases, reaches a minimum, and sharply increases. The decreasing part of U_{LJ} is due to the term $-(\sigma/r)^6$, which represents an attractive force, and the sharply increasing part is due to the term $(\sigma/r)^{12}$, which represents a repulsive core. The Lennard–Jones energy reaches a minimum value of $-\epsilon$ when $r = 2^{1/6}\sigma$ (Exercise 1.20). The two van der Waals parameters, a and b , are related to ϵ and σ respectively, the former being a measure of the molecular attractive force and the latter a measure of the molecular size. In fact, using the principles of statistical thermodynamics, for a given ϵ and σ the values of a and b can be calculated. Such a relationship between the molecular interaction potential and the parameters in the van der Waals equation of state gives us an insight into the limitations of the law of corresponding states, which depends on just two parameters, a and b . If more than two parameters are needed to describe the forces between two molecules adequately, then we can also expect the equation of state to depend on more than two parameters. Lennard–Jones-type potentials that use two parameters are good approximations for small molecules; for larger molecules the interaction energy depends not only on the distance between the molecules but also on their relative orientation and other factors that require more parameters. Thus, significant deviation from the law of corresponding states can be observed for larger molecules.

1.6 An Introduction to the Kinetic Theory of Gases

When Robert Boyle published his study on the nature of the ‘spring of the air’ (what we call pressure today) and argued that heat was an ‘intense commotion of the parts’, he did not know how pressure in a gas actually arose. During the seventeenth century, a gas was thought to be a continuous substance. A century later, Daniel

Bernoulli (1700–1782) published the idea that the mechanism that caused pressure is the rapid collisions of molecules with the walls of the container [5]. In his 1738 publication, *Hydrodynamica*, Bernoulli presented his calculation of the average force on the container walls due to molecular collisions and obtained a simple expression for the pressure: $p = (mnv_{\text{avg}}^2/3)$, in which m is the molecular mass, n is the number of molecules per unit volume and v_{avg} is the average speed of molecules. At that time, no one had any idea how small gas molecules were or how fast they moved, but Bernoulli's work was an important step in explaining the properties of a gas in terms of molecular motion. It was the beginnings of a subject that came to be known as the kinetic theory of gases.

The kinetic theory of gases was largely developed in the late nineteenth century. Its goal was to explain the observed properties of gases by analyzing the random motion of molecules. Many quantities, such as pressure, diffusion constant and the coefficient of viscosity, could be related to the average speed of molecules, their mass, size and the average distance they traversed between collisions (called the mean free path). As we shall see in this section, the names of James Clerk Maxwell (1831–1879) and Ludwig Boltzmann (1844–1906) are associated with some of the basic concepts in this field, while, as is often the case in science, several others contributed to its development [4, 5]. In this introductory section we shall deal with some elementary aspects of kinetic theory, such as the mechanism that causes pressure and the relation between average kinetic energy and temperature.

1.6.1 Kinetic Theory of Pressure

As Daniel Bernoulli showed, using the basic concepts of force and randomness, it is possible to relate the pressure of a gas to molecular motion: pressure is the average force per unit area exerted on the walls by colliding molecules.

We begin by noting some aspects of the random motion of molecules. First, if all directions have the same physical properties, then we must conclude that motion along all directions is equally probable: the properties of molecules moving in one direction will be the same as the properties of molecules moving in any other direction. Let us assume that the average speed of the gas molecules is v_{avg} . We denote its x , y and z components by $v_{x\text{avg}}$, $v_{y\text{avg}}$, and $v_{z\text{avg}}$. Thus:

$$v_{\text{avg}}^2 = v_{x\text{ avg}}^2 + v_{y\text{ avg}}^2 + v_{z\text{ avg}}^2 \quad (1.6.1)$$

Because all directions are equivalent, we must have

$$v_{x\text{ avg}}^2 = v_{y\text{ avg}}^2 = v_{z\text{ avg}}^2 = \frac{v_{\text{avg}}^2}{3} \quad (1.6.2)$$

The following quantities are necessary for obtaining the expression for pressure:

- N_A = Avogadro number
- N = amount of gas in moles
- V = gas volume
- M = molar mass of the gas
- m = mass of a single molecule = M/N_A
- n = number of molecules per unit volume = NN_A/V

Now we calculate the pressure by considering the molecular collisions with the wall. In doing so, we will approximate the random motion of molecules with molecules moving with an average speed v_{avg} . (A rigorous

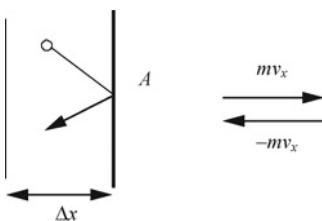


Figure 1.8 Rapid collisions of gas molecules with the walls of the container give rise to pressure. By computing the average momentum transferred to the wall by colliding molecules, pressure can be related to the average of the square of molecular velocity.

derivation gives the same result.) Consider a layer of a gas, of thickness Δx , close to the wall of the container (see Figure 1.8). When a molecule collides with the wall, which we assume is perpendicular to the x axis, the change in momentum of the molecule in the x direction equals $2mv_{x\text{avg}}$. In the layer of thickness Δx and area A , because of the randomness of molecular motion, about half the molecules will be moving towards the wall; the rest will be moving away from the wall. Hence, in a time $\Delta t = \Delta x/v_{\text{avg}}$, about half the molecules in the layer will collide with the wall. The number of molecules in the layer is $(\Delta x A)n$ and the number of molecules colliding with the walls is $(\Delta x A)n/2$. Now, since each collision imparts a momentum $2mv_{x\text{avg}}$, in a time Δt , the total momentum imparted to the wall is $2mv_{x\text{avg}}(\Delta x A)n/2$. Thus, the average force F on the wall of area A is

$$F = \frac{\text{Momentum imparted}}{\Delta t} = \frac{2mv_{x\text{avg}}\Delta x A}{\Delta t} \frac{n}{2} = \frac{mv_{x\text{avg}}\Delta x An}{\Delta x/v_{x\text{avg}}} = mv_{x\text{avg}}^2 n A \quad (1.6.4)$$

Pressure p , which is the force per unit area, is thus

$$p = \frac{F}{A} = mv_{x\text{avg}}^2 n \quad (1.6.5)$$

Since the direction x is arbitrary, it is better to write this expression in terms of the average speed of the molecule rather than its x component. By using Equation (1.6.2) and the definitions (1.6.3), we can write the pressure in terms the macroscopic variables M , V and N :

$$p = \frac{1}{3}mnv_{\text{avg}}^2 = \frac{1}{3}M\frac{N}{V}v_{\text{avg}}^2 \quad (1.6.6)$$

This expression relates the pressure to the square of the average speed. A rigorous description of the random motion of molecules leads to the same expression for the pressure with the understanding that v_{avg}^2 is to be interpreted as the average of the square of the molecular velocity, a distinction that will become clear when we discuss the Maxwell velocity distribution.

When Daniel Bernoulli published the above result in 1738, he did not know how to relate the molecular velocity to temperature; that connection had to wait until Avogadro stated his hypothesis in 1811 and the formulation of the ideal gas law based on an empirical temperature that coincides with the absolute temperature that we use today (see Equation (1.4.9)). On comparing expression (1.6.6) with the ideal gas equation, $pV = NRT$, we see that

$$RT = \frac{1}{3}Mv_{\text{avg}}^2 \quad (1.6.7)$$

Using the Boltzmann constant $k_B = R/N_A = 1.3807 \times 10^{-23} \text{ J K}^{-1}$ and noting $M = mN_A$, we can express Equation (1.6.7) as a relation between the gas molecule's kinetic energy and temperature:

$$\frac{1}{2}mv_{\text{avg}}^2 = \frac{3}{2}k_B T \quad (1.6.8)$$

This is a wonderful result because it relates temperature to molecular motion, in agreement with Robert Boyle's intuition. It shows us that the average kinetic energy of a molecule equals $3k_B T/2$. It is an important step in our understanding of the meaning of temperature at the molecular level.

From Equation (1.6.8) we see that the total kinetic energy of 1 mol of a gas equals $3RT/2$. Thus, for monatomic gases, whose atoms could be thought of as point particles that have neither internal structure nor potential energy associated with intermolecular forces (He and Ar are examples), the total molar energy of the gas is entirely kinetic; this implies $U_m = 3RT/2$. The molar energy of a gas of polyatomic molecules is larger. A polyatomic molecule has additional energy in its rotational and vibrational motion. In the nineteenth century, as kinetic theory progressed, it was realized that random molecular collisions result in an equal distribution of energy among each of the independent modes of motion. According to this **equipartition theorem**, the energy associated with each independent mode of motion equals $k_B T/2$. For a point particle, for example, there are three independent modes of motion, corresponding to motion along each of the three independent spatial directions x , y and z . According to the equipartition theorem, the average kinetic energy for motion along the x direction is $mv_x^2/2 = k_B T/2$, and similarly for the y and z directions, making the total kinetic energy $3(k_B T/2)$ in agreement with Equation (1.6.8). For a diatomic molecule, which we may picture as two spheres connected by a rigid rod, there are two independent modes of rotational motion in addition to the three modes of kinetic energy of the entire molecule. Hence, for a diatomic gas the molar energy $U_m = 5RT/2$, as we noted in the context of Equation (1.4.8). The independent modes of motion are often called **degrees of freedom**.

1.6.2 The Maxwell–Boltzmann Velocity Distribution

A century after Bernoulli's *Hydrodynamica* was published, the kinetic theory of gases began to make great inroads into the nature of the randomness of molecular motion. Surely molecules in a gas move with different velocities. According to Equation (1.6.8), the measurement of pressure only tells us the average of the square of the velocities. It does not tell us what fraction of molecules have velocities with a particular magnitude and direction. In the latter half of the nineteenth century, James Clerk Maxwell (1831–1879) directed his investigations to the **probability distribution of molecular velocity** that specifies such details. We shall denote the probability distribution of the molecular velocity \mathbf{v} by $P(\mathbf{v})$. The meaning of $P(\mathbf{v})$ is as follows:

$P(\mathbf{v}) dv_x dv_y dv_z$ is the fraction of the total number of molecules whose velocity vectors have their components in the range $(v_x, v_x + dv_x)$, $(v_y, v_y + dv_y)$ and $(v_z, v_z + dv_z)$.

As shown in the Figure 1.9, each point in the velocity space corresponds to a velocity vector; $P(\mathbf{v}) dv_x dv_y dv_z$ is the probability that the velocity of a molecule lies within an elemental volume dv_x , dv_y and dv_z at the point (v_x, v_y, v_z) . $P(\mathbf{v})$ is called the **probability density** in the velocity space.

The mathematical form of $P(\mathbf{v})$ was obtained by James Clerk Maxwell; the concept was later generalized by Ludwig Boltzmann (1844–1906) to the probability distribution of the total energy E of the molecule. According to the principle discovered by Boltzmann, when a system reaches thermodynamic equilibrium, the

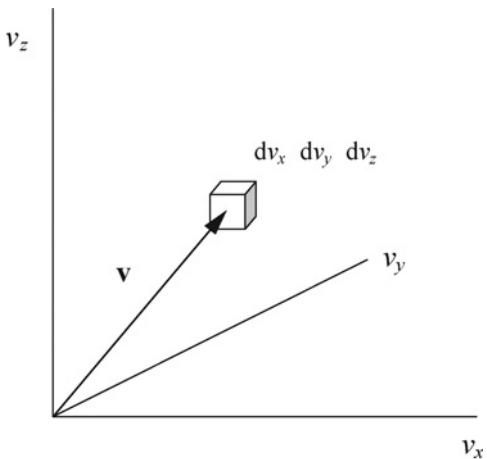


Figure 1.9 The probability distribution for the velocity is defined in the velocity space. $P(\mathbf{v})dv_x \, dv_y \, dv_z$ is the probability that the velocity of a molecule is within the shown cube.

probability that a molecule is in a state with energy E is proportional to $\exp(-E/k_B T)$. If $\rho(E)$ is the number of different states in which the molecule has energy E , then

$$P(E) \propto \rho(E) e^{-E/k_B T} \quad (1.6.9)$$

The quantity $\rho(E)$ is called the **density of states**. Relation (1.6.9), called the **Boltzmann principle**, is one of the fundamental principles of physics. Using this principle, equilibrium thermodynamic properties of a substance can be derived from molecular energies E – a subject called statistical thermodynamics, presented in a later chapter. In this introductory section, however, we will only study some elementary consequences of this principle.

The energy of a molecule $E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{int}} + \dots$, in which E_{trans} is the kinetic energy of translational motion of the whole molecule, E_{rot} is the energy of rotational motion, E_{vib} is the energy of vibrational motion, E_{int} is the energy of the molecule's interaction with other molecules and fields such as electric, magnetic or gravitational fields, and so on. According to the Boltzmann principle, the probability that a molecule will have a translational kinetic energy E_{trans} is proportional to $\exp(-E_{\text{trans}}/k_B T)$ (the probabilities associated with other forms of energy are factors that multiply this term). Since the kinetic energy due to translational motion of the molecule is $mv^2/2$, we can write the probability as a function of the velocity \mathbf{v} by which we mean probability that a molecule's velocity is in an elemental cube in velocity space, as shown in the Figure 1.9. For a continuous variable, such as velocity, we must define a probability density $P(\mathbf{v})$ so that the probability that a molecule's velocity is in an elemental cube of volume $dv_x \, dv_y \, dv_z$ located at the tip of the velocity vector \mathbf{v} is $P(\mathbf{v}) \, dv_x \, dv_y \, dv_z$. According to the Boltzmann principle, this probability is

$$P(\mathbf{v})dv_x \, dv_y \, dv_z = \frac{1}{z} e^{-mv^2/2k_B T} dv_x \, dv_y \, dv_z \quad (1.6.10)$$

in which $v^2 = v_x^2 + v_y^2 + v_z^2$. Here, z is the **normalization factor**, defined by

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-mv^2/2k_B T} dv_x \, dv_y \, dv_z = z \quad (1.6.11)$$

so that a requirement of the very definition of a probability

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(\mathbf{v}) dv_x dv_y dv_z = 1$$

is met. The normalization factor z , as defined in Equation (1.6.11), can be calculated using the definite integral:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{a} \right)^{1/2}$$

which gives

$$\frac{1}{z} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \quad (1.6.12)$$

(Some integrals that are often used in kinetic theory are listed at the end of this chapter in Appendix 1.2.) With the normalization factor thus determined, the probability distribution for the velocity can be written explicitly as

$$P(\mathbf{v}) dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} dv_x dv_y dv_z \quad (1.6.13)$$

This is the **Maxwell velocity distribution**. Plots of this function show the well-known Gaussian or ‘bell-shaped’ curves shown in Figure 1.10a. It must be noted that this velocity distribution is that of a gas at thermodynamic equilibrium. The width of the distribution is proportional to the temperature. A gas not in thermodynamic equilibrium has a different velocity distribution and the very notion of a temperature may not be well defined, but such cases are very rare. In most situations, even if the temperature changes with location, the velocity distribution locally is very well approximated by Equation (1.6.13). Indeed, in computer simulations of gas dynamics it is found that any initial velocity distribution evolves into the Maxwell distribution very quickly, in the time it takes a molecule to undergo few collisions, which in most cases is less than 10^{-8} s.

1.6.3 The Maxwell Speed Distribution

The average velocity of a molecule is clearly zero because every direction of velocity and its opposite are equally probable (but the average of the square of the velocity is not zero). However, the average speed, which depends only on the magnitude of the velocity, is not zero. From the Maxwell velocity distribution (1.6.13) we can obtain the probability distribution for molecular speed, i.e. the probability that a molecule will have a speed in the range $(v, v + dv)$ regardless of direction. This can be done by summing or integrating $P(\mathbf{v})$ over all the directions in which the velocity of a fixed magnitude can point. In spherical coordinates, since the volume element is $v^2 \sin \theta d\theta d\phi dv$, the probability is written as $P(\mathbf{v})v^2 \sin \theta d\theta d\phi dv$. The integral over all possible directions is

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} P(\mathbf{v})v^2 \sin \theta d\theta d\phi dv = 4\pi P(\mathbf{v})v^2 dv \quad (1.6.14)$$

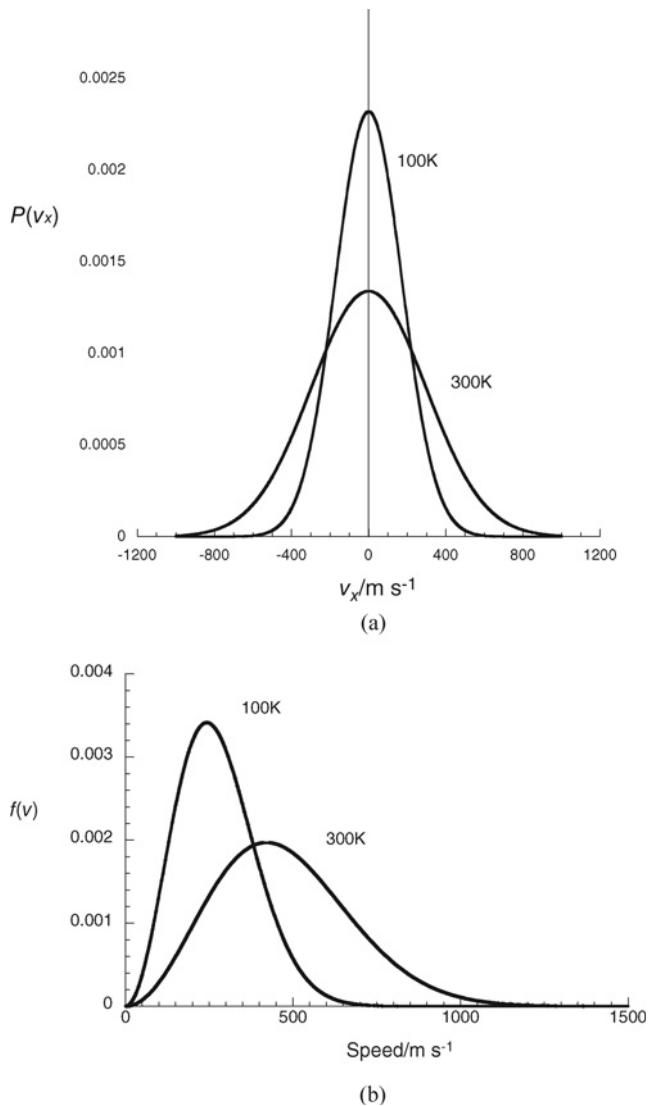


Figure 1.10 Probability distributions of nitrogen. (a) Maxwell velocity distribution of the x -component of the velocity v_x at $T = 100$ K and 300 K. At the value of $P(v_x)$ at which $P(v_x)/P(0) = 1/2$ or $1/e$, the width of the distribution is proportional to \sqrt{T} . (b) $f(v)$ versus speed at $T = 100$ K and 300 K.

The quantity $4\pi P(\mathbf{v})v^2$ is the probability density for the molecular speed. We shall denote it by $f(v)$. With this notation, the probability distribution for molecular speeds can be written explicitly as

$$f(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta v^2} v^2 dv \quad (1.6.15)$$

$$\beta = \frac{m}{2k_B T}$$

Because the molar mass $M = mN_A$ and $R = k_B N_A$, the above expressions can also be written as

$$\begin{aligned} f(v)dv &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\beta v^2} v^2 dv \\ \beta &= \frac{M}{2RT} \end{aligned} \quad (1.6.16)$$

The shape of the function $f(v)$ is shown in Figure 1.10b. This graph shows that, at a given temperature, there are a few molecules with very low speeds and a few with large speeds; we can also see that $f(v)$ becomes broader as T increases. The speed v at which $f(v)$ reaches its maximum is the most probable speed.

With the above probability distributions we can calculate several average values. We shall use the notation in which the average value of a quantity X is denoted by $\langle X \rangle$. The average speed is given by the integral

$$\langle v \rangle = \int_0^\infty vf(v)dv \quad (1.6.17)$$

For the probability distribution (1.6.15), such integrals can be calculated using integral tables, *Mathematica* or *Maple*. While doing such calculations, it is convenient to write the probability $f(v)$ as

$$\begin{aligned} f(v)dv &= \frac{4\pi}{z} e^{-\beta v^2} v^2 dv \\ \beta &= \frac{M}{2RT}, \quad \frac{1}{z} = \left(\frac{M}{2\pi RT} \right)^{3/2} \end{aligned} \quad (1.6.18)$$

Using the appropriate integral in Appendix 1.2 at the end of this chapter, the average speed can be obtained in terms of T and the molar mass M (Exercise 1.23):

$$\langle v \rangle = \frac{4\pi}{z} \int_0^\infty v^3 e^{-\beta v^2} dv = \frac{4\pi}{z} \frac{1}{2\beta^2} = \sqrt{\frac{8RT}{\pi M}} \quad (1.6.19)$$

Similarly, one can calculate the average energy of a single molecule using m and k_B instead of M and R (Exercise 1.23):

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{m4\pi}{2z} \int_0^\infty v^4 e^{-\beta v^2} dv = \frac{m2\pi}{z} \frac{3\sqrt{\pi}}{8\beta^{5/2}} = \frac{3}{2}k_B T \quad (1.6.20)$$

A rigorous calculation of the pressure using the Maxwell–Boltzmann velocity distribution leads to the expression (1.6.6) in which $v_{\text{avg}}^2 = \langle v^2 \rangle$. Also, the value of v at which $f(v)$ has a maximum is the most probable speed. This can easily be determined by setting $df/dv = 0$, a calculation left as an exercise.

What do the above calculations tell us? First, we see that the average speed of a molecule is directly proportional to the square root of the absolute temperature and inversely proportional to its molar mass. This is one of the most important results of the kinetic theory of gases. Another point to note is the simple dependence of the average kinetic energy of a molecule on the absolute temperature (1.6.20). It shows that the average kinetic energy of a gas molecule depends only on the temperature and is independent of its mass.

Appendix 1.1 Partial Derivatives

Derivatives of Many Variables

When a variable such as energy $U(T, V, N_k)$ is a function of many variables V, T and N_k , its *partial derivative* with respect to each variables is defined by holding all other variables constant. Thus, for example, if $U(T, V, N) = (5/2)NRT - a(N^2/V)$, then the partial derivatives are

$$\left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{5}{2}NR \quad (\text{A1.1.1})$$

$$\left(\frac{\partial U}{\partial N}\right)_{V,T} = \frac{5}{2}RT - a\frac{2N}{V} \quad (\text{A1.1.2})$$

$$\left(\frac{\partial U}{\partial V}\right)_{N,T} = a\frac{N^2}{V^2} \quad (\text{A1.1.3})$$

The subscripts indicate the variables that are held constant during the differentiation. In cases where the variables being held constant are understood, the subscripts are often dropped. The change in U , i.e. the differential dU , due to changes in N, V and T is given by

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV + \left(\frac{\partial U}{\partial N}\right)_{V,T} dN \quad (\text{A1.1.4})$$

For functions of many variables, there is a second derivative corresponding to every pair of variables: $\partial^2 U / \partial T \partial V$, $\partial^2 U / \partial N \partial V$, $\partial^2 U / \partial T^2$, etc. For the ‘cross-derivatives’ such as $\partial^2 U / \partial T \partial V$, which are derivatives with respect to two different variables, the order of differentiation does not matter. That is:

$$\frac{\partial^2 U}{\partial T \partial V} = \frac{\partial^2 U}{\partial V \partial T} \quad (\text{A1.1.5})$$

The same is valid for all higher derivatives, such as $\partial^3 U / \partial T^2 \partial V$; i.e. the order of differentiation does not matter.

Basic Identities

Consider three variables x, y and z , each of which can be expressed as a function of the other two variables, $x = x(y, z)$, $y = y(z, x)$ and $z = z(x, y)$ (p, V and T in the ideal gas equation $pV = NRT$ is an example). Then the following identities are valid:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y / \partial x)_z} \quad (\text{A1.1.6})$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (\text{A1.1.7})$$

Consider a function of x and y , $f = f(x, y)$, other than z . Then:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \quad (\text{A1.1.8})$$

Appendix 1.2 Elementary Concepts in Probability Theory

In the absence of a deterministic theory that enables us to calculate the quantities of interest to us, one uses probability theory. Let x_k , in which $k = 1, 2, 3, \dots, n$, represent all possible n values of a random variable x . For example, x could be the number of molecules at any instant in a small volume of 1 nm^3 within a gas or the number of visitors at a website at any instant of time. Let the corresponding probabilities for these n values of x be $P(x_k)$. Since $x_k, k = 1, 2, \dots, n$, represents all possible states:

$$\sum_{k=1}^n P(x_k) = 1 \quad (\text{A1.2.1})$$

Average Values

We shall denote the average value of a quantity A by $\langle A \rangle$. Thus, the average value of x would be

$$\langle x \rangle = \sum_{k=1}^n x_k P(x_k) \quad (\text{A1.2.2})$$

Similarly, the average value of x^2 would be

$$\langle x^2 \rangle = \sum_{k=1}^n x_k^2 P(x_k) \quad (\text{A1.2.3})$$

More generally, if $f(x_k)$ is a function of x , its average value would be

$$\langle f \rangle = \sum_{k=1}^n f(x_k) P(x_k)$$

If the variable x takes continuous values in the range (a, b) , then the average values are written as integrals:

$$\langle x \rangle = \int_a^b x P(x) dx, \quad \langle f \rangle = \int_z^b f(x) P(x) dx \quad (\text{A1.2.4})$$

For a given probability distribution, s , the **standard deviation**, is defined as

$$s = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} \quad (\text{A1.2.5})$$

Some Common Probability Distributions

Binomial distribution. This is the probability distribution associated with two outcomes, H and T (such as a coin toss) with probabilities p and $(1 - p)$ respectively. The probability that, in N trials, m are H and $(N - m)$ are T is given by

$$P(N, m) = \frac{N!}{m!(N-m)!} p^m (1-p)^{N-m} \quad (\text{A1.2.6})$$

Poisson distribution. In many random processes the random variable is a number n . For example, the number of gas molecules in a small volume within a gas will vary randomly around an average value. Similarly, so

is the number of molecules undergoing chemical reaction in a given volume per unit time. The probability of n in such processes is given by the Poisson distribution:

$$P(n) = e^{-\alpha} \frac{\alpha^n}{n!} \quad (\text{A1.2.7})$$

The Poisson distribution has one parameter, α ; it is equal to the average value of n , i.e. $\langle n \rangle = \alpha$.

Gaussian distribution. When a random variable x is a sum of many variables, its probability distribution is generally a Gaussian distribution. If x is a real number in the range $(-\infty, \infty)$ the probability distribution is given by

$$P(x)dx = \left(\frac{1}{2\pi\sigma^2} \right)^{1/2} \exp \left(-\frac{(x-x_0)^2}{2\sigma^2} \right) dx \quad (\text{A1.2.8})$$

The Gaussian distribution has two parameters, x_0 and σ . The average value of x is equal to x_0 and the standard deviation equals σ .

Some Useful Integrals

a. $\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}$

b. $\int_0^\infty x e^{-ax^2} dx = \frac{1}{a}$

c. $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a} \right)^{1/2}$

d. $\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$

More generally:

e. $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \times 3 \times 5 \times \dots \times (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a} \right)^{1/2}$

f. $\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2} \left(\frac{1}{a^{n+1}} \right)$

Appendix 1.3 Mathematica Codes

The following *Mathematica* codes show how to define functions, plot them using the **Plot** command, produce dynamic graphics using **Manipulate** command, create numerical text output files using **Export** command and do algebraic calculations and evaluate derivatives.

CODE A: EVALUATING AND PLOTTING PRESSURE USING THE EQUATION OF STATE AND GENERATING DYNAMIC PLOTS

We define the van der Walls pressure (PVW) and the ideal gas pressure (PID) as shown below as functions of V and T setting $N = 1$. The parameters a and b are set for CO₂. Then, using the defined functions the pressures at $V = 1.5 \text{ L}$, $T = 300 \text{ K}$ and T_c are evaluated.

```
(* Values of a and b set for CO2; We set N=1 *)
a=3.658; (* L^2.bar.mol^-2*)
b=0.0429; (* L.mol^-1*)
R=0.0831; (* L.bar.K^-1.mol^-1 *)

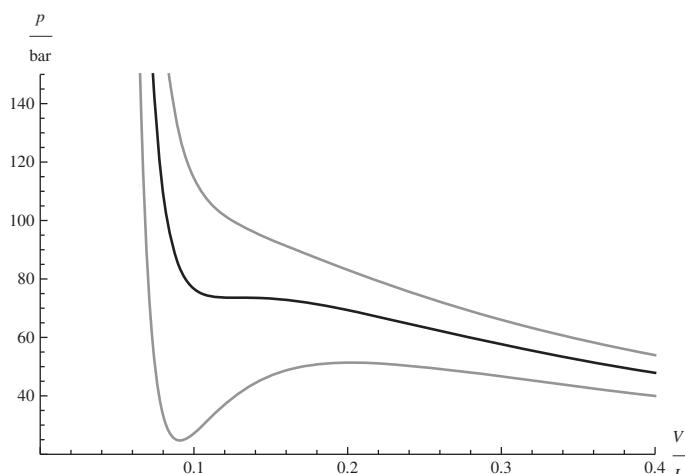
PVW[V_,T_]:= (R*T/(V-b)) - (a/(V^2));
PID[V_,T_]:= R*T/V;

PID[1.5,300]
PVW[1.5,300]
TC=(8/27)*(a/(R*b))

16.62
15.4835
304.027
```

Using the functions defined above, p - V curves could be plotted using the Plot command. The options **PlotRange**, **PlotStyle** and **AxesLabel** are also used to format the plot. If these are not specified, *Mathematica* uses default values. Drawing Tools under the Graphics menu could be used to add text and figures to the plots. For more options see online manual.

```
Plot[{PVW[V,270],PVW[V,304],PVW[V,330]}, {V,0.06,0.4},
PlotRange->{{0,0.4},{20,150}},
PlotStyle->{{Gray,Thick},{Black,Thick},{Gray,Thick}},
AxesLabel->{V/L,p/bar}]
```

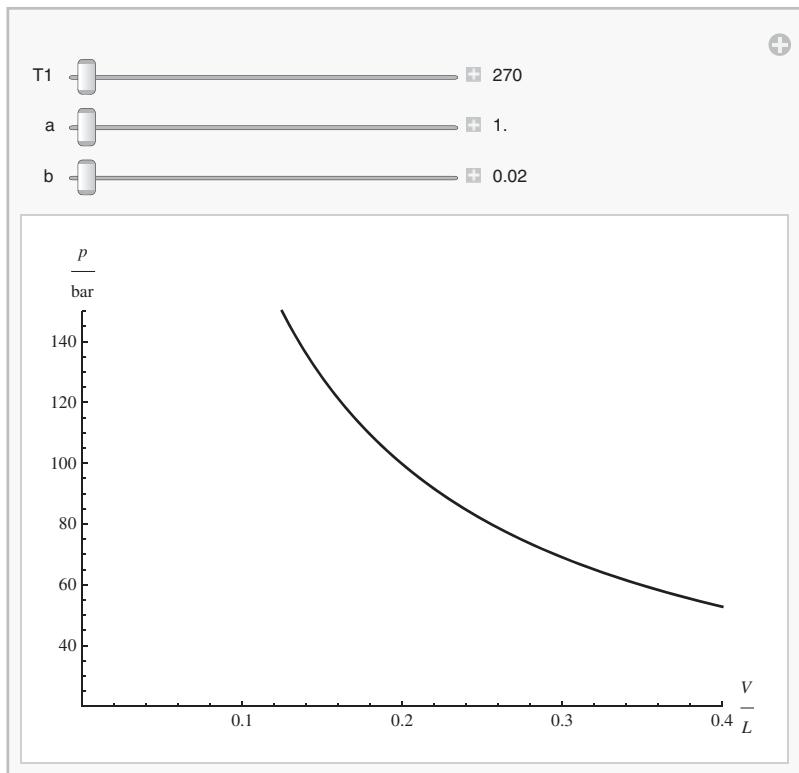


The above plot can also be made a dynamic plot by using the **Manipulate** command. Using this command, one can see how the p - V curve changes when a , b and T are changed. Using the table in the text, appropriate ranges of values are specified for a and b .

In the cell shown below, the value of the parameters are displayed when the option **Appearance** is specified as '**Labeled**'. When the option **SaveDefinitions->True** is included, all the definitions outside the **Manipulate** command (such as $R = 0.0831$) are associated with the graphic that is generated. Then the stand-alone graphic can be used in a CDF (Computable Document Format) file without the code that generated the graphic.

```
Clear[a,b,R,T1,V];
R=0.0831;(*L.bar.K^-1.mol^-1*)
PVW[V_,T_,a_,b_]:=(R*T/(V-b))-(a/(V^2));

Manipulate[
Plot[PVW[V,T1,a,b],{V,0.06,0.4},
PlotRange->{{0,0.4},{20,150}},
PlotStyle->{Black,Thick},AxesLabel->{V/L,p/bar}],
{T1,270, 330, Appearance->"Labeled"},{a,1.0,10.0, Appearance->"Labeled"},{b,0.02,0.09, Appearance->"Labeled"},SaveDefinitions->True]
```



To write output files for spreadsheets use the ‘Export’ command and the file format ‘CSV’. For more detail for the Export command use the help menu and online documentation. In the command below, the output FileName is data.txt. This file can be read by most spreadsheets and graphing software.

```
Export["data.txt", Table[{x,PVW[x,270],PVW[x,304],PVW[x,350]}, {x,0.07,0.6,0.005}], "CSV"]
```

data.txt

Using the Table command, we can also generate a table of values of V and p , as shown below:

```
Table[{x,PVW[x,300]},{x,0.06,0.1,0.01}]//TableForm
```

0.06	441.784
0.07	173.396
0.08	100.405
0.09	77.6944
0.1	70.8025

CODE B: OBTAINING CRITICAL CONSTANTS FOR THE VAN DER WAALS EQUATION

```
Clear[a,b,R,T,V];
p[V_,T_]:=(R*T/(V-b)) - (a/V^2);

(* At the critical point the first and second derivatives of p with respect to
V are zero*)

(* First derivative *)
D[p[V,T],V]

(2 a)/V^3 - (R T)/(-b+V)^2

(* Second derivative *)
D[p[V,T],V,V]

- ((6 a)/V^4) + (2 R T)/(-b+V)^3

Solve[{(-6*a)/V^4 + (2*R*T)/(-b + V)^3 == 0,
(2*a)/V^3 - (R*T)/(-b + V)^2 == 0}, {T, V}]

{{T -> (8 a)/(27 b R), V -> 3 b}}
```

Now we can substitute these values in the equation for p and obtain p_c .

```
T = (8*a)/(27*b*R); V = 3*b;
p[V,T]
```

$$a/(27 b^2)$$

Thus we have all the critical variables: $p_c = a/(27*b^2)$, $T_c = (8*a)/(27*b*R)$, $V_c = 3*b$.

CODE C: THE LAW OF CORRESPONDING STATES

```

Clear[a,b,R,T,V];
T = Tr*(8*a)/(27*b*R); V = Vr*3*b; pc = a/(27*b^2);

(* In terms of these variables the reduced pressure pr = p/pc. This can now be
calculated*)

p[V,T]/pc

(27 b2 ((-a/(9 b2 Vr2))+(8 a Tr)/(27 b (-b+3 b Vr))))/a

FullSimplify[(27 b2 ((-a/(9 b2 Vr2))+(8 a Tr)/(27 b (-b+3 b Vr))))/a]

-(3/Vr2)+(8 Tr)/(-1+3 Vr)

```

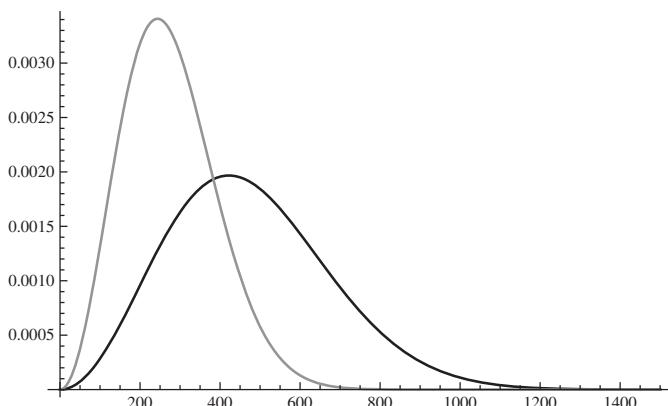
Thus we have the following relation for the reduced variables, which is the law of corresponding states: $pr = (8*Tr)/(3*Vr - 1) - 3/Vr^2$.

CODE D: PLOTTING THE MAXWELL–BOLTZMANN SPEED DISTRIBUTION FOR A GAS OF MOLAR MASS M AT TEMPERATURE T

```

Clear[a,b,R2,T,V];
M=28.0*10-3; (*molar mass of N2 in kg*)
R2=8.314(*J/K.mol*);
b=M/(2*R2);
p[v_,T_]:=(4.0*Pi)*(M/(2*Pi*R2*T))3/2 v2*Exp[(-b*v2)/T];
Plot[{p[v,300],p[v,1001]},{v,0,1500},
PlotStyle->{{Black,Thick},{Gray,Thick}}]

```



As in Code A one can also produce a dynamic plot of the Maxwell–Boltzmann velocity distributions with T as the dynamic variable.

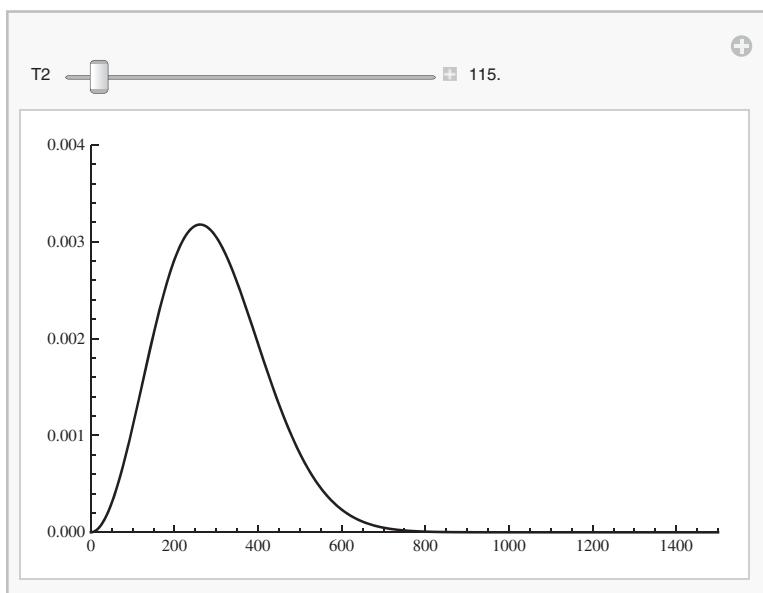
```

Clear[a,bb,R2,T2];
M=28.0*10-3; (*molar mass of N2 in kg*)

```

```
R2=8.314 (*J/K.mol*) ;
bb=M/(2*R2) ;
p[v_,T_]:= (4.0*Pi) (M/(2*Pi*R2*T))3/2 v2*Exp[(-bb*v2)/T] ;

Manipulate[
Plot[p[v,T2],{v,0,1500},
PlotStyle->{Black,Thick},
PlotRange->{{0,1500},{0.,0.004}}],
{T2,100,400,Appearance->"Labeled"}]
```



References

1. Prigogine, I., Stengers, I., *Order Out of Chaos*. 1984, Bantam: New York.
2. Mach, E., *Principles of the Theory of Heat*. 1986, D. Reidel: Boston, MA.
3. Conant, J.B. (ed.), *Harvard Case Histories in Experimental Science*, Vol. 1. 1957, Harvard University Press: Cambridge, MA.
4. Mason, S.F., *A History of the Sciences*. 1962, Collier Books: New York.
5. Segrè, E., *From Falling Bodies to Radio Waves*. 1984, W.H. Freeman: New York; 188.

Examples

Example 1.1 The atmosphere consists of 78.08% by volume of N₂ and 20.95% of O₂. Calculate the partial pressures due to the two gases.

Solution The specification ‘percentage by volume’ may be interpreted as follows. If the components of the atmosphere were to be separated, at the pressure of 1 atm, the volume occupied by each component is

specified by the volume percent. Thus, if we isolate the N₂ in 1.000 L of dry air, at a pressure of 1 atm, its volume will be 0.781 L. According to the ideal gas law, at a fixed pressure and temperature, the amount of gas $N = V(p/RT)$; i.e. the molar amount is proportional to the volume. Hence, the percentage by volume is the same as the percentage in N , i.e. 1.000 mol of air consists of 0.781 mol of N₂. According to Dalton's law (see Equation (1.4.5)), the partial pressure is proportional to N ; therefore, the partial pressure of N₂ is 0.781 atm and that of O₂ is 0.209 atm.

Example 1.2 Using the ideal gas approximation, estimate the change in the total internal energy of 1.00 L of N₂ at $p = 2.00$ atm and $T = 298.15$ K if its temperature is increased by 10.0 K. What is the energy required to heat 1.00 mol of N₂ from 0.0 K to 298 K?

Solution The energy of an ideal gas depends only on the amount of gas N and the temperature T . For a diatomic gas such as N₂ the energy per mole equals $(5/2)RT + U_0$. Hence, for N moles of N₂ the change in energy ΔU for a change in temperature from T_1 to T_2 is

$$\Delta U = N(5/2)R(T_2 - T_1)$$

In the above case

$$N = \frac{pV}{RT} = \frac{2.00 \text{ atm} \times 1.00 \text{ L}}{0.821 \text{ L atm mol}^{-1} \text{ K}^{-1} (298.15 \text{ K})} = 8.17 \times 10^{-2} \text{ mol}$$

Hence:

$$\begin{aligned}\Delta U &= (8.17 \times 10^{-2} \text{ mol}) \frac{5}{2} (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (10.0 \text{ K}) \\ &= 17.0 \text{ J}\end{aligned}$$

(Note the different units of R used in this calculation.)

The energy required to heat 1.00 mol of N₂ from 0 K to 298 K is

$$(5/2)RT = (5/2)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = 6.10 \text{ kJ mol}^{-1}$$

Example 1.3 At $T = 300$ K, 1.00 mol of CO₂ occupies a volume of 1.50 L. Calculate the pressures given by the ideal gas equation and the van der Waals equation. (The van der Waals constants a and b can be obtained from Table 1.1.)

Solution The ideal gas pressure is

$$p = \frac{1.00 \text{ mol} \times 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1.50 \text{ L}} = 16.4 \text{ atm}$$

The pressure according to the van der Waals equation is

$$p = \frac{NRT}{V - Nb} - a \frac{N^2}{V^2}$$

Since the van der Waals constants a and b given in Table 1.1 are in units of L² atm mol⁻² and L mol⁻² respectively, we will use the value or $R = 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}$. This will give the pressure in atmospheres:

$$p = \frac{1.00(0.0821)300}{1.50 - 1.00(0.0421)} - 3.59 \frac{1.00}{1.50^2} = 15.3 \text{ atm}$$

Exercises

- 1.1** Describe an experimental method, based on the ideal gas law, to obtain the molecular mass of a gas.
- 1.2** The density of dry air at $p = 1.0$ bar and $T = 300$ K is 1.161 kg m^{-3} . Assuming that it consists entirely of N_2 and O_2 and using the ideal gas law, determine the amount of each gas in moles in a volume of 1 m^3 and their mole fractions.
- 1.3** The molecular density of interstellar gas clouds is about 10^4 molecules/mL. The temperature is approximately 10 K. Calculate the pressure. (The lowest vacuum obtainable in the laboratory is about three orders of magnitude larger.)
- 1.4** A sperm whale dives to a depth of more than 1.5 km into the ocean to feed. Estimate the pressure the sperm whale must withstand at this depth. (Express your answer in atmospheres.)
- 1.5** (a) Calculate the amount of gas in moles per cubic meter of atmosphere at $p = 1 \text{ atm}$ and $T = 298 \text{ K}$ using the ideal gas equation.
 (b) The atmospheric content of CO_2 is about 360 ppmv (parts per million by volume). Assuming a pressure of 1.00 atm, estimate the amount of CO_2 in a 10.0 km layer of the atmosphere at the surface of the Earth. The radius of the Earth is 6370 km. (The actual amount of CO_2 in the atmosphere is about $6.0 \times 10^{16} \text{ mol}$.)
 (c) The atmospheric content of O_2 is 20.946% by volume. Using the result in part (b), estimate the total amount of O_2 in the atmosphere.
 (d) Life on Earth consumes about $0.47 \times 10^{16} \text{ mol}$ of O_2 per year. What percentage of the O_2 in the atmosphere does life consume in a year?
- 1.6** The production of fertilizers begins with the Haber processes, which is the reaction $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$ conducted at about 500 K and a pressure of about 300 atm. Assume that this reaction occurs in a container of fixed volume and temperature. If the initial pressure due to 300.0 mol H_2 and 100.0 mol N_2 is 300.0 atm, what will the final pressure be? What will the final pressure be if initially the system contained 240.0 mol H_2 and 160.0 mol N_2 ? (Use the ideal gas equation even though the pressure is high.)
- 1.7** The van der Waals constants for N_2 are $a = 1.370 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.0387 \text{ L mol}^{-1}$. Consider 0.5 mol of $\text{N}_2(\text{g})$ is in a vessel of volume 10.0 L. Assuming that the temperature is 300 K, compare the pressures predicted by the ideal gas equation and the van der Waals equation.
 (a) What is the percentage error in using the ideal gas equation instead of the van der Waals equation?
 (b) Keeping $V = 10.0 \text{ L}$, use *Maple/Mathematica* to plot p versus N for $N = 1$ to 100, using the ideal gas and the van der Waals equations. What do you notice regarding the difference between the pressure predicted by the two equations?
- 1.8** For 1.00 mol of Cl_2 in a volume of 2.50 L, calculate the difference in the energy between U_{ideal} and U_{vw} . What is the percentage difference when compared with U_{ideal} ?
- 1.9** (a) Using the ideal gas equation, calculate the volume of 1 mol of a gas at a temperature of 25 °C and a pressure of 1 atm. This volume is called the *Avogadro volume*.
 (b) The atmosphere of Venus is 96.5% CO_2 (g). The surface temperature is about 730 K and the pressure is about 90 atm. Using the ideal gas equation, calculate the volume of 1 mol of CO_2 (g) under these conditions (Avogadro volume on Venus).
 (c) Use *Maple/Mathematica* and the van der Waals equation to obtain the Avogadro volume on Venus and compare it (find the percentage difference) with the result obtained using the ideal gas equation.

- 1.10** The van der Waals parameter b is a measure of the volume excluded due to the finite size of the molecules. Estimate the size of a single molecule from the data in Table 1.1.
- 1.11** For the van der Waals equation, express the pressure as a power series in $1/V_m$. Using this expression, determine the Boyle temperature T_B at which $p \approx RT_B/V_m$.
- 1.12** For the Redlich–Kwong equation

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}$$

show that there is a critical temperature above which there is no transition to a liquid state.

- 1.13** Though the van der Waals equation was a big improvement over the ideal gas equation, its validity is also limited. Compare the following experimental data with the predictions of the van der Waals equation for 1 mol of CO₂ at $T = 40^\circ\text{C}$. (Source: I. Prigogine and R. Defay, *Chemical Thermodynamics*, 1967, Longmans: London.)

P (atm)	V_m (L mol ⁻¹)
1	25.574
10	2.4490
25	0.9000
50	0.3800
80	0.1187
100	0.0693
200	0.0525
500	0.0440
1000	0.0400

- 1.14** Use *Mathematica/Maple* to plot the van der Waals p – V curves for Ar, N₂ and C₃H₈ using the data listed in Table 1.1 (see Appendix 1.3 for sample programs). In particular, compare the van der Waals curves for CO₂ and He and the ideal gas equation.
- 1.15** For CO₂, plot the compressibility factor $Z = pV_m/RT$ as a function of the reduced pressure p_r for fixed reduced temperatures $T_r = 1.2$ and $T_r = 1.7$. Verify that the Z – p_r curves are the same for all van der Waals' gases. (This can be plotted using Parametric Plots.)
- 1.16** Show that the pressure given by the van der Waals equation can become negative only when T is less than the critical temperature T_c .
- 1.17** (a) From the van der Waals equation, using Equation (1.5.2) obtain Equations (1.5.3) and (1.5.4). (These calculations may also be done using *Mathematica/Maple*). (b) Show that $Z_c = (p_c V_{mc}/RT_c) = 3/8$, a constant for all van der Waals gases.
- 1.18** Using *Mathematica/Maple*, obtain Equation (1.5.6) from Equation (1.5.5).
- 1.19** For CO₂, plot p – V isotherms for the van der Waals and Redlich–Kwong equations on the same graph for $T = 280\text{ K}$, 300 K and 330 K and comment on the difference between the two equations. The table

below lists some constants a and b for the Redlich–Kwong equation. (Source: J.H. Noggle, *Physical Chemistry*, 1996, Harper Collins.)

	A (bar L ² mol ⁻² K ^{1/2})	B (L mol ⁻¹)
Ar	16.71	0.0219
CO ₂	64.48	0.0296
O ₂	17.36	0.0221

- 1.20** Show that the Lennard–Jones energy

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

has a minimum value equal to $-\epsilon$ at $r = 2^{1/6}\sigma$.

- 1.21** Estimate the average distance between molecules at $T = 300$ K and $p = 1.0$ atm. (Hint: consider a cube of side 10 cm in which the molecules occupy points on a three-dimensional cubic lattice.)
- 1.22** According to Graham's law of diffusion, the rate of diffusion of gas molecules is inversely proportional to the square root of its mass. Explain why this is so using the kinetic theory of gases. How would you expect the diffusion coefficient to depend on the temperature?
- 1.23** (a) Using the integrals in Appendix 1.2, obtain the square of average speed and compare it with the average of v^2 .
 (b) Using the Maxwell probability distribution $f(v)$, obtain the most probable speed of a molecule of molar mass M at a temperature T .
- 1.24** Consider N₂ at a temperature of 350 K. Use the Maxwell speed distribution to calculate the fraction of molecules that have speeds greater than 600 m/s. You may use *Mathematica* to evaluate the needed integrals.

2

The First Law of Thermodynamics

The Idea of Energy Conservation Amidst New Discoveries

The concepts of kinetic energy, associated with motion, and potential energy, associated with conservative forces such as gravitation, were well known at the beginning of the nineteenth century. For a body in motion, the conservation of the sum of kinetic energy and potential energy is a direct consequence of Newton's laws (Exercise 2.1). However, this concept had no bearing on the multitude of thermal, chemical and electrical phenomena that were being investigated at that time. In addition, during the final decades of the eighteenth century and the initial decades of the nineteenth century, new phenomena were being discovered at a rapid pace.

The Italian physician Luigi Galvani (1737–1798) discovered that a piece of charged metal could make the leg of a dead frog twitch! The amazed public was captivated by the idea that electricity can generate life as dramatized by Mary Shelley (1797–1851) in her *Frankenstein*. Summarizing the results of his investigations in a paper published in 1791, Galvani attributed the source of electricity to animal tissue. However, it was the physicist Alessandro Volta (1745–1827) who recognized that the 'galvanic effect' is due to the passage of electric current. In 1800, Volta went on to construct the so-called Volta's pile, the first 'chemical battery'; electricity could now be generated from chemical reactions. The inverse effect, the driving of a chemical reaction by electricity, was demonstrated by Michael Faraday (1791–1867) in the 1830s. The newly discovered electric current could also produce heat and light. To this growing list of interrelated phenomena, the Danish physicist Hans Christian Oersted (1777–1851) added the generation of magnetic field by an electrical current in 1819. In Germany, in 1822, Thomas Seebeck (1770–1831) (who helped Goethe in his scientific investigations) demonstrated the 'thermoelectric effect', the generation of electricity by heat. The well-known Faraday's law of induction, the generation of an electrical current by a changing magnetic field, came in 1831. All these discoveries presented a great web of interrelated phenomena in heat, electricity, magnetism and chemistry to the nineteenth century scientists (Figure 2.1).

Soon, within the scientific community that faced this multitude of new phenomena, the idea that all these effects really represented the transformation of one indestructible quantity, 'the energy', began to take shape [1]. This law of conservation of energy is the First Law of thermodynamics. We will see details of its formulation in the following sections.

The mechanical view of nature holds that all energy is ultimately reducible to kinetic and potential energy of interacting particles. Thus, the law of conservation of energy may be thought of as essentially the law of conservation of the sum of kinetic and potential energies of all the constituent particles. A cornerstone for the

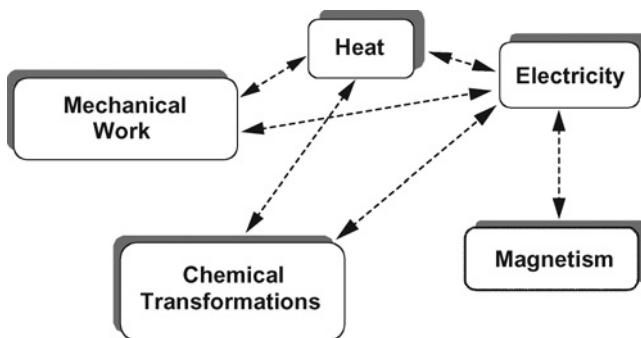


Figure 2.1 Interrelations between various phenomena discovered in the nineteenth century.

formulation of the First Law is the decisive experiments of James Prescott Joule (1818–1889) of Manchester, a brewer and an amateur scientist. Here is how Joule expressed his view of conservation of energy [2, 3]:

Indeed the phenomena of nature, whether mechanical, chemical or vital, consist almost entirely in a continual conversion of attraction through space,¹ living force² and heat into one another. Thus it is that order is maintained in the universe – nothing is deranged, nothing ever lost, but the entire machinery, complicated as it is, works smoothly and harmoniously. And though, as in the awful vision of Ezekiel, ‘... wheel may be in the middle of wheel ...’, and everything may appear complicated and involved in the apparent confusion and intricacy of an almost endless variety of causes, effects, conversion, and arrangements, yet is the most perfect regularity preserved – the whole being governed by the sovereign will of God.

In practice, however, we measure energy in terms of heat and changes in macroscopic variables, such as chemical composition, electrical voltage and current, not the kinetic and potential energies of molecules. Energy can take many forms, e.g. mechanical work, heat, chemical energy, and it can reside in electric, magnetic and gravitational fields. For each of these forms we can specify the energy in terms of macroscopic variables, and the changes of energy in each form have a mechanical equivalent.

2.1 The Nature of Heat

Though the distinction between temperature and heat was recognized in the eighteenth century as a result of the work of Joseph Black and others, the nature of heat was not clearly understood until the middle of the nineteenth century. Robert Boyle, Isaac Newton and others held the view that heat was the microscopic chaotic motion of particles. An opposing view, which prevailed in France, was that heat was an indestructible fluid-like substance without mass that was exchanged between material bodies. This indestructible substance was called **caloric** and it was measured in ‘calories’ (see Box 2.1). In fact, such figures as Antoine-Laurent Lavoisier (1743–1794), Jean Baptiste Joseph Fourier (1768–1830), Pierre-Simon de Laplace (1749–1827) and Siméon-Denis Poisson (1781–1840) all supported the caloric theory of heat. Even Sadi Carnot (1796–1832), in whose insights the Second Law originated, initially used the concept of caloric, though he later rejected it.

¹Potential energy.

²Kinetic energy.

Box 2.1 Basic definitions

Heat can be measured by the change in temperature it causes in a body. In this text we shall mostly use the SI units in which heat is measured in joules, though the calorie is an often-used unit of heat.

The calorie. The calorie, a word derived from the caloric theory of heat, was originally defined as the amount of heat required to increase the temperature of 1 g of water by 1 °C. When it was realized that this amount depended on the initial temperature of the water, the following definition was adopted: a calorie is the amount of heat required to increase the temperature of 1 g of water from 14.5 °C to 15.5 °C at a pressure of 1 bar. **The current practice is to define 1 cal as 4.184 J.** In fact, the International Union of Pure and Applied Chemistry (IUPAC) defines three types of calorie: the thermochemical calorie, $\text{cal}_{\text{th}} = 4.184 \text{ J}$; the international calorie, $\text{cal}_{\text{IT}} = 4.1868 \text{ J}$; the 15 °C calorie, $\text{cal}_{15} \approx 4.1855 \text{ J}$.

Work and heat. In classical mechanics, when a body undergoes a displacement $\text{d}s$ by a force \mathbf{F} , the mechanical work done $\text{d}W = \mathbf{F} \cdot \text{d}s$. Work is measured in joules. Dissipative forces, such as friction between solids in contact, or viscous forces in liquids, convert mechanical energy to heat. Joule's experiments demonstrated that a certain amount of mechanical work, regardless of the manner in which it is performed, always produces the same amount of heat. Thus, an equivalence between work and heat was established.

Heat capacity. The heat capacity C of a body is the ratio of the heat absorbed $\text{d}Q$ to the resulting increase in temperature $\text{d}T$:

$$C = \frac{\text{d}Q}{\text{d}T}$$

For a given $\text{d}Q$, the change in temperature $\text{d}T$ depends on whether the substance is maintained at constant volume or at constant pressure. The corresponding heat capacities are denoted by C_V and C_p respectively. Heat capacities are generally functions of temperature.

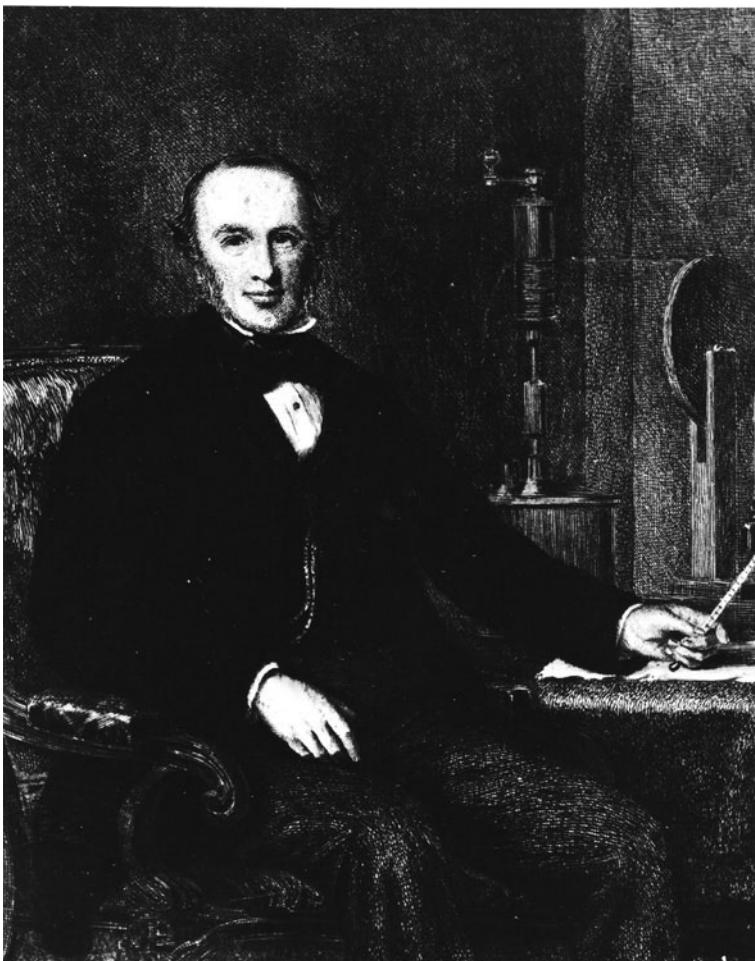
Molar heat capacity. It is the heat capacity of 1 mol of the substance. We shall denote it by C_{mV} or C_{mp} .

Specific heat. It is the heat required to change the temperature of a unit mass (usually 1.0 g or 1.0 kg) of the substance by 1 °C.

The true nature of heat as a form of energy that can interconvert to other forms of energy was established after much debate. One of the most dramatic demonstrations of the conversion of mechanical energy to heat was performed by Benjamin Thompson, an American born in Woburn, Massachusetts, whose adventurous life took him to Bavaria where he became Count Rumford (1753–1814) [4]. Rumford immersed metal cylinders in water and drilled holes in them. The heat produced due to mechanical friction could bring the water to a boil! He even estimated that the production of 1 cal of heat requires about 5.5 J of mechanical work [5].

It was the results of the careful experiments of James Prescott Joule, reported in 1847, that established beyond doubt that heat was not an indestructible substance, that, in fact, it can be transformed to mechanical energy and vice versa [5, 6]. Furthermore, Joule showed that there is an equivalence between heat and mechanical energy in the following sense: a certain amount of mechanical energy, regardless of the particular means of conversion, always produces the same amount of heat (4.184 J produce 1 cal of heat). This meant heat and mechanical energy can be thought of as different manifestations of the same physical quantity, the 'energy'.

But still, what is heat? One could say that physical and chemical processes have a natural tendency to convert all other forms of energy to heat. In the classical picture of particle motion, it is the kinetic energy



James Prescott Joule (1818–1889).

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associated with chaotic motion, as we saw in Chapter 1. Molecules in incessant motion collide and randomize their kinetic energy and the Maxwell–Boltzmann velocity distribution is quickly established; the average kinetic energy, which equals $3k_B T/2$, generally increases with absorption of heat. However, heat does not change the temperature of the body during phase transformations, but transforms the phase.

That is not all we can say about heat. In addition to particles, we also have fields. The interaction between the particles is described by fields, such as electromagnetic fields. Classical physics had established that electromagnetic radiation was a physical quantity that can carry energy and momentum. So when particles gain or lose energy, some of it can transform into the energy of the field. The energy associated with electromagnetic radiation is an example. The interaction between matter and radiation also leads to a state of thermal equilibrium in which a temperature can be associated with radiation. Radiation in thermal equilibrium with matter is called ‘heat radiation’ or ‘thermal radiation’. So heat can also be in the form of radiation. We shall study the thermodynamics of thermal radiation in some detail in Chapter 11.

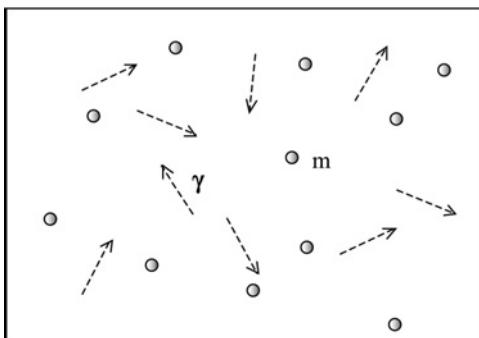


Figure 2.2 Classical picture of a gas of molecules (*m*) at low temperatures in equilibrium with radiation (γ).

During the twentieth century, our view of particles and fields has been unified by quantum field theory. According to quantum field theory, all particles are excitations of quantum fields. We now know, for example, that the electromagnetic field is associated with particles we call photons, though it also has a wave nature. Similarly, other fields, such as those associated with nuclear forces, have corresponding particles. Just as photons are emitted or absorbed by molecules undergoing a transition from one state to another (see Figure 2.2) – which in the classical picture corresponded to emission or absorption of radiation – other particles, such as mesons, can be absorbed and emitted by nuclear particles in high-energy processes. The energy density of thermal radiation depends only on the temperature.

One of the most remarkable discoveries of modern physics is that every particle has an antiparticle. When a particle encounters its antiparticle they may annihilate each other, converting their energy into other forms, such as photons. All this has expanded our knowledge of the possible states of matter. As mentioned above, the average kinetic energy of particles is proportional to temperature. At the temperatures we normally experience, collisions between molecules result in the emission of photons, but not other particles. At sufficiently high temperatures (greater than 10^{10} K), other particles can also be similarly created as a result of collisions. Particle creation is often in the form of particle–antiparticle pairs (see Figure 2.3). Thus, there are states of matter in which there is incessant creation and annihilation of particle–antiparticle pairs, a state in which the

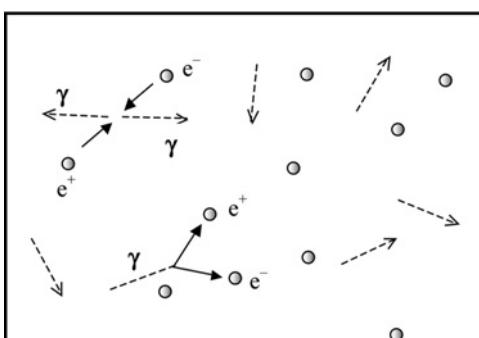


Figure 2.3 A gas of electrons (e^-) and positrons (e^+) in equilibrium with radiation (γ) at very high temperatures. At temperatures over 10^{10} K, particle–antiparticle pair creation and annihilation begins to occur and the total number of particles is no longer a constant. At these temperatures, electrons, positrons and photons are in a state called thermal radiation. The energy density of thermal radiation depends only on temperature.

number of particles does not remain constant. This state of matter is a highly excited state of a field. The notion of thermodynamic equilibrium and a temperature should apply to such a state as well.

Fields in thermal equilibrium can be more generally referred to as **thermal radiation**. One of the characteristic properties of thermal radiation is that its energy density is only a function of temperature; unlike the ideal gas, the number of particles of each kind itself depends on the temperature. ‘Blackbody radiation’, the study of which led Max Planck (1858–1947) to the quantum hypothesis, is thermal radiation associated with the electromagnetic field. At high enough temperatures, all particles (electrons and positrons, protons and antiprotons) can exist in the form of thermal radiation. Immediately after the big bang, when the temperature of the universe was unimaginably high, the state of matter in the universe was in the form of thermal radiation. As the universe expanded and cooled, the photons remained in the state of thermal radiation, which can be associated with a temperature, but the protons, electrons and neutrons are no longer in that state. In its present state, the electromagnetic radiation that fills the universe is in an equilibrium state of temperature about 2.7 K, but the observed abundance of elements in the universe is not that expected in a state of thermodynamic equilibrium [7].

2.2 The First Law of Thermodynamics: The Conservation of Energy

As mentioned at the beginning of this chapter, though mechanical energy (kinetic energy plus potential energy) and its conservation was known from the time of Newton and Leibnitz, energy was not thought of as a general and universal quantity until the nineteenth century [5, 8].

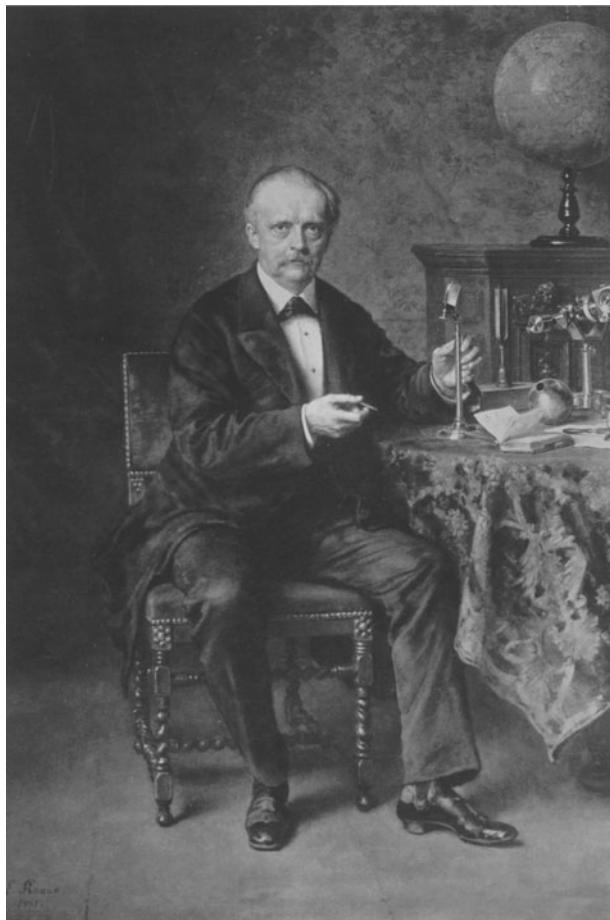
With the establishment of the mechanical equivalence of heat by Joule, it became accepted that heat is a form of energy that could be converted to work and vice versa. It was in the second half of the nineteenth century that the concept of *conservation* of energy was clearly formulated. Many contributed to this idea, which was very much ‘in the air’ at that time. For example, the law of ‘constant summation of heats of reaction’ was formulated in 1840 by the Russian chemist Germain Henri Hess (1802–1850). This was essentially the law of energy conservation in chemical reactions. This law, now called Hess’s law, is routinely used to calculate heats of chemical reactions.

It can be said that the most important contributions to the idea of conservation of energy as a universal law of nature came from Julius Robert von Mayer (1814–1878), James Prescott Joule (1818–1889) and Hermann von Helmholtz (1821–1894). Two of the landmarks in the formulation of the law of conservation of energy are a paper by Robert von Mayer titled ‘Bermerkungen über die Kräfte der unbelebten Natur’ (‘Remarks on the forces of inanimate nature’), published in 1842, and a paper by Helmholtz titled ‘Über die Erhaltung der Kraft’ (‘On the conservation of force’), which appeared in 1847 [5, 6].

The law of conservation of energy can be stated and utilized entirely in terms of macroscopic variables. A transformation of state may occur due to an exchange of heat, performance of work and change in chemical composition and other such macroscopic processes. Each of these processes is associated with a change in energy, and the First Law of thermodynamics could be stated as:

When a system undergoes a transformation of state, the algebraic sum of the different energy changes, heat exchanged, work done, etc., is independent of the manner of the transformation. It therefore depends only on the initial and final states of the transformation.

For example, as shown in Figure 2.4, when N_k is constant, a transformation of volume and temperature of a gas mixture from the state O to the state X may occur via different paths, each following different intermediate volumes and temperatures. For each path, the total amount of heat exchanged and the mechanical work done will be different. However, as the First Law states, the sum of the two will be the same, independent of the path. Since the total change in energy is independent of the path, the infinitesimal change dU associated



Hermann von Helmholtz (1821–1894).

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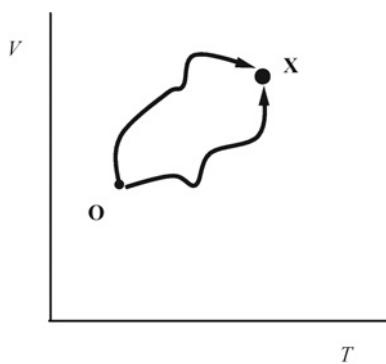


Figure 2.4 The change of energy U_X during a transformation from a normal or reference state 'O' to the state 'X' is independent of the manner of transformation. In the figure, the state of a system is specified by its volume V and temperature T .

with any transformation must depend solely on the initial and final states. An alternative way of stating this assertion is that in every cyclic process (closed path) that restores the system to its initial state, the integral of the energy change is zero:

$$\oint dU = 0 \quad (2.2.1)$$

Equation (2.2.1) may also be considered a statement of the First Law. Since changes in U are independent of the transformation path, its change from a fixed state O to any final state X is entirely specified by X. The state X of many systems is specified by the state variables T , V and N_k . For such systems, if the value of U at the state O is arbitrarily defined as U_0 , then U is a function of the state X:

$$U = U(T, V, N_k) + U_0 \quad (2.2.2)$$

If more variables (such as electric or magnetic fields) are needed to specify the state of a system, then U will be a function of those variables as well. In this formulation, the energy U can only be defined up to an arbitrary additive constant. Its absolute value cannot be specified.

Yet another way of stating the First Law is as an ‘impossibility’, a restriction nature imposes on physical processes. For example, in Max Planck’s treatise [9], the First Law is stated thus:

... it is in no way possible, either by mechanical, thermal, chemical, or other devices, to obtain perpetual motion, i.e. it is impossible to construct an engine which will work in a cycle and produce continuous work, or kinetic energy, from nothing (author’s italics).

It is easy to see that this statement is equivalent to the above formulation summarized in Equation (2.2.1). We note again that this statement is entirely in macroscopic, operational terms and has no reference whatsoever to the microscopic structure of matter. The process described above is called *perpetual motion of the first kind*.

For a closed system, the energy exchanged with its exterior in a time dt may be divided into two parts: dQ , the amount of heat, and, dW , the amount of mechanical energy. Unlike the change in total energy dU , the quantities dQ and dW are *not independent* of the manner of transformation; we cannot specify dQ or dW simply by knowing the initial and final states because their values depend on the path or the process that causes the energy exchange. Hence, it is not possible to define a function Q that depends only on the initial and final states, i.e. heat is not a state function. While every system can be said to possess a certain amount of energy U , the same cannot be said of heat Q or work W . However, there is no difficulty in specifying the amount of heat exchanged in a particular transformation. The process that causes the heat exchange enables us to specify dQ as the heat exchanged in a time interval dt .

Most introductory texts on thermodynamics do not include irreversible processes; they describe all transformations of state as idealized, infinitely slow changes. In that formulation, dQ cannot be defined in terms of a time interval dt because the transformation does not occur in finite time; in fact, classical thermodynamics does not contain time at all. This point is clearly stated in the well-known physical chemistry text by Alberti and Silbey [10]: ‘Thermodynamics is concerned with equilibrium states of matter and has nothing to do with time.’ It is a theory based solely on *states* with no explicit inclusion of irreversible *processes*, such as heat conduction. This poses a problem: because Q is not a state function, the heat exchanged dQ cannot be uniquely specified by initial and final states. To overcome this difficulty, an ‘imperfect differential’ dQ is defined to represent the heat exchanged in a transformation, a quantity that depends on the initial and final states *and* the path of transformation. In our approach we will avoid the use of imperfect differentials. The heat flow is described by processes that occur at a finite time and, with the assumption that the rate of heat flow is known, the heat exchanged dQ in a time dt is well defined. The same is true for the work dW . Idealized, infinitely

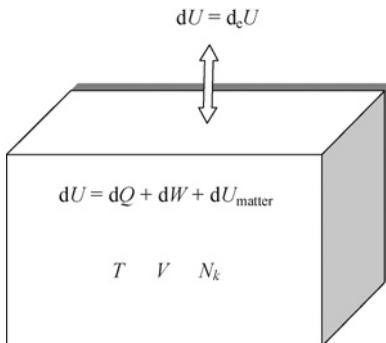


Figure 2.5 The law of conservation of energy: the total energy of an isolated system U remains a constant. The change in the energy dU of a system, in a time dt , can only be due to exchange of energy $d_e U$ with the exterior in the form of heat, mechanical work dW and through the exchange of matter dU_{matter} . The energy change of the system is equal and opposite to that of the exterior.

slow reversible processes still remain useful for some conceptual reasons and we will use them occasionally, but we will not restrict our presentation to reversible processes as many texts do.

The total change in energy dU of a closed system in a time dt is

$$dU = dQ + dW \quad (2.2.3)$$

The quantities dQ and dW can be specified in terms of the rate laws for heat transfer and the forces that do the work. For example, the heat supplied in a time dt by a heating coil of resistance R carrying a current I is given by $dQ = VI dt = (I^2 R) dt$, in which V is the voltage drop across the coil.

For open systems there is an additional contribution due to the flow of matter dU_{matter} (Figure 2.5):

$$dU = dQ + dW + dU_{\text{matter}} \quad (2.2.4)$$

Also, for open systems we define the volume not as the volume occupied by a fixed amount of substance but by the boundary of the system, e.g. a membrane. Since the flow of matter into and out of the system can be associated with mechanical work (as, for instance, the flow of molecules into the system through a semipermeable membrane due to excess external pressure), dW is not necessarily associated with changes in the system volume. The calculation of changes in energy dU in open systems does not pose any fundamental difficulty. In any process, if changes in T , V and N_k can be computed, then the change in energy can be calculated. The total change in the energy can then be obtained by integrating $U(T, V, N_k)$ from the initial state A to the final state B:

$$\int_A^B dU = U_B - U_A \quad (2.2.5)$$

Because U is a state function, this integral is independent of the path.

Let us now consider some specific examples of exchange of energy in forms other than heat.

- For closed systems, if dW is the mechanical work due to a volume change, then we may write

$$dW_{\text{mech}} = -p dV \quad (2.2.6)$$

in which p is the pressure at the moving surface and dV is the change in volume (see Box 2.2).

- For transfer of charge dq across a potential difference ϕ

$$dU_q = \phi dq \quad (2.2.7)$$

- For dielectric systems, the change of electric dipole moment dP in the presence of an electric field E is associated with a change of energy

$$dU_{\text{elect}} = -E dP \quad (2.2.8)$$

- For magnetic systems, the change of magnetic dipole moment dM in the presence of a magnetic field B is associated with a change of energy

$$dU_{\text{mag}} = -B dM \quad (2.2.9)$$

- For a change of surface area $d\Sigma$ with an associated interfacial energy γ (interfacial energy per unit area)

$$dU_{\text{surf}} = \gamma d\Sigma \quad (2.2.10)$$

In general, the quantity dW is a sum of all the various forms of ‘work’, each term being a product of an intensive variable and a differential of an extensive variable.

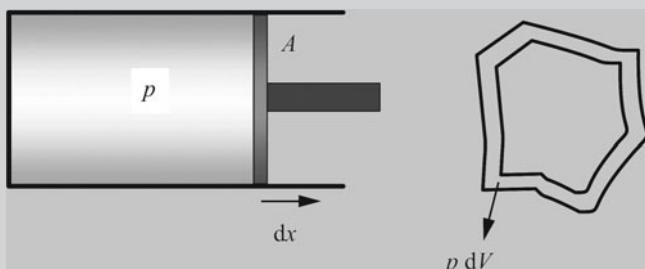
Thus, in general, the change in the total internal energy may be written as

$$dU = dQ - p dV + \varphi dq - EdP + \dots \quad (2.2.11)$$

This change of energy of a system is a function of state variables such as T , V and N_k .

Box 2.2 Mechanical work due to a change in volume

Mechanical work: $dW = \mathbf{F} \cdot d\mathbf{s}$



The force on the piston of area A due to a pressure p is pA . An expanding gas does work; hence, its energy decreases. The decrease in the energy when the gas pressure moves the piston by an amount dx is

$$dW = -pA dx = -p dV$$

in which dV is the change in volume of the gas. The negative sign is used to ensure that the energy of the gas decreases when V increases. By considering small displacements of the surface of a body at pressure

p (the figure on the right), the above expression for the work done by a gas can be shown to be generally valid for any system.

Isothermal Volume Change

By keeping a gas in contact with a reservoir at temperature T and slowly changing its volume, a constant-temperature or *isothermal* process can be realized. For such a process, the change in the energy of the gas equals the isothermal work given by the expression:

$$\text{Work} = \int_{V_i}^{V_f} -p \, dV = \int_{V_i}^{V_f} -\frac{NRT}{V} \, dV = -NRT \ln\left(\frac{V_f}{V_i}\right)$$

The negative sign indicates that an expanding gas transfers its energy to the exterior. During an isothermal expansion, flow of heat from the reservoir to the gas keeps T constant.

For systems undergoing chemical transformations, the total energy $U = U(T, V, N_k)$ may be expressed as a function of T , V and the molar amounts of the constituents N_k . As a function of T , V and N_k , the total differential of U can be written as

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_{V, N_k} dT + \left(\frac{\partial U}{\partial V}\right)_{T, N_k} dV + \sum_k \left(\frac{\partial U}{\partial N_k}\right)_{V, T, N_{i \neq k}} dN_k \\ &= dQ + dW + dU_{\text{matter}} \end{aligned} \quad (2.2.12)$$

The exact form of the function $U(T, V, N_k)$ for a particular system is obtained empirically. One way of obtaining the temperature dependence of U is the measurement of the *molar heat capacity* C_{mV} at *constant volume* (see Box 2.1 for basic definitions of heat capacity and specific heat). At constant volume, since no work is performed, $dU = dQ$. Hence:

$$C_{mV}(T, V) \equiv \left(\frac{dQ}{dT}\right)_{V=\text{const}} = \left(\frac{\partial U}{\partial T}\right)_{V, N=1} \quad (2.2.13)$$

If C_{mV} is determined experimentally (Box 2.3), then the internal energy $U(T, V)$ is obtained through integration of C_{mV} :

$$U(T, V, N) - U(T_0, V, N) = N \int_{T_0}^T C_{mV}(T, V) dT \quad (2.2.14)$$

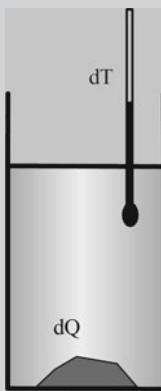
in which T_0 is the temperature of a reference state. If, for example, C_{mV} is independent of temperature and volume, as is the case for an ideal gas, then we have

$$U_{\text{ideal}} = C_{mV}NT + U_0 \quad (2.2.15)$$

in which U_0 is an arbitrary additive constant. As noted earlier, U can only be defined up to an additive constant. For ideal monatomic gases $C_{mV} = (3/2)R$ and for diatomic gases $C_{mV} = (5/2)R$.

Box 2.3 Calorimetry

Calorimeter. Heat evolved or absorbed during a transformation, such as a chemical reaction, is measured using a calorimeter. The transformation of interest is made to occur inside a chamber that is well insulated from the environment to keep heat loss to a minimum. To measure the heat generated by a process, first the heat capacity of the calorimeter, C_{cal} should be determined. This is done by noting the increase in the temperature of the calorimeter due to a process for which the heat evolved is known. The heat produced by a current-carrying resistor, for example, is known to be I^2R joules per second, in which I is the current in amps and R is the resistance in ohms. (Using Ohm's law, $V = IR$, in which V is the voltage across the resistor in volts, the heat generated per second may also be written as VI .) If the heat capacity C_{cal} of the calorimeter is known, then one only needs to note the change in the temperature of the calorimeter to determine the heat generated by a process.



Calorimetry is widely used in present-day laboratories.

Bomb calorimeter. The heat of combustion of a compound is determined in a bomb calorimeter. In a bomb calorimeter, the combustion takes place in a chamber pressurized to about 20 atm with pure oxygen to ensure that the combustion is complete.

Isothermal calorimeter. In this type of calorimeter, the sample that absorbs or generates heat due to a physicochemical process is maintained at a constant temperature using a sensitive heat exchanger that can record the amount of heat exchanged. This technique is highly developed and sensitive enough to measure enthalpy changes as low as a few nanojoules. It is a method widely used to study the thermodynamics of biological systems.

The notion of total internal energy is not restricted to homogeneous systems in which quantities such as temperature are uniform. For many systems, temperature is locally well defined but may vary with the position x and time t . In addition, the equations of state may remain valid in every elemental volume δV (i.e. in a small-volume element defined appropriately at every point x) in which all the state variables are specified as densities. For example, corresponding to the energy $U(T, V, N_k)$ we may define the energy destiny $u(x, T)$, energy per unit volume, at the point x at time t , which can be expressed as a function of the local temperature $T(x, t)$ and the molar density $n_k(x, t)$ (moles of k per unit volume, also called number density), which in general are functions of both position x and time t :

$$u(x, t) = u(T(x, t), n_k(x, t)) \quad (2.2.16)$$

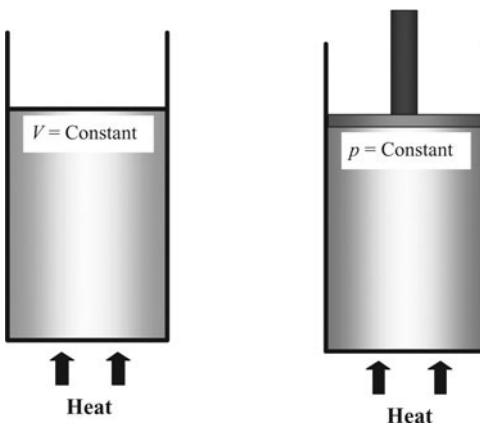


Figure 2.6 Molar heat capacity at constant pressure is larger than that at a constant volume.

The law of conservation of energy is a *local conservation law*: the change in energy in a small volume can only be due to a flow of energy into or out of the volume. Two spatially separated regions cannot exchange energy unless the energy passes through the region connecting the two parts.³

2.3 Elementary Applications of the First Law

2.3.1 Relation between C_{mp} and C_{mV}

The First Law of thermodynamics leads to many simple and useful conclusions. It leads to a relation between the *molar heat capacities* at constant pressure C_{mp} and at constant volume C_{mV} (Figure 2.6 and Table 2.1). Consider a one-component substance. Then, using Equations (2.2.3) and (2.2.6), and the fact that U is a function of the volume and temperature, the change in the energy dU can be written as

$$dU = dQ - p dV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (2.3.1)$$

From this it follows that the heat exchanged by the gas can be written as

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad (2.3.2)$$

If the gas is heated at a constant volume, then, since no work is done, the change in the energy of the gas is entirely due to the heat supplied. Therefore:

$$C_V \equiv \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (2.3.3)$$

³One might wonder why energy conservation does not take place nonlocally, disappearing at one location and simultaneous appearing at another. Such conservation, it turns out, is not compatible with the theory of relativity. According to relativity, events that are simultaneous but occurring at different locations to one observer may not be simultaneous to another. Hence, the simultaneous disappearance and appearance of energy as seen by one observer will not be simultaneous for all. For some observers, energy would have disappeared at one location first and only some time later would it reappear at the other location, thus violating the conservation law during the time interval separating the two events.

Table 2.1 Molar heat capacities C_{mV} and C_{mp} for some substances at $T = 298.15\text{ K}$ and $p = 1\text{ bar}$.

Substance	C_{mp} (J mol $^{-1}$ K $^{-1}$)	C_{mV} (J mol $^{-1}$ K $^{-1}$)
Ideal monatomic	$(5/2)R$	$(3/2)R$
Ideal diatomic	$(7/2)R$	$(5/2)R$
Noble gases (He, Ne, Ar, Kr, Xe)	20.8	12.5
$\text{N}_2(\text{g})$	29.17	20.82
$\text{O}_2(\text{g})$	29.43	21.07
$\text{CO}_2(\text{g})$	37.44	28.93
$\text{H}_2(\text{g})$	28.83	20.52
$\text{H}_2\text{O}(\text{l})$	75.33	
$\text{CH}_3\text{OH}(\text{l})$	81.21	
$\text{C}_6\text{H}_6(\text{l})$	132.9	
$\text{Cu}(\text{s})$	24.47	
$\text{Fe}(\text{s})$	25.09	

Source: P.J. Linstrom and W.G. Mallard (eds), *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, June 2005, National Institute of Standards and Technology, Gaithersburg, MD (<http://webbook.nist.gov>).

On the other hand, if the gas is heated at constant pressure, then from Equation (2.3.2) we have

$$C_p \equiv \left(\frac{dQ}{dT} \right)_p = \left(\frac{\partial U}{\partial T} \right)_V + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p \quad (2.3.4)$$

Comparing Equations (2.3.3) and (2.3.4), we see that C_V and C_p are related by

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p \quad (2.3.5)$$

The right-hand side of Equation (2.3.5) is equal to the additional amount of heat required to raise the temperature in a constant-pressure, or ‘isobaric’, process to compensate for the energy expended due to expansion of the volume.

Relation (2.3.5) is generally valid for all substances. For an ideal gas, it reduces to a simple form. As mentioned in Chapter 1 (see Equations (1.4.6) and (1.4.8)), the energy U is only a function of the temperature and is independent of the volume. Hence, in Equation (2.3.5), $(\partial U / \partial V)_T = 0$; for 1 mol of an ideal gas, since $pV = RT$, the remaining term $p(\partial V / \partial T)_p = R$. Therefore, for the molar heat capacities, Equation (2.3.5) reduces to the simple relation

$$C_{mp} - C_{mV} = R \quad (2.3.6)$$

2.3.2 Adiabatic Processes in an Ideal Gas

In an **adiabatic process**, the state of a system changes without any exchange of heat. Using the equation $dU = dQ - p dV$, we can write

$$dQ = dU + pdV = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + pdV = 0 \quad (2.3.7)$$

For an ideal gas, since U is a function of temperature but not of volume, and because $(\partial U / \partial T)_V = NC_{mV}$, Equation (2.3.7) reduces to

$$C_{mV}N dT + p dV = 0 \quad (2.3.8)$$

If the change in volume occurs so that the ideal gas equation is valid during the process of change, then we have

$$C_{mV}dT + \frac{RT}{V}dV = 0 \quad (2.3.9)$$

(For very rapid changes in volume, the relation between p , V and T may deviate from the ideal gas law.) However, since $R = C_{mp} - C_{mV}$ for an ideal gas, we can write Equation (2.3.9) as

$$\frac{dT}{T} + \frac{C_{mp} - C_{mV}}{C_{mV}V}dV = 0 \quad (2.3.10)$$

Integration of Equation (2.3.10) gives

$$TV^{(\gamma-1)} = \text{constant} \quad \text{where} \quad \gamma = \frac{C_{mp}}{C_{mV}} \quad (2.3.11)$$

Using $pV = NRT$, the above relation can be transformed into

$$pV^\gamma = \text{constant} \quad \text{or} \quad T^\gamma p^{1-\gamma} = \text{constant} \quad (2.3.12)$$

Thus, the First Law gives us Equations (2.3.11) and (2.3.12), which characterize adiabatic processes in an ideal gas. Table 2.2 lists the ratio of heat capacities γ for some gases. We shall discuss adiabatic processes in real gases in Chapter 6.

2.3.3 Sound Propagation

An example of an adiabatic process in nature is the rapid variations of pressure during the propagation of sound. These pressure variations, which are a measure of the sound intensity, are small. A measure of these pressure variations is p_{rms} , the root-mean-square value of the sound pressure with respect to the atmospheric

Table 2.2 Ratios of molar heat capacities and speed of sound C_{sound} at $T = 298.15 \text{ K}$ and $p = 1 \text{ bar}$.

Gas	C_{mp} (J mol $^{-1}$ K $^{-1}$)	C_{mV} (J mol $^{-1}$ K $^{-1}$)	$\gamma = C_{mp}/C_{mV}$	C_{sound} (m s $^{-1}$)
Ar(g)	20.83	12.48	1.669	321.7
CO ₂ (g)	37.44	28.93	1.294	268.6
H ₂ (g)	28.83	20.52	1.405	1315
He(g)	20.78	12.47	1.666	1016
N ₂ (g)	29.17	20.82	1.401	352.1
O ₂ (g)	29.43	21.07	1.397	328.7

Source: E.W. Lemmon, M.O. McLinden and D.G. Friend, Thermophysical properties of fluid systems. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, P.J. Linstrom and W.G. Mallard (eds), June 2005, National Institute of Standards and Technology, Gaithersburg, MD (<http://webbook.nist.gov>).

pressure, i.e. p_{rms} is the square root of the average value of $(p - p_{\text{atms}})^2$. The unit for measuring sound intensity is the *bel* (B, named in honor of Alexander Graham Bell). The usual practice is to express the intensity in units of *decibels* (dB). The decibel can be expressed as a logarithmic measure of the pressure variations defined by

$$I = 10 \log_{10} \left(\frac{p_{\text{rms}}^2}{p_0^2} \right) \quad (2.3.13)$$

in which the reference pressure $p_0 = 2 \times 10^{-8}$ kPa ($= 2 \times 10^{-10}$ bar) roughly corresponds to audibility threshold in humans – an astoundingly low threshold, which in units of energy intensity equals a mere 2×10^{-12} W m⁻². The logarithmic scale is used because it corresponds roughly to the sensitivity of the ear. We normally encounter sound whose intensity is in the range 10–100 dB, corresponding to a pressure variations in the range 6×10^{-10} to 2×10^{-5} bar. These small variations of pressure for audible sound occur in the frequency range 20 Hz–20 kHz (music being in the range 40–4000 Hz).

Owing to the rapidity of pressure variations, hardly any heat is exchanged by the volume of air that is undergoing the pressure variations and its surroundings. It is essentially an adiabatic process. As a first approximation, we may assume that the ideal gas law is valid for these rapid changes. In introductory physics texts it is shown that the speed of sound C_{sound} in a medium depends on the bulk modulus B and the density ρ according to the relation

$$C_{\text{sound}} = \sqrt{\frac{B}{\rho}} \quad \text{in which} \quad B = -\frac{\delta p}{\delta V/V} \quad (2.3.14)$$

The bulk modulus B relates the relative change in the volume of a medium $\delta V/V$ due to a change in pressure δp ; the negative sign indicates that for positive δp the change δV is negative. If the propagation of sound is an adiabatic process, in the ideal gas approximation, then the changes in volume and pressure are such that $pV^\gamma = \text{constant}$. By differentiating this relation, one can easily see that the bulk modulus B for an adiabatic process is

$$B = -V \frac{dp}{dV} = \gamma p \quad (2.3.15)$$

For an ideal gas of density ρ and molar mass M , we have

$$p = \frac{NRT}{V} = \frac{NM}{V} \frac{RT}{M} = \frac{\rho RT}{M}$$

Hence:

$$B = \frac{\gamma \rho RT}{M} \quad (2.3.16)$$

Using this expression in the relation (2.3.14) we arrive at the conclusion that, if the propagation of sound is an adiabatic process, the velocity C is given by

$$C_{\text{sound}} = \sqrt{\frac{\gamma RT}{M}} \quad (2.3.17)$$

Experimental measurements of sound confirm this conclusion to a good approximation. The velocities of sound in some gases are listed in Table 2.2.

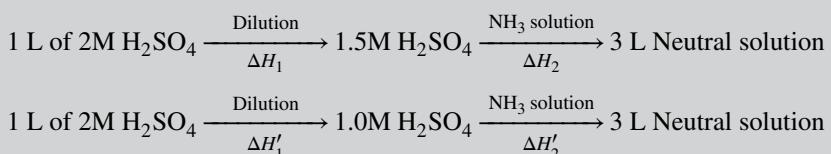
2.4 Thermochemistry: Conservation of Energy in Chemical Reactions

During the first half of the nineteenth century, chemists mostly concerned themselves with the analysis of compounds and chemical reactions and paid little attention to the heat evolved or absorbed in a chemical reaction. Though the early work of Lavoisier (1743–1794) and Laplace (1749–1827) established that heat absorbed in a chemical reaction was equal to the heat released in the reverse reaction, the relation between heat and chemical reactions was not investigated very much. The Russian chemist Germain Henri Hess (1802–1850) was rather an exception among the chemists of his time in regard to his interest in the heat released or absorbed by chemical reactions [11]. Hess conducted a series of studies in neutralizing acids and measuring the heats released (see Box 2.4). This, and several other experiments on the heats of chemical reactions, led Hess to his ‘law of constant summation’, which he published in 1840, 2 years before the appearance of Robert von Mayer’s paper on the conservation of energy:

The amount of heat evolved during the formation of a given compound is constant, independent of whether the compound is formed directly or indirectly in one or in a series of steps [12].

Box 2.4 The experiments of Germain Henry Hess

Hess conducted a series of studies in which he first diluted sulfuric acid with different amounts of water and then neutralized the acid by adding a solution of ammonia. Heat was released in both steps. Hess found that, depending on the amount of water added during the dilution, different amounts of heat were released during the dilution and the subsequent neutralization with ammonia. However, the sum of the heats released in the two processes was found to be the same [11]. The following example, in which ΔH are the heats released, illustrates Hess’s experiments:



Hess found that $\Delta H_1 + \Delta H_2 = \Delta H'_1 + \Delta H'_2$ to a good approximation.

Hess’s work was not very well known for many decades after its publication. The fundamental contribution of Hess to thermochemistry was made known to chemists largely through Wilhelm Ostwald’s (1853–1932) *Textbook of General Chemistry*, published in 1887. The above statement, known as **Hess’s law**, was amply confirmed in the detailed work of Mercellin Berthelot (1827–1907) and Julius Thomsen (1826–1909) [13]. As we shall see below, Hess’s law is a consequence of the law of conservation of energy and is most conveniently formulated in terms of a state function called *enthalpy*.

Hess’s law refers to the heat evolved in a chemical reaction under constant (atmospheric) pressure. Under such conditions, a part of the energy released during the reaction may be converted to work $W = \int_{V_1}^{V_2} -p \, dV$, if there is a change in volume from V_1 to V_2 . Using the basic equation of the First Law, $dU = dQ - V \, dp$, the heat evolved, ΔQ_p , during a chemical transformation at a constant pressure can be written as

$$\Delta Q_p = \int_{U_1}^{U_2} dU + \int_{V_1}^{V_2} p \, dV = (U_2 - U_1) + p(V_2 - V_1) \quad (2.4.1)$$



Germain Henri Hess (1802–1850).

(Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library.)

From this we see that the heat released can be written as a difference between two terms, one referring to the initial state (U_1, V_1), the other to the final state (U_2, V_2):

$$\Delta Q_p = (U_2 + pV_2) - (U_1 + pV_1) \quad (2.4.2)$$

Since U , p and V are specified by the state of the system and are independent of the manner in which that state was reached, the quantity $U + pV$ is a state function, fully specified by the state variables. According to Equation (2.4.2), the heat evolved, ΔQ_p , is the difference between the values of the function $(U + pV)$ at the initial and final states. The state function $(U + pV)$ is called **enthalpy** H :

$$H \equiv U + pV \quad (2.4.3)$$

The heat released by a chemical reaction at constant pressure $\Delta Q_p = H_2 - H_1$. Since ΔQ_p depends only on the values of enthalpy at the initial and final states, it is independent of the ‘path’ of the chemical transformation, in particular if the transformation occurs ‘directly or indirectly in one or in a series of steps’, as Hess concluded.

As a simple example, consider the reaction



in which 2 mol of P reacts with 5 mol of Cl₂ to produce 2 mol of PCl₅. In this reaction, 886 kJ of heat is released. The reaction can occur directly when an adequate amount of Cl₂ is present or it could be made to occur in two steps:



In reactions (b) and (c), for the molar quantities shown in the reaction, the heats evolved are 640 kJ and 246 kJ respectively. If the change in the enthalpies between the initial and final states of reactions (a), (b) and (c) are denoted by ΔH_{ra}, ΔH_{rb} and ΔH_{rc} respectively, then we have:

$$\Delta H_{\text{ra}} = \Delta H_{\text{rb}} + \Delta H_{\text{rc}} \quad (2.4.4)$$

The heat evolved or enthalpy change in a chemical reaction under constant pressure is usually denoted by ΔH_r and is called the **enthalpy of reaction**. The enthalpy of reaction is *negative for exothermic reactions* and it is *positive for endothermic reactions*.

The First Law of thermodynamics applied to chemical reactions in the form of Hess's law gives us a very useful way of predicting the heat evolved or absorbed in a chemical reaction if we can formally express it as a sum of chemical reactions for which the enthalpies of reaction are known. In fact, if we can assign a value for the enthalpy of 1 mol of each compound, then the heats of reactions can be expressed as the difference between the sums of enthalpies of the initial reactants and the final products. In reaction (c), for example, if we can assign enthalpies for a mole of PCl₃(g), Cl₂(g) and PCl₅(s), then the enthalpy of this reaction will be the difference between the enthalpy of the product PCl₅(s) and the sum of the enthalpies of the reactants PCl₃(g) and Cl₂(g). However, from the definition of enthalpy in Equation (2.4.3) it is clear that it could only be specified with respect to a reference or normal state because U can only be defined in this way.

A convenient way to calculate enthalpies of chemical reactions at a specified temperature has been developed by defining a **standard molar enthalpy of formation** ΔH_f⁰[X] for each compound X as described in Boxes 2.5 and 2.6.

Box 2.5 Basic definitions of standard states

Like the energy U, the quantitative specification of enthalpy and other thermodynamic quantities that we will discuss in later chapters can be done with reference to a **standard state** at a specified temperature T, standard pressure p⁰, standard molality m⁰ and standard concentration c⁰. Though the choice of p⁰, m⁰ and c⁰ depends on the system under consideration, the most common choice for tabulating data is

$$T = 298.15, \quad p^0 = 1 \text{ bar} = 10^5 \text{ Pa}, \quad m^0 = 1 \text{ mol kg}^{-1} \text{ and } c^0 = 1 \text{ mol dm}^{-3}$$

The standard state of a pure substance at a particular temperature is its most stable state (gas, liquid or solid) at a pressure of 1 bar (10⁵ Pa).

Notation used to indicate the standard state: g = gas; l = liquid; s = pure crystalline solid.

In a **gas phase**, the standard state of a substance, as a pure substance or as a component in a gas mixture, is the hypothetical state exhibiting ideal gas behavior at p = 1 bar. (Note that this definition implies that real gases at p = 1 bar are not in their standard state.*)

In a **condensed phase** (solid or liquid), the standard state of a substance, as a pure substance or as component of a mixture, is the state of the pure substance in the liquid or solid phase at the standard pressure p^0 .

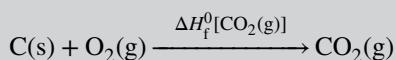
For a **solute** in a solution, the standard state is a hypothetical ideal solution of standard concentration c^0 at the standard pressure p^0 . Notation used to indicate the standard state: a_i = completely dissociated electrolyte in water; a_o = undissociated compound in water.

*Since the energy of an ideal gas depends only on the temperature, the standard state energy and enthalpy of a gas depend only on the temperature. This implies that real gases at a pressure of 1 bar are not in their standard state; their energies and enthalpies differ from that of the standard state of a gas at that temperature. For a real gas, at a temperature T and pressure of 1 bar, the energy $U_{\text{real}}(T) = U_{\text{ideal}}^0(T) + \Delta U(T)$, in which $\Delta U(T)$ is the correction due to the nonideality of the gas; it is sometimes called ‘internal energy imperfection’. Similarly, the enthalpy of a real gas at a temperature T and pressure of 1 bar is $H_{\text{real}}(T) = H_{\text{ideal}}^0(T) + \Delta H(T)$. The corrections, $\Delta U(T)$ and $\Delta H(T)$, are small, however, and they can be calculated using the equation of state such as the van der Waals equation.

Box 2.6 Basic definitions used in thermochemistry

Standard reaction enthalpies at a specified temperature are reaction enthalpies in which the reactants and products are in their standard states.

Standard molar enthalpy of formation $\Delta H_f^0[X]$ of a compound X, at a specified temperature T , is the enthalpy of formation of the compound X from its constituent elements in their standard state. Consider the example where X = CO₂(g):



The enthalpies of formation of elements in their standard state are defined to be zero at any temperature.

Thus, the enthalpies of formation $\Delta H_f^0[\text{H}_2]$, $\Delta H_f^0[\text{O}_2]$ and $\Delta H_f^0[\text{Fe}]$ are defined to be zero at all temperatures.

The consistency of the above definition is based on the fact that in ‘chemical reactions’ elements do not transform among themselves, i.e. reactions between elements do not result in the formation of other elements (though energy is conserved in such a reaction).

Standard enthalpies of formation of compounds can be found in tables of thermodynamic data [14]. Using these tables and Hess’s law, the standard enthalpies of reactions can be computed by viewing the reaction as ‘dismantling’ of the reactants to their constituent elements and recombining them to form the products. Since the enthalpy for the dismantling step is the negative of the enthalpy of formation, the enthalpy of the reaction



for example, can be written as

$$\Delta H_r^0 = -a\Delta H_f^0[X] - b\Delta H_f^0[Y] + c\Delta H_f^0[W] + d\Delta H_f^0[Z] \quad (2.4.5b)$$

Enthalpies of various chemical transformations are discussed in detail in later chapters and in the exercises at the end of this chapter.

Though it is most useful in thermochemistry, the enthalpy H , as defined in Equation (2.4.3), is a function of state that has a wider applicability. For example, we can see that the constant-pressure heat capacity C_p

can be expressed in terms of H as follows. Since the heat exchanged in a process that takes place at constant pressure is equal to the change in the system's enthalpy,

$$dQ_p = dU + p dV = dH_p \quad (2.4.6)$$

in which the subscripts denote a constant-pressure process. If the system consists of 1 mol of a substance, and if the change in temperature due to the exchange of heat is dT , then it follows that

$$\left(\frac{dQ}{dT}\right)_p = C_{mp} = \left(\frac{\partial H_m}{\partial T}\right)_p \quad (2.4.7)$$

Also, in general, the change in enthalpy in a chemical reaction (not necessarily occurring at constant pressure) can be written as

$$\begin{aligned} \Delta H_r &= H_f - H_i = (U_f - U_i) + (p_f V_f - p_i V_i) \\ &= \Delta U_r + (p_f V_f - p_i V_i) \end{aligned} \quad (2.4.8)$$

in which the subscripts 'i' and 'f' denote the initial and final states. In an isothermal process occurring at temperature T , if all the gaseous components in the reaction can be approximated to be ideal gases and if the change in volume of the nongaseous components can be neglected, then the changes of enthalpy and energy are related by

$$\Delta H_r = \Delta U_r + \Delta N_r RT \quad (2.4.9)$$

in which ΔN_r is the change in the total molar amount of the gaseous reactants, a relation used in obtaining enthalpies of combustion using a bomb calorimeter.

2.4.1 Variation of Enthalpy with Temperature

Being a state function, enthalpy is a function of T . Using the relation (2.4.7), the dependence of enthalpy on T can be expressed in terms of the molar heat capacity C_{mp} :

$$H(T, p, N) - H(T_0, p, N) = N \int_{T_0}^T C_{mp}(T) dT \quad (2.4.10)$$

Though the variation of C_{mp} with temperature is generally small, the following equation, called the Shomate equation, is often used:

$$C_{mp} = A + BT + CT^2 + DT^3 + \frac{E}{T^2} \quad (2.4.11)$$

Values of the coefficients A , B , C , D and E for some gases are shown in Table 2.3.

Table 2.3 Values of constants A , B , C , D and E in Equation (2.4.11) for some gases. The range of validity is 300 to 1200 K ($p = 1$ bar).

Gas	A ($J \text{ mol}^{-1} \text{ K}^{-1}$)	B ($10^{-3} \text{ J mol}^{-1} \text{ K}^{-2}$)	C ($10^{-6} \text{ J mol}^{-1} \text{ K}^{-3}$)	D ($10^{-9} \text{ J mol}^{-1} \text{ K}^{-4}$)	E ($10^6 \text{ J mol}^{-1} \text{ K}^{-5}$)
$\text{O}_2(\text{g})$	29.66	6.137	-1.186	0.0958	-0.2197
$\text{N}_2(\text{g})$	29.09	8.218	-1.976	0.1592	0.0444
$\text{CO}_2(\text{g})$	24.99	55.19	-33.69	7.948	-0.1366

Source: P.J. Linstrom and W.G. Mallard (eds), *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, June 2005, National Institute of Standards and Technology, Gaithersburg, MD (<http://webbook.nist.gov>).

From Equations (2.2.14) and (2.4.10) it is clear that the temperature dependence of the total internal energy U and enthalpy H of any particular gas can be obtained if its heat capacity is known as a function of temperature. Sensitive calorimetric methods are available to measure heat capacities experimentally.

Using the relation (2.4.10), if the reaction enthalpy at a pressure p_0 (which could be the standard pressure $p^0 = 1$ bar) is known at one temperature T_0 , then the reaction enthalpy at any other temperature T can be obtained if the molar heat capacities, C_{mp} , for the reactants and the products are known. The enthalpies of reactants or products X at the temperatures T and T_0 are related according to the relation (2.4.10) as

$$H_X(T, p_0, N_X) - H_X(T_0, p_0, N_X) = N_X \int_{T_0}^T C_{mp}(T) dT \quad (2.4.12)$$

in which the subscript X identifies the reactants or products. Then, by subtracting the sum of the enthalpies of reactants from the sum of the enthalpies of the products (as shown in Equation (2.4.5b)) we arrive at the following relation between the reaction enthalpies $\Delta H_r(T, p_0)$ and $\Delta H_r(T_0, p_0)$:

$$\Delta H_r(T, p_0) - \Delta H_r(T_0, p_0) = \int_{T_0}^T \Delta C_p(T) dT \quad (2.4.13)$$

in which ΔC_p is the difference in the heat capacities of the products and the reactants. Thus, $\Delta H_r(T, p_0)$ at any arbitrary temperature T can be obtained knowing $\Delta H_r(T_0, p_0)$ at a reference temperature T_0 . Relation (2.4.13) was first noted by Gustav Kirchhoff (1824–1887) and is sometimes called **Kirchhoff's law**. The change in reaction enthalpy with temperature is generally small.

2.4.2 Variation of Enthalpy with Pressure

The variation of H with pressure, at a fixed temperature, can be obtained from the definition $H = U + pV$. Generally, H and U can be expressed as functions of p , T and N . For changes in H we have

$$\Delta H = \Delta U + \Delta(pV) \quad (2.4.14)$$

At constant T_0 and N , in the ideal gas approximation $\Delta H = 0$ for gases. This is because U and the product pV are functions only of temperature (see Chapter 1); hence $H = U + pV$ is a function only of T and is independent of pressure. The change in H due to a change in p is mainly due to intermolecular forces and it becomes significant only for large densities. These changes in H can be calculated, for example, using the van der Waals equation.

For most solids and liquids, at a constant temperature, the total energy U does not change much with pressure. Since the change in volume is rather small unless the changes in pressure are very large, the change in enthalpy ΔH due to a change in pressure Δp can be approximated by

$$\Delta H \approx V\Delta p \quad (2.4.15)$$

A more accurate estimate can be made from a knowledge of the compressibility of the compound.

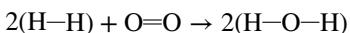
The First Law thus provides a powerful means of understanding the heats of chemical reactions. It enables us to compute the heats of reactions of an enormous number of reactions using the heats of formation of compounds at a standard temperature and pressure. The table entitled 'Standard Thermodynamic Properties' at the end of the book lists the standard heats of formation of some compounds. In addition, with a knowledge of

heat capacities and compressibilities, the heats of reactions at any temperature and pressure can be calculated given those at a reference temperature and pressure.

2.4.3 Computation of ΔH_r Using Bond Enthalpies

The concept of a chemical bond gives us a better understanding of the nature of a chemical reaction: it is essentially the breaking and making of bonds between atoms. The heat evolved or absorbed in a chemical reaction can be obtained by adding the heat absorbed in the breaking of bonds and the heat evolved in the making of bonds. The heat or enthalpy needed to break a bond is called the **bond enthalpy**.

For a particular bond, such as a C—H bond, the bond enthalpy varies from compound to compound, but one can meaningfully use an average bond enthalpy to estimate the enthalpy of a reaction. For example, the reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ can be written explicitly indicating the bonds as



This shows that the reaction involves the breaking of two H—H bonds and one O=O bond and the making of four O—H bonds. If the bond enthalpy of the H—H bond is denoted by $\Delta H[\text{H—H}]$, etc., the reaction enthalpy ΔH_r may be written as

$$\Delta H_r = 2\Delta H[\text{H—H}] + \Delta H[\text{O=O}] - 4\Delta H[\text{O—H}]$$

This is a good way of estimating the reaction enthalpy of a large number of reactions using a relatively small table of average bond enthalpies. Table 2.4 lists some average bond enthalpies which can be used to estimate the enthalpies of a large number of reactions.

Table 2.4 Average bond enthalpies for some common bonds.

	Bond enthalpy (kJ mol ⁻¹)										
	H	C	N	O	F	Cl	Br	I	S	P	Si
H	436										
C (single)	412	348									
C (double)		612									
C (triple)		811									
C (aromatic)		518									
N (single)	388	305	163								
N (double)		613	409								
N (triple)		890	945								
O (single)	463	360	157	146							
O (double)		743		497							
F	565	484	270	185	155						
Cl	431	338	200	203	254	252					
Br	366	276				219	193				
I	299	238				210	178	151			
S	338	259				250	212		264		
P	322									172	
Si	318		374								176

Source: L. Pauling, *The Nature of the Chemical Bond*, 1960, Cornell University Press: Ithaca, NY.

2.5 Extent of Reaction: A State Variable for Chemical Systems

In each chemical reaction, the changes in the mole numbers N_k are related through the stoichiometry of the reaction. In fact, *only one parameter is required to specify the changes in N_k resulting from a particular chemical reaction*. This can be seen as follows. Consider the elementary chemical reaction:



which is of the form



In this case the changes in the molar amounts dN_A , dN_B and dN_C of the components A, B and C are related by the stoichiometry. We can express this relation as

$$\frac{dN_A}{-1} = \frac{dN_B}{-1} = \frac{dN_C}{2} \equiv d\xi \quad (2.5.3)$$

in which we have introduced a single variable $d\xi$ that expresses all the changes in the mole numbers due to the chemical reaction. This variable ξ introduced by Theophile De Donder [15, 16] is basic for the thermodynamic description of chemical reactions and is called the **extent of reaction** or **degree of advancement**. The **rate of conversion** (or reaction velocity) is the rate at which the extent of reaction changes with time:

$$\text{Rate of conversion (or reaction velocity)} = \frac{d\xi}{dt} \quad (2.5.4)$$

If the initial values of N_k are written as N_{k0} , then the values of all N_k during the reactions can be specified by the extent of reaction ξ :

$$N_k = N_{k0} + v_k \xi \quad (2.5.5)$$

in which v_k is the stoichiometric coefficient of the reacting component N_k ; v_k is negative for reactants and positive for products. In this definition $\xi = 0$ for the initial state.

If the changes in N_k in a system are due to chemical reactions, then the total internal energy U of such a system can be expressed in terms of the initial N_{k0} , which are constants, and the extents of reaction ξ_i defined for each of the reactions. For example, consider a system consisting of three substances A, B and C undergoing a single reaction (see Equation (2.5.2)). Then the molar amounts can be expressed as: $N_A = N_{A0} - \xi$, $N_B = N_{B0} - \xi$ and $N_C = N_{C0} + 2\xi$. The value of ξ completely specifies all the molar amounts N_A , N_B and N_C . Hence, the total energy U may be regarded as a function $U(T, V, \xi)$ with the understanding that the initial molar amounts N_{A0} , N_{B0} and N_{C0} are constants in the function U . If more than one chemical reaction is involved, then an extent of reaction ξ_i is defined for each independent reaction i and each mole number is specified in terms of the extents of reaction of all the chemical reactions in which it takes part. Clearly, the ξ_i are state variables and internal energy can be expressed as a function of T , V and ξ_i : $U(T, V, \xi_i)$.

In terms of the state variables T , V and ξ_i , the total differential of U becomes

$$dU = \left(\frac{\partial U}{\partial T} \right)_{V, \xi_k} dT + \left(\frac{\partial U}{\partial V} \right)_{T, \xi_k} dV + \sum_k \left(\frac{\partial U}{\partial \xi_k} \right)_{V, T, \xi_{i \neq k}} d\xi_k \quad (2.5.6)$$

Using the First Law, the partial derivatives of U can be related to ‘thermal coefficients’, which characterize the system’s response to heat under various conditions. Consider a system with one chemical reaction. We have one extent of reaction ξ . Then, by using the First Law:

$$dQ - p dV = dU = \left(\frac{\partial U}{\partial T} \right)_{V,\xi} dT + \left(\frac{\partial U}{\partial V} \right)_{T,\xi} dV + \left(\frac{\partial U}{\partial \xi} \right)_{T,V} d\xi \quad (2.5.7)$$

which can be written as

$$dQ = \left(\frac{\partial U}{\partial T} \right)_{V,\xi} dT + \left[p + \left(\frac{\partial U}{\partial V} \right)_{T,\xi} \right] dV + \left(\frac{\partial U}{\partial \xi} \right)_{T,V} d\xi \quad (2.5.8)$$

Just as the partial derivative $(\partial U / \partial T)_V$ has the physical meaning of being the heat capacity at constant volume C_V , the other derivatives, called thermal coefficients, can be related to experimentally measurable quantities. The derivative $r_{T,V} \equiv (\partial U / \partial \xi)_{V,T}$, for example, is the amount of *heat evolved* per unit change in the extent of reaction (one equivalent of reaction) at constant V and T . If it is negative, then the reaction is exothermic; if it is positive, then the reaction is endothermic. Just as we derived the relation (2.3.6) between the thermal coefficients C_p and C_V , several interesting relations can be derived between these thermal coefficients as a consequence of the First Law [17].

Also, since the extent of reaction is a state variable, the enthalpy of a reacting system can be expressed as a function of the extent of reaction:

$$H = H(p, T, \xi) \quad (2.5.9)$$

The heat of reaction per unit change of ξ , which we shall denote as $h_{p,T}$, is the derivative of H with respect to ξ :

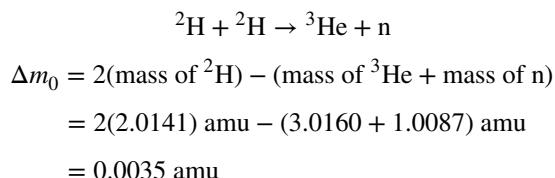
$$h_{p,T} = \left(\frac{\partial H}{\partial \xi} \right)_{p,T} \quad (2.5.10)$$

2.6 Conservation of Energy in Nuclear Reactions and Some General Remarks

At terrestrial temperatures, transformations of states of matter are mostly chemical, radioactivity being an exception. Just as molecules collide and react at terrestrial temperatures, at very high temperatures that exceed 10^6 K, typical of temperatures attained in the stars, nuclei collide and undergo nuclear reactions. At these temperatures, the electrons and nuclei of atoms are completely torn apart. Matter turns into a state that is unfamiliar to us and the transformations that occur are between nuclei, which is why it is called ‘nuclear chemistry’.

All the elements heavier than hydrogen on our and other planets are a result of nuclear reactions, generally referred to as nucleosynthesis, which occurred in stars [18]. Just as we have unstable molecules that dissociate into other more stable molecules, some of the nuclei that were synthesized in the stars are unstable and disintegrate; these are the ‘radioactive’ elements. The energy released by radioactive elements turns into heat, which is a source of heat for the Earth’s interior. For example, the natural radioactivity in granite due to ^{238}U , ^{235}U , ^{232}Th and ^{40}K produces a small amount of heat equal to about 5 μcal per gram of granite per year; however, accumulation of such heat over billions of years in the interior of the Earth makes a significant contribution to geothermal energy.

Under special circumstances, nuclear reactions can occur on the Earth, as in the case of nuclear fission of uranium and in the nuclear fusion of hydrogen in special reactors. Nuclear reactions release vastly greater amounts of energy than chemical reactions. The energy released in a nuclear reaction can be calculated from the difference in the rest mass of the reactants and the products using the famous relation $E^2 = p^2c^2 + m_0^2c^4$, derived by Einstein, in which E is the total energy of a particle, p is its momentum, m_0 its rest mass and c the velocity of light *in vacuo*. If the total rest mass of the products is lower than the total rest mass of the reactants, then the difference in energy due to change in the rest mass turns into the kinetic energy of the products. This excess kinetic energy turns into heat due to collisions. If the difference in the kinetic energy of the reactants and products is negligible, then the heat released $\Delta Q = \Delta m_0 c^2$, in which Δm_0 is the difference in the rest mass between the reactants and the products. In nuclear fusion, two deuterium nuclei, ${}^2\text{H}$, can combine to form a helium nucleus, ${}^3\text{He}$, and a neutron, n , is released:



where amu stands for atomic mass unit. Since $1 \text{ amu} = 1.6605 \times 10^{-27} \text{ kg}$, when 2 mol of ${}^2\text{H}$ react to produce 1 mol of ${}^3\text{He}$ and 1 mol of n , the difference in mass $\Delta m_0 = 3.5 \times 10^{-6} \text{ kg}$. The corresponding heat released is

$$\Delta E = \Delta m_0 c^2 = 3.14 \times 10^8 \text{ kJ mol}^{-1}$$

If a nuclear process occurs at constant pressure, then the heat released is equal to the enthalpy and all the thermodynamic formalism that applies to the chemical reactions also applies to nuclear reactions. Needless to say, in accordance with the First Law, Hess's law of additivity of reaction enthalpies is also valid for nuclear reactions.

2.6.1 General Remarks

Thermodynamically, energy is only defined up to an additive constant. In physical processes, it is only the change in energy (Equation (2.2.11)) that can be measured, which leaves the absolute value of energy undetermined. With the advent of the theory of relativity, which has given us the relation between rest mass, momentum and energy, $E^2 = p^2c^2 + m_0^2c^4$, the definition of energy has become as absolute as the definition of mass and momentum. The absolute value of the energy of elementary particles can be used to describe matter in the state of thermal radiation that we discussed in Section 2.1.

The conservation of energy has become the founding principle of physics. During the early days of nuclear physics, studies of β radiation, or ' β decay' as it is often called, showed initially that the energy of the products was not equal to the energy of the initial nucleus. This resulted in some reexamination of the law of conservation of energy, with some physicists wondering if it could be violated in some processes. Asserting the validity of the conservation of energy, Wolfgang Pauli (1900–1958) suggested in 1930 that the missing energy was carried by a new particle that interacted extremely weakly with other particles and, hence, was difficult to detect. This particle later acquired the name neutrino. Pauli was proven right 26 years later. Experimental confirmation of the existence of the neutrino came in 1956 from the careful experiments conducted by Frederick Reines and (the now late) Clyde Cowen. Since then our faith in the law of conservation of energy has become stronger than ever. Frederick Reines received the Physics Nobel Prize in 1995 for

the discovery of the elusive neutrino; for the interesting history behind the discovery of the neutrino, see Reference [19].

2.7 Energy Flows and Organized States

In Nature, the role of energy is much more than just a conserved quantity: *energy flows* are crucial to life, ecosystems and human activity that we call ‘economy’. It could be said that energy flows have a creative role, in that out of these flows emerge complex processes that range from global biogeochemical cycles to photosynthetic bacteria. In this section, we present a brief introduction to energy flow and some of its consequences. We will discuss more about nonequilibrium systems that become organized spontaneously in Chapter 19.

2.7.1 Self-organization

At the outset we must note that what is of interest to us in a thermodynamic system is not only its *state* but also the *processes* that take place in it and the way the system interacts with its exterior. The state of thermodynamic equilibrium is static, devoid of processes; in this state there is no flow of energy or matter from one point to another and no chemical change takes place. When a system is driven out of equilibrium by energy and matter flows, however, *irreversible* processes begin to emerge within the system. These processes are ‘irreversible’ in that the transformations they cause have a definite direction. Heat conduction is an example of an irreversible process: heat always flows towards a region at a lower temperature, never in the opposite direction. The concept of entropy, which will be introduced in the following chapters, makes the notion of irreversibility more precise; but even without the concept of entropy, one can see through simple examples how irreversible processes can create structure and organization in a system. One such example involving heat flow is illustrated in Figure 2.7. It consists of a fluid placed between two metal plates. The lower plate is maintained at a temperature T_h , which is higher than that of the upper plate temperature T_c . The temperature difference will cause a flow of heat through the fluid. If the difference in the temperature $\Delta T = (T_h - T_c)$ is increased, there is a point at which a well-organized pattern of convection cells emerges. The threshold value of ΔT depends on the fluid properties, such as the thermal expansion coefficient and viscosity. What is remarkable about this familiar convection pattern is that it emerges entirely out of chaotic motion associated with heat. Furthermore, the fluid’s organized convection pattern now serves a ‘function’: it increases the rate of heat flow. This is an example in which the energy flow drives a system to an organized state which in turn increases the energy flow.

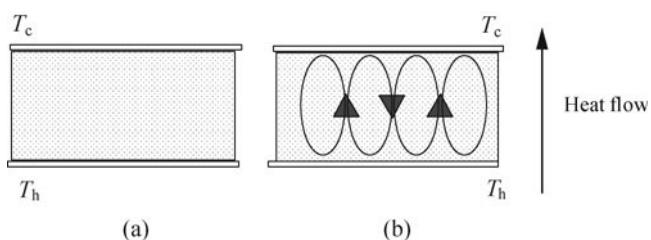


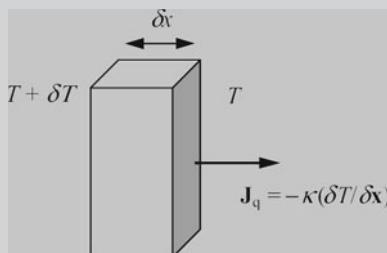
Figure 2.7 Energy flows can cause self-organized patterns to emerge. A fluid is placed between two plates and heated from below. The temperature difference $\Delta T = T_h - T_c$ between the two plates drives a heat flow. (a) When ΔT is small, the heat flow is due to conduction and the fluid is static. (b) When ΔT exceeds a critical value, organized convection patterns emerge spontaneously.

The convection pattern exists as long as there is heat flow; if the heat flow is stopped, then the system evolves to equilibrium and the pattern disappears. Such patterns in nonequilibrium systems should be distinguished from patterns that we might see in a system in equilibrium, such as layers of immiscible fluids separated by differences in density. Organized states in nonequilibrium systems are maintained by the flow of energy and matter and, as we shall see in later chapters, production of entropy.

In the formulation of modern thermodynamics, flows of matter and energy are thermodynamic flows. The laws that govern them can be formulated in thermodynamic terms, as described in later chapters. Empirical laws governing heat flow and radiative cooling have been known for centuries. Some commonly used laws are summarized in Box 2.7. These laws can be used to analyze heat flows in various systems.

Box 2.7 Laws of heat flow

Heat flow or heat current \mathbf{J}_q is defined as the amount of heat flowing per unit surface area per unit time.



Conduction

Jean Baptiste Joseph Fourier (1768–1830) proposed a general law of heat conduction in his 1807 memoir, which states that the heat current is proportional to the gradient of temperature:

$$\mathbf{J}_q = -\kappa \nabla T = -\kappa \left(\hat{\mathbf{i}} \frac{\partial T}{\partial x} + \hat{\mathbf{j}} \frac{\partial T}{\partial y} + \hat{\mathbf{k}} \frac{\partial T}{\partial z} \right)$$

in which k ($\text{W m}^{-1} \text{K}^{-1}$) is the thermal conductivity and $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ are unit vectors. The SI units of \mathbf{J}_q are W m^{-2} .

Convection

A law of cooling due to convection, attributed to Newton, states that the rate of heat loss dQ/dt of a body at temperature T surrounded by a fluid at temperature T_0 is proportional to the difference $(T - T_0)$ and the body's surface area A :

$$\frac{dQ}{dt} = -hA(T - T_0)$$

in which h ($\text{W m}^{-2} \text{K}^{-1}$) is the heat transfer coefficient. This law is a good approximation when heat loss is mainly due to convection and that due to radiation can be ignored.

Radiation

When thermal equilibrium between matter and radiation (Chapter 12) is analyzed, it is found that heat radiated by a body at temperature T is proportional to T^4 and the heat radiation absorbed from the surroundings at temperature T_0 is proportional to T_0^4 . The net radiative heat loss is equal to

$$\frac{dQ}{dt} = -\sigma e A (T^4 - T_0^4)$$

in which $\sigma = 5.67 \cdot 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is the Stefan–Boltzmann constant, A is the surface area of the body and e is the body's emissivity (the maximum $e = 1$ for a blackbody). At high temperatures, the cooling of bodies is due to convective and radiative heat losses.

2.7.2 Process Flows

An important application of the First Law is to the analysis of energy flows associated with fluids in industrial processes and engines. Energy flows in this case include the kinetic and potential energies of the fluid in addition to the thermodynamic internal energy U . The First Law applies to the total energy

$$E = U + \frac{1}{2} M v^2 + \Psi \quad (2.7.1)$$

in which M is the mass of the system and Ψ is its potential energy. In describing energy flows, it is convenient to use energy and mass densities:

Internal energy density	$u (\text{J m}^{-3})$
Mass density	$\rho (\text{kg m}^{-3})$

When the change in potential energy is insignificant, the energy flowing in and out of a system is in the form of heat, mechanical work, kinetic energy and internal energy of matter (Figure 2.8). Let us assume that matter with energy density u_i is flowing into the system under a pressure p_i and velocity v_i . Consider a displacement $dx_i = v_i dt$ of the matter flowing in through an inlet with area of cross-section A_i , in time dt (see Figure 2.8). The amounts of the various forms of energy entering the system through the inlet due to this displacement are:

Internal energy:	$u_i A_i dx_i$
Kinetic energy:	$\frac{1}{2} \rho v_i^2 A_i dx_i$
Mechanical work:	$p_i A_i dx_i$

Similar considerations apply for the energy flowing through the outlet, for which we use the subscript ‘o’ instead of ‘i’. In addition, we assume, in time dt , that there is a net heat output dQ and mechanical energy output dW that are not associated with matter flow (which are positive for a net output and negative for a net input). Taking all these into consideration, we see that the total change in energy dU in a time dt is

$$dU = -dW - dQ + u_i A_i dx_i + \frac{1}{2} \rho_i v_i^2 A_i dx_i + p_i A_i dx_i - u_o A_o dx_o - \frac{1}{2} \rho_o v_o^2 A_o dx_o - p_o A_o dx_o \quad (2.7.2)$$

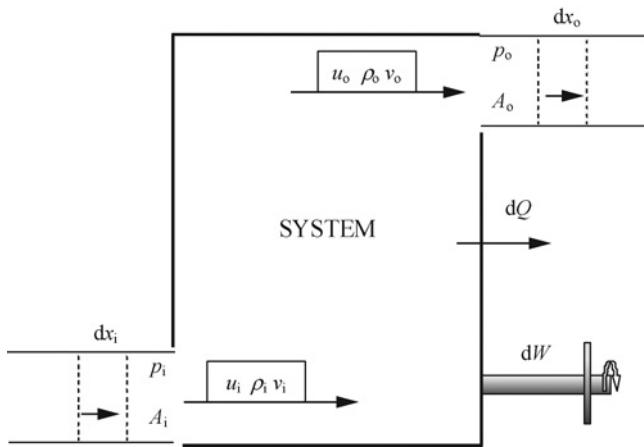


Figure 2.8 Energy flow through a system. The subscripts i and o identify the variables for the inflow and outflow respectively; p is the pressure, A is the area of cross-section, u is the energy density, ρ is the mass density and v is the flow velocity. The change in the energy of the system in a time dt is given by Equation (2.7.3), in which h is the enthalpy density.

By defining enthalpy per unit volume $h = u + p$, and by noting that $dx_i = v_i dt$ and $dx_o = v_o dt$, the above expression can be written as

$$\frac{dU}{dt} = -\frac{dW}{dt} - \frac{dQ}{dt} + \left(h_i + \frac{1}{2}\rho_i v_i^2 \right) A_i v_i - \left(h_o + \frac{1}{2}\rho_o v_o^2 \right) A_o v_o \quad (2.7.3)$$

In many situations, the system may reach a *steady state* in which all its thermodynamic quantities are constant, i.e. $dU/dt = 0$. Also, in such a state, the mass of matter flowing into the system is equal to the mass flowing out. Since the mass of matter flowing into and out of the system in time dt is $(\rho_i v_i A_i) dt$ and $(\rho_o v_o A_o) dt$ respectively, we have $(\rho_i v_i A_i) dt = (\rho_o v_o A_o) dt$ for a steady state. Hence, we can rewrite (2.7.3) as

$$\frac{dW}{dt} + \frac{dQ}{dt} = \left[\left(\frac{h_i}{\rho_i} + \frac{v_i^2}{2} \right) - \left(\frac{h_o}{\rho_o} + \frac{v_o^2}{2} \right) \right] \frac{dm}{dt} \quad (2.7.4)$$

in which $dm/dt = \rho_i v_i A_i = \rho_o v_o A_o$ is the mass flow rate. In this expression, dW/dt is the rate of work output and dQ/dt is the rate of heat output. Thus, we obtain a relation between the work and heat output and the change of enthalpy densities and the kinetic energy of the matter flowing through the system.

This general equation can be applied to various situations. In a steam turbine, for example, steam enters the system at a high pressure and temperature and leaves the system at a lower pressure and temperature, delivering its energy to the turbine, which converts it to mechanical energy. In this case the heat output dQ/dt is negligible. We then have

$$\frac{dW}{dt} = \left[\left(\frac{h_i}{\rho_i} + \frac{v_i^2}{2} \right) - \left(\frac{h_o}{\rho_o} + \frac{v_o^2}{2} \right) \right] \frac{dm}{dt} \quad (2.7.5)$$

The ratio h/ρ is the **specific enthalpy** (enthalpy per unit mass) and its values at a given pressure and temperature are tabulated in ‘steam tables’. The term dm/dt (kg s^{-1}) is the rate of mass flow through the system in the form of steam and, in many practical situations, the term $(v_i^2 - v_o^2)$ is small compared with the

other terms in Equation (2.7.5). Thus, the rate of work output in a turbine is related to the rate of steam flow and the specific enthalpy through the simple relation

$$\frac{dW}{dt} \approx \left[\left(\frac{h_i}{\rho_i} \right) - \left(\frac{h_o}{\rho_o} \right) \right] \frac{dm}{dt} \quad (2.7.6)$$

Using steam tables, the expected work output can be calculated. Note that if there are heat losses, i.e. if $dQ/dt > 0$, then the work output dW/dt is correspondingly less. Explicit examples of the application of Equation (2.7.4) are given at the end of this chapter.

2.7.3 Solar Energy Flow

In discussing energy flows, it is useful to have a quantitative idea of the energy flows on a global scale. Figure 2.9 summarizes the flows that result from the solar energy incident on the Earth. The energy from the sun traverses 150×10^6 km (93 million miles) before it reaches the Earth's atmosphere. The amount of solar energy reaching the Earth, called the 'total solar radiance', is about 1300 W m^{-2} , which amounts to a total of about $54.4 \times 10^{20} \text{ kJ year}^{-1}$. About 30% of this energy is reflected back into space by clouds and other reflecting surfaces, such as snow. A significant fraction of the solar energy entering the Earth's surface goes to drive the water cycle, the evaporation and condensation as rain (Exercise 2.20). Of the solar energy not lost due to reflection, it is estimated that only a small fraction, about $0.08 \times 10^{20} \text{ kJ year}^{-1}$, or 0.21%, goes into the biosphere through photosynthesis. The energy consumed by human economies is estimated to

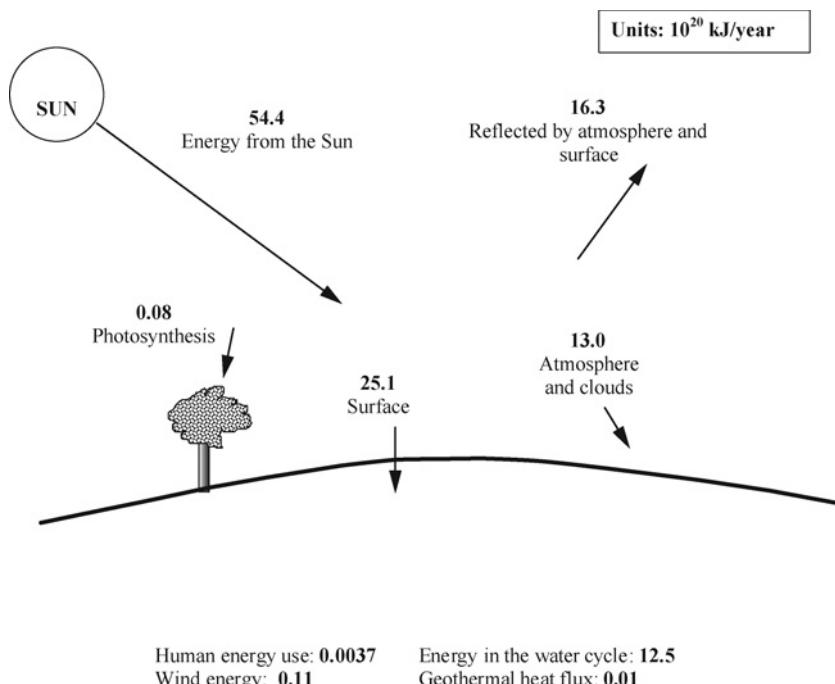


Figure 2.9 Annual solar energy flow through the Earth's atmosphere and the surface. (Numerical Data from T.G. Spiro and W.M. Stiglani, Chemistry of the Environment, second edition, 2003, Prentice Hall: Upper Saddle River, NJ.)

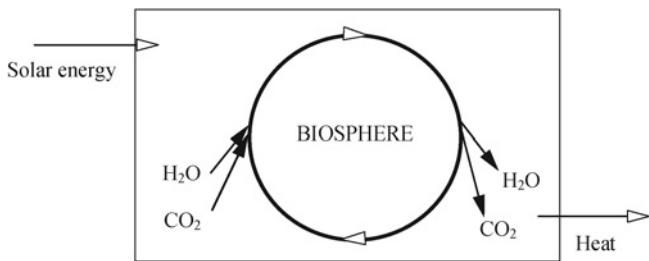


Figure 2.10 Energy flow through the biosphere.

be about 0.0037×10^{20} kJ year⁻¹, which is about 5% of the energy that flows into photosynthesis. Thus, there is ample solar energy to run human economies. The interior of the Earth also has a vast amount of geothermal energy that flows to the surface at a rate of about 0.01×10^{20} kJ year⁻¹. The solar energy entering the Earth system is ultimately radiated back into space, and the total energy contained in the crust and the atmosphere is essentially in a steady state, which is not a state of thermodynamic equilibrium. This flow of 38.1×10^{20} kJ year⁻¹ drives the winds, creates rains and drives the cycle of life.

2.7.4 Energy Flows in Biological Systems

The process of life is a consequence of energy flow. Energy enters the biosphere through photosynthesis, which results in the production of biochemical compounds, such as carbohydrates, from CO₂, H₂O and other simple compounds containing nitrogen and other elements. Photosynthesis releases O₂ into the atmosphere while removing CO₂ (Figure 2.10). The solar energy is captured in the biomolecules, which contain more energy than the compounds from which they are synthesized. The ‘high-energy’ products of photosynthesis are in turn the energy source for organisms that feed on them. Photosynthesis, the primary source of ‘food’, drives a complex food chain that sustains ‘higher organisms’ and ultimately a complex ecosystem. The energy flow in higher organisms is through the conversion of carbohydrates back to CO₂ and H₂O; this flow drives life processes: feeding, reproducing, flying, running, etc. While living cells do not exist in a steady state but go through a cycle of life and death, the ecosystems as a whole could be in a self-sustaining ‘steady state’ on a long timescale. As energy flows through the biosphere, it is converted to heat and is returned to the atmosphere. The metabolic processes in a human, for example, generate about 100 J s⁻¹ of heat. The heat generated in the biosphere is ultimately radiated back into space.

Let us look at some quantitative aspects of energy captured in photosynthesis. When a plant grows, it not only synthesizes compounds but also absorbs water. For this reason, to estimate the amount of substance produced in photosynthesis it is necessary to separate the ‘dry mass’ from the water. By measuring the energy in the dry mass generated in the presence of a known flux of radiation, the efficiency of photosynthesis in various conditions could be estimated. When the dry mass is combusted, it is converted back to its initial reactants, CO₂, H₂O and other small compounds, and the energy captured in photosynthesis is released. Combustion of carbohydrates releases about 15.6 kJ mol⁻¹, proteins about 24 kJ mol⁻¹ and fats 39 kJ mol⁻¹ [20]. Plant cells contain many other compounds that yield less energy upon combustion. On the whole, plant dry mass yields about 17.5 kJ mol⁻¹. Under optimal conditions rapidly growing plants could produce around 50 g m⁻² day⁻¹, which equals 875 kJ m⁻² day⁻¹. During this observed plant growth, the amount of solar energy that was incident on the plants averaged about 29×10^3 kJ m⁻² day⁻¹. From these figures we can estimate that plants capture solar energy with an efficiency of about $(875/29 \times 10^3) = 0.03$, a rather low value. A much larger fraction, about 0.33, of solar energy that enters the Earth’s atmosphere, goes into the water cycle (see Figure 2.8). A part of the reason for such a low efficiency of photosynthetic capture of solar energy is the low amounts of CO₂ in the atmosphere (about 0.04% by volume). Plants grow faster at higher levels of CO₂.

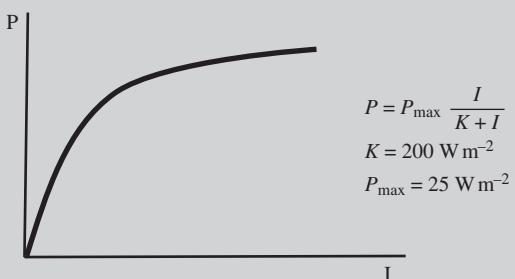
The rate of photosynthesis depends on the intensity of incident radiation, I (W m^{-2}). In a leaf exposed to radiation of intensity I , the rate of photosynthesis could be measured in terms of the energy captured P (W m^{-2}). At low intensities P increases with I but at high intensities P reaches a saturation value P_{\max} (see Box 2.8). The empirical relationship between P and I could be expressed as [20]

$$P = P_{\max} \frac{I}{K + I} \quad (2.7.7)$$

in which K is a constant and is approximately 200 W m^{-2} . A representative value of P_{\max} is about 25 W m^{-2} . It is found that P_{\max} depends on the temperature and the CO_2 concentration. On a bright sunny day $I \approx 1000 \text{ W m}^{-2}$. Using Equation (2.7.7) one can estimate the photosynthetic efficiency at various intensities.

Box 2.8 Photosynthesis

- Satellite measurements of **solar radiant flux** just outside the atmosphere give a value of 1370 W m^{-2} (area perpendicular to the flux). The maximum radiation reaching Earth's surface is about 1100 W m^{-2} . For the purposes of estimation, the maximum flux at the ground surface during a clear day $\approx 800 \text{ W m}^{-2}$.
- It is estimated that 90% of photosynthesis takes place in the oceans in algae, bacteria, diatoms and other organisms. Approximately $4.7 \times 10^{15} \text{ mol of O}_2$ is generated per year by photosynthesis. Microorganisms in the oceans and soil consume over 90% of all the oxygen consumed by life.
- The energy captured, P , by photosynthesis varies with the incident solar energy intensity, I , according to the approximate equation shown below.



- The rate of photosynthesis is considered to be primary production. It is quantified as either energy captured or new biomass formed. Gross primary production is the rate at which biomass is being synthesized. The process of respiration degrades biomass into CO_2 . Net primary production is the difference between the rate at which biomass is being synthesized and the rate at which it is being degraded into carbon dioxide; it is the rate at which biomass is accumulating. For example, sugarcane growth corresponds to about $37 \text{ g m}^{-2} \text{ day}^{-1}$.

Source: R.M. Alexander, *Energy for Animals*, 1999, Oxford University Press: New York.

The energy captured by plants moves up the food chain, sustaining the process of life at the micro level and ecosystems on the macro level. Ultimately this 'food' reacts with O_2 and turns into CO_2 and H_2O , thus completing the cycle. The cycle, however, has an awesome complexity, which is the process of life. Finally, when an organism 'dies' its complex constituents are converted to simpler molecules by bacteria.

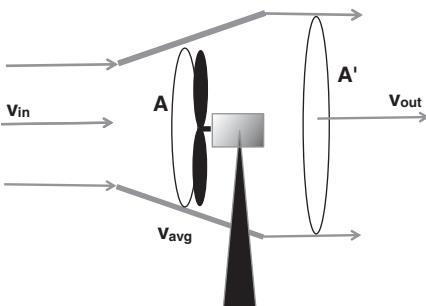


Figure 2.11 Wind flowing into a turbine at speed v_{in} transfers some of its energy to the blades of the turbine and flows out at a velocity v_{out} . The area swept by the turbine blades is A . At steady state, the wind flowing behind the turbine has a larger cross-sectional area A' and lower speed v_{out} . Energy is transferred to the turbine at an average wind speed $v_{avg} = (v_{in} + v_{out})/2$.

2.7.5 Wind Energy and the Betz Law

A part of the solar energy that the Earth receives converts to wind energy. Differences in pressure and temperature that are caused by the location-dependent heating and cooling cause the flow of wind. In the last few decades, there has been a steady increase using wind energy for generating electric power.

The amount of energy flowing into a wind turbine when the wind speed is v can be determined as follows. Consider wind flowing at a speed v_{in} into a wind turbine (Figure 2.11) whose area of cross-section is A . If the density of air is ρ , the kinetic energy carried by a unit volume wind is $\rho v^2/2$. In one second, a column of air of volume Av_{in} will be incident on the wind turbine. Hence the incident power on the turbine is

$$P_{in} = A\rho v_{in}^3/2 \quad (2.7.8)$$

Because the wind delivers some of its energy to the turbine blades, its velocity, v_{out} , behind the blades will be lower and its area of cross-section will also increase to A' , so that, at steady state, the mass of air flowing in to the turbine equals the mass flowing past it. This leads to the mass balance equation:

$$\rho Av_{in} = \rho A' v_{out} \quad (2.7.9)$$

Here we have assumed that the density of air, which depends on its pressure, does not change significantly as it flows past the turbine; v_{out} and A' depend on the design of the blades.

The kinetic energy transferred to the wind turbine per unit volume of air is

$$\rho (v_{in}^2 - v_{out}^2)/2 \quad (2.7.10)$$

Albert Betz, a German physicist, noted that there is an upper limit to the amount of power that can be extracted from wind. This can be seen as follows. Since the wind slows down from v_{in} to v_{out} as it flows past the turbine, the average speed of the wind $v_{avg} = (v_{in} + v_{out})/2$. Hence the average rate at which energy is delivered to the turbine for power generation is

$$P = A\rho (v_{in}^2 - v_{out}^2) (v_{in} + v_{out})/4 \quad (2.7.11)$$

As Equation (2.7.9) indicates, the ratio of wind speeds, v_{out}/v_{in} , depends on the design and the efficiency of the turbine blades, which capture the wind energy. Let us assume that

$$\beta = v_{out}/v_{in}$$

In terms of this parameter β , the power P can be written as

$$P = A\rho v_{\text{in}}^3(1 - \beta^2)(1 + \beta)/4 \quad (2.7.12)$$

Now we can determine the maximum value P as function of the parameter β . It is easy to see that P reaches its maximum value when $\beta = 1/3$, which is

$$P = (16/27) (1/2) A \rho v_{\text{in}}^3 \quad (2.7.13)$$

Thus we see that the maximum power a wind turbine can capture from the incident wind power is given by the factor 16/27, which is about 59%. This result is called the **Betz law**. The energy transferred to the turbine is converted to electrical energy with further losses. Currently, the overall conversion efficiency of wind power to electrical power is about 40%. Wind turbines in the diameter range 20–120 m are available commercially.

Appendix 2.1 Mathematica Codes

CODE A: MATHEMATIC CODE FOR EVALUATING WORK DONE IN AN ISOTHERMAL EXPANSION OF A GAS

While evaluating integrals, *Mathematica* assumes that the parameters in the integral and limits could be complex numbers. Therefore the output may look complex, as shown below. This can be avoided by using the **Assumptions** option as shown in the commands below

```
Integrate[1/x,{x,x1,x2}]
ConditionalExpression[-Log[x1]+Log[x2],((Im[x1]>=Im[x2]&&Im[x2]
Re[x1]<=Im[x1] Re[x2])|| (Im[x2]>=Im[x1]
Re[x2]&&Im[x1]<=Im[x2]))&&((Re[x1/(-x1+x2)]>=0&&x1^2!=x1 x2)||x1/(x1-x2)notin
Reals||Re[x1/(x1-x2)]>=1)]
```

```
Integrate[1/x,{x,x1,x2},Assumptions->{x1>0,x2>0}]
ConditionalExpression[Log[x2/x1],x1<x2]
```

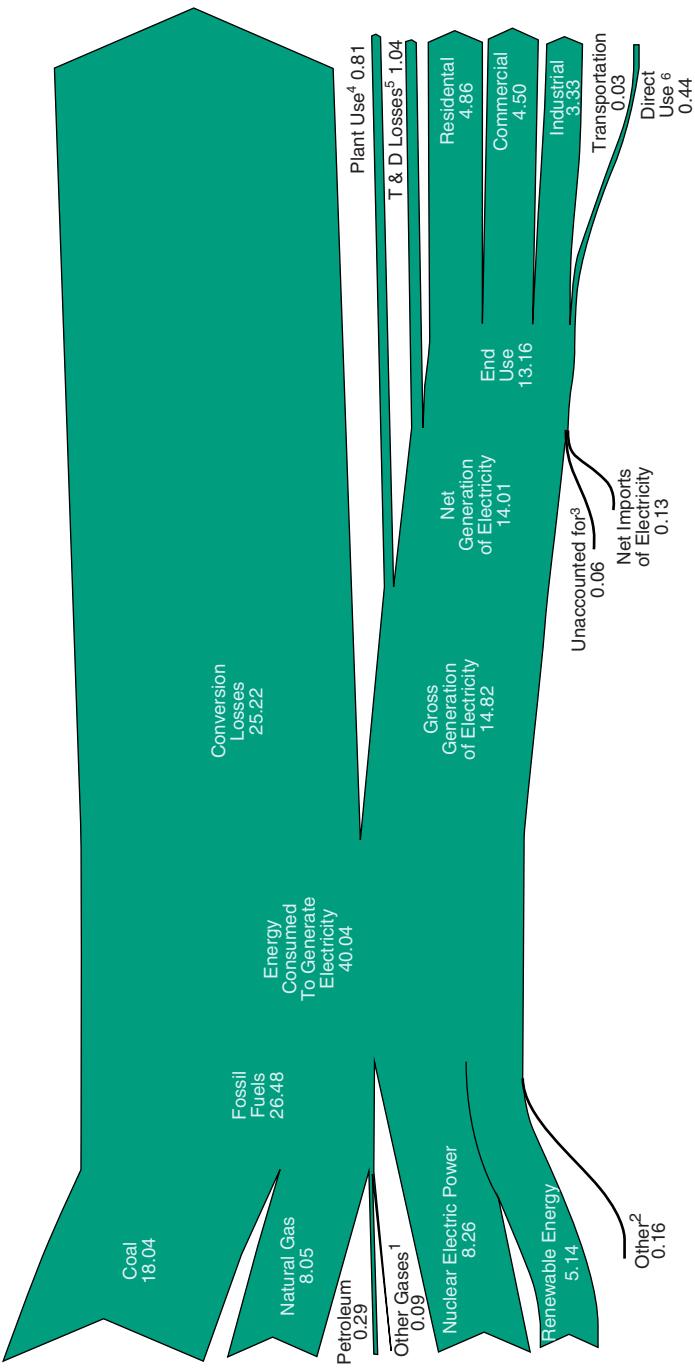
Using the **Assumptions** command we can now calculate the work done in an isothermal expansion of a van der Waals gas.

```
Clear[p,V,T,a,b]
p[V_,T_]:= (R*T/(V-b)) - (a/V^2);
Integrate[p[V,T],{V,v1,v2}, Assumptions->{v1>0,v2>0,b>0,a>0}]
ConditionalExpression[
a(-(1/v1)+1/v2)+RT(-Log[-b+v1]+Log[-b+v2]),
v1<v2&&(b<=v1||b>=v2)]
```

Appendix 2.2 Energy Flow in the USA for the Year 2013

Energy flows are essential for economies and ecosystems. The figure below shows the estimated electricity and energy flow from various sources in the United States for the year 2011 in units of quadrillion Btu/year or 10^{15} Btu/year. 1 Btu = 1.055 kJ. The estimated total energy flow for 2013 is 97.4 quads/year. For the years 2008–2012, the total energy flow was in the range 99–94 quads/year. Flow charts such as this may be found at the website of Lawrence Livermore National Labs: <https://flowcharts.llnl.gov>.

US Electricity Flow, 2011



¹ Blast furnace gas, propane gas, and other manufactured and waste gases derived from fossil fuels.

² Batteries, chemicals, hydrogen, pitch, purchased steam, sulfur, miscellaneous technologies, and non-renewable waste (municipal solid waste from non-biogenic sources, and tire-derived fuels).

³ Data collection frame differences and nonsampling error. Derived for the diagram by subtracting the "T & D Losses" estimated from "T & D Losses and Unaccounted for" derived from Table 8.1.

⁴ Electric energy used in the operation of power plants.

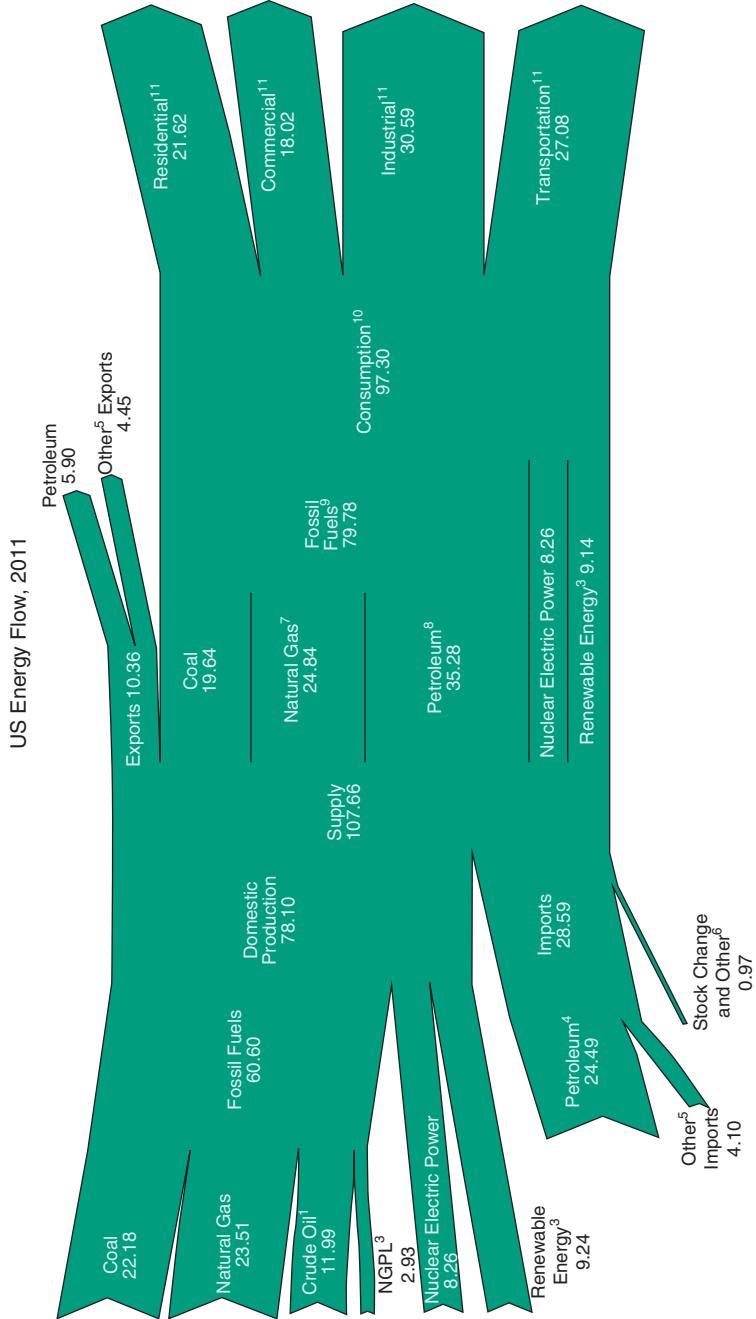
⁵ Transmission and distribution losses (electricity losses that occur between the point of delivery and the point of end-use).

generation and delivery to the customer) are estimated as 7 percent of gross generation.

⁶ Use of electricity that is 1) self-generated, 2) produced by either the same entity that consumes the power or an affiliate, and 3) used in direct support of a service or industrial process located within the same facility or group of facilities that house the generating equipment. Direct use is exclusive of station use.

Notes: • See Note, "Electrical System Energy Losses," at the end of Section 2. • Net generation of electricity includes pumped storage facilities producing net energy used for pumping. • Values are derived from source data prior to rounding for publication. • Totals may not equal sum of components due to independent rounding.

Sources: Tables 8.1, 8.4.a, 8.9, A6 (column 7), and U.S. Energy Information Administration, Form EIA-923, "Power Plant Operations Report."



¹ Includes lease condensate.

² Natural gas plant liquids.

³ Conventional hydroelectric power, biomass, geothermal, solar/photovoltaic, and wind.

⁴ Crude oil and petroleum products. ⁵ Includes imports into the Strategic Petroleum Reserve.

⁵ Natural gas, coal, coke, liquids, and unaccounted for.

⁶ Adjustments, losses, and unaccounted for.

⁷ Natural gas only; excludes supplemental gaseous fuels.

⁸ Petroleum products, including natural gas plant liquids, and crude oil burned as fuel.

⁹ Includes 0.01 quadrillion Btu of coal coke net imports.

¹⁰ Includes 0.13 quadrillion Btu of electricity net imports.

¹¹ Total energy consumption, which is the sum of primary energy consumption, electricity retail sales, and electrical system energy losses. Losses are allocated to the end-use sectors in proportion to each sector's share of total electricity retail sales. See Note, "Electrical Systems Energy Losses," at end of Section 2.

Notes: • Data are preliminary. • Values are derived from source data prior to rounding for publication. • Totals may not equal sum of components due to independent rounding.

Sources: Tables 1.1, 1.2, 1.3, 1.4, and 2.1a.

Data Source: Lawrence Livermore National Laboratories and the Department of Energy.

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Examples

Example 2.1 A bullet of mass 20.0 g moving at a speed of 350.0 m s⁻¹ is lodged into a block of wood. How many calories of heat are generated in this process?

Solution In this process, the kinetic energy (KE) of the bullet is converted to heat.

$$\begin{aligned} \text{KE}_{\text{bullet}} &= mv^2/2 = (1/2)20.0 \times 10^{-3} \text{ kg} \times (350 \text{ m s}^{-1})^2 = 1225 \text{ J} \\ 1225 \text{ J} &= 1225 \text{ J}/4.184 \text{ J cal}^{-1} = 292.6 \text{ cal} \end{aligned}$$

Example 2.2 Calculate the energy ΔU required to increase the temperature of 2.50 mol of an ideal monatomic gas from 15.0 °C to 65.0 °C.

Solution Since the specific heat $C_V = (\partial U/\partial T)_V$, we see that

$$\Delta U = \int_{T_i}^{T_f} C_V dT = C_V(T_f - T_i)$$

Since C_V for a monatomic ideal gas is $(3/2)R$:

$$U = (3/2)(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(2.5 \text{ mol})(65.0 - 15.0) \text{ K} = 1559 \text{ J}$$

Example 2.3 The velocity of sound in CH₄ at 41.0 °C was found to be 466.0 m s⁻¹. Calculate the value of γ , the ratio of specific heats, at this temperature.

Solution Equation (2.3.17) gives the relation between γ and the velocity of sound:

$$\gamma = \frac{MC_{\text{sound}}^2}{RT} = \frac{16.04 \times 10^{-3} \text{ kg} \times (466 \text{ m s}^{-1})^2}{8.314 \times 314.15 \text{ K}} = 1.33$$

Example 2.4 1 mol of N₂(g) at 25.0 °C and a pressure of 1.0 bar undergoes an isothermal expansion to a pressure of 0.132 bar. Calculate the work done.

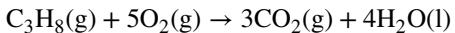
Solution For an isothermal expansion:

$$\text{Work} = -NRT \ln \left(\frac{V_f}{V_i} \right)$$

For an ideal gas, at constant T , $p_i V_i = p_f V_f$. Hence:

$$\begin{aligned} \text{Work} &= -NRT \ln \left(\frac{V_f}{V_i} \right) \\ &= -NRT \ln \left(\frac{p_i}{p_f} \right) = -1.0(8.314 \text{ J K}^{-1}) \ln \left(\frac{1.0 \text{ bar}}{0.132 \text{ bar}} \right) = -5.03 \text{ kJ} \end{aligned}$$

Example 2.5 Calculate the heat of combustion of propane in the reaction at 25 °C:



Solution From the table of heats of formation at 298.15 K we obtain

$$\begin{aligned} \Delta H_r^0 &= -\Delta H_f^0[\text{C}_3\text{H}_8] - 5\Delta H_f^0[\text{O}_2] + 3\Delta H_f^0[\text{CO}_2] + 4\Delta H_f^0[\text{H}_2\text{O}] \\ &= -(-103.85 \text{ kJ}) - (0) + 3(-393.51 \text{ kJ}) + 4(-285.83 \text{ kJ}) = -2220 \text{ kJ} \end{aligned}$$

Example 2.6 For the reaction N₂(g) + 3H₂(g) → 2NH₃(g), at $T = 298.15$ K the standard enthalpy of reaction is $-46.11 \text{ kJ mol}^{-1}$. At constant volume, if 1.0 mol of N₂(g) reacts with 3.0 mol of H₂(g), what is the energy released?

Solution The standard enthalpy of reaction is the heat released at constant pressure of 1.0 bar. At constant volume, since no mechanical work is done, the heat released equals the change in internal energy ΔU . From Equation (2.4.9) we see that

$$\Delta H_r = \Delta U_r + \Delta N_r RT$$

In the above reaction, $\Delta N_r = -2$. Hence:

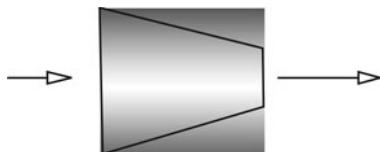
$$\Delta U_r = \Delta H_r - (-2)RT = -46.11 \text{ kJ} + 2(8.314 \text{ J K}^{-1})298.15 = -41.15 \text{ kJ}$$

Example 2.7 Apply the energy flow equation to a thermal power station for which the energy flow is as shown in the figure below. The power station takes in heat to run an electrical power generator.



Solution A thermal power plant may be considered as a system with the following properties: heat flows into the system, a part of it is converted to mechanical energy that runs an electrical power generator, and the unused heat is expelled. There is no flow of matter. Applying Equation (2.7.4) to this system, we see that $dm/dt = 0$, and we are left with $dW/dt = -dQ/dt$. Since dQ/dt is the *net* outflow of heat, a negative value of dQ/dt means that the inflow of heat is larger than the outflow, i.e. part of the heat flowing into the system is converted to mechanical energy that runs the power generator. What fraction of the heat energy flowing into the system is converted to mechanical energy depends on the efficiency of the power plant. In Chapter 3 we will discuss Sadi Carnot's discovery that conversion of heat to mechanical energy has limitations; it is impossible to convert 100% of the heat flowing into the system into mechanical energy.

Example 2.8 N_2 is flowing into a nozzle with a velocity $v_i = 35.0 \text{ m s}^{-1}$ at $T = 300.0 \text{ K}$. The temperature of the gas flowing out of the nozzle is 280.0 K . Calculate the velocity of the gas flowing out of the nozzle. (Assume the ideal gas law for the flowing gas.)



Solution For flow through a nozzle, there is no net output of heat or work. Applying Equation (2.7.4) to this system, we see that $dW/dt = 0$ and $dQ/dt = 0$. Hence:

$$\frac{h_i}{\rho_i} + \frac{v_i^2}{2} = \frac{h_o}{\rho_o} + \frac{v_o^2}{2}$$

in which the subscripts ‘i’ and ‘o’ denote the quantities for inflow and outflow respectively. Using the given values of T for the flows, the specific enthalpies h/ρ of the gas flowing in and out of the nozzle can be calculated as follows. For an ideal gas, enthalpy $H = U + pV = cNRT + NRT = (c + 1)RTN$ ($c = 5/2$ for a diatomic gas such as N_2). If the molar mass of the gas is M , then

$$h = \frac{H}{V} = \frac{(c + 1)RT}{M} \frac{NM}{V} = \frac{(c + 1)RT}{M} \rho$$

i.e.

$$\frac{h}{\rho} = \frac{(c + 1)RT}{M}$$

Now we can write the specific enthalpies in terms of temperature in the above expression and obtain

$$\frac{v_o^2}{2} = \frac{v_i^2}{2} + \frac{(c + 1)R}{M}(T_i - T_o)$$

For a diatomic gas N_2 , $c = 5/2$. We have $v_i = 35.0 \text{ m s}^{-1}$, $M = 28 \times 10^{-3} \text{ kg mol}^{-1}$, $T_i = 300.0 \text{ K}$ and $T_0 = 280.0 \text{ K}$. Using these values, v_o can be calculated: $v_o = 206 \text{ m s}^{-1}$.

Example 2.9 A steam turbine operates under the following conditions: steam flows into a turbine through an inlet pipe of radius 2.50 cm, at a velocity 80.0 m s^{-1} , at $p = 6.0 \text{ MPa}$ and $T = 450.0 \text{ }^\circ\text{C}$. The spent steam flows out at $p = 0.08 \text{ MPa}$ and $T = 93.0 \text{ }^\circ\text{C}$ through an outlet pipe of radius 15.0 cm. Assuming steady-state conditions, calculate the power output using the following data from steam tables

At $p = 6.0 \text{ MPa}$, $T = 450.0 \text{ }^\circ\text{C}$, the specific volume $1/\rho = 0.052 \text{ m}^3 \text{ kg}^{-1}$ and $h/\rho = 3301.4 \text{ kJ kg}^{-1}$.

At $p = 0.08 \text{ MPa}$, $T = 93.0 \text{ }^\circ\text{C}$, the specific volume $1/\rho = 2.087 \text{ m}^3 \text{ kg}^{-1}$ and $h/\rho = 2665.4 \text{ kJ kg}^{-1}$.

Solution At steady state, the mass flowing in must equal the mass flowing out (mass balance). Hence, $A_i v_i \rho_i = A_o v_o \rho_o$. Using this equation and the given data, we can calculate the velocity of the steam in the outlet:

$$v_o = \frac{\pi(0.025 \text{ m})^2(19.2 \text{ kg m}^{-3})}{\pi(0.15 \text{ m})^2(0.479 \text{ kg m}^{-3})} 80.0 \text{ m s}^{-1} = 89.0 \text{ m s}^{-1}$$

The rate of mass flow is

$$\frac{dm}{dt} = A_i v_i \rho_i = \pi(0.025 \text{ m})^2(19.2 \text{ kg m}^{-3}) 80 \text{ m s}^{-1} = 3.01 \text{ kg s}^{-1}$$

Now we can apply Equation (2.7.4) to calculate the power output. In this case, mechanical energy is the output and we may assume negligible heat losses, i.e. $dQ/dt = 0$. We then have

$$\frac{dW}{dt} = \left[\left(\frac{h_i}{\rho_i} + \frac{v_i^2}{2} \right) - \left(\frac{h_o}{\rho_o} + \frac{v_o^2}{2} \right) \right] \frac{dm}{dt}$$

Using the steam table data, we see that $h_i/\rho_i = 3301.4 \text{ kJ kg}^{-1}$ and $h_o/\rho_o = 2665.4 \text{ kJ kg}^{-1}$. Thus, the power output is

$$\frac{dW}{dt} = [(3301.4 - 2665.4)10^3 + 0.5(80.0^2 - 89.0^2)]3.01 = 1915 \text{ kJ s}^{-1} = 1.9 \text{ MW}$$

Exercises

- 2.1 For a conservative force $F = -\partial V(x)/\partial x$, in which $V(x)$ is the potential, using Newton's laws of motion, show that the sum of kinetic energy and potential energy is a constant.
- 2.2 How many joules of heat are generated by the brakes of a 1000 kg car when it is brought to rest from a speed of 50 km h^{-1} ? If we use this amount of heat to heat 1.0 L of water from an initial temperature of $30 \text{ }^\circ\text{C}$, estimate the final temperature assuming that the heat capacity of water is about 1 cal mL^{-1} ($1 \text{ cal} = 4.184 \text{ J}$).
- 2.3 The manufacturer of a heater coil specifies that it is a 500 W device.
 - (a) At a voltage of 110 V, what is the current through the coil?
 - (b) Given that the latent heat of fusion of ice is about 6.0 kJ mol^{-1} , how long will it take for this heater to melt 1.0 kg of ice at $0 \text{ }^\circ\text{C}$.

2.4 Use the relation $dW = -p dV$ to show that:

- (a) The work done in an *isothermal* expansion of N moles of an ideal gas from initial volume V_i to the final volume V_f is Work = $-NRT \ln(V_f/V_i)$.
- (b) For 1 mol of an ideal gas, calculate the work done in an isothermal expansion of 1 mol from $V_i = 10.0\text{ L}$ to $V_f = 20.0\text{ L}$ at temperature $T = 350\text{ K}$.
- (c) Repeat the calculation of part (a) using the van der Waals equation in place of the ideal gas equation and show that

$$\text{Work} = -NRT \ln\left(\frac{V_f - Nb}{V_i - Nb}\right) + aN^2 \left(\frac{1}{V_i} - \frac{1}{V_f}\right)$$

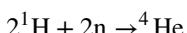
- 2.5** Given that for the gas Ar the heat capacity $C_V = (3R/2) = 12.47\text{ J K}^{-1}\text{ mol}^{-1}$, calculate the velocity of sound in Ar at $T = 298\text{ K}$ using the ideal-gas relation between C_p and C_V . Do the same for N₂, for which $C_V = 20.74\text{ J K}^{-1}\text{ mol}^{-1}$.
- 2.6** Calculate the sound velocities of He, N₂ and CO₂ using Equation (2.3.17) and the values of γ in Table 2.2 and compare them with the experimentally measured velocities shown in the same table.
- 2.7** The human ear can detect an energy intensity of about $2 \times 10^{-12}\text{ W m}^{-2}$. Consider a light source whose output is 100 W. At what distance is its intensity equal to $2 \times 10^{-12}\text{ W m}^{-2}$?
- 2.8** A **monatomic** ideal gas is initially at $T = 300\text{ K}$, $V = 2.0\text{ L}$ and $p = 1.0\text{ bar}$. If it is expanded adiabatically to $V = 4.0\text{ L}$, what will its final T be?
- 2.9** We have seen (Equation (2.3.5)) that, for any system,

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p$$

For the van der Waals gas the energy $U_{\text{vw}} = U_{\text{ideal}} - a(N/V)^2V$, in which $U_{\text{ideal}} = C_V NT + U_0$ (Equation (2.2.15)). Use these two expressions and the van der Waals equation to obtain an explicit expression for the difference between C_p and C_V for a van der Waals gas.

- 2.10** For nitrogen at $p = 1\text{ atm}$ and $T = 298\text{ K}$, calculate the change in temperature when it undergoes an adiabatic compression to a pressure of 1.5 atm; $\gamma = 1.404$ for nitrogen.
- 2.11** Using Equation (2.4.11) and Table 2.3, calculate the change in enthalpy of 1.0 mol of CO₂(g) when it is heated from 350.0 K to 450.0 K at $p = 1\text{ bar}$.
- 2.12** Using the Standard Thermodynamic Properties table at the back of the book, which contains heats of formation of compounds at $T = 298.15\text{ K}$, calculate the standard heats of reaction for the following reactions:
- (a) H₂(g) + F₂(g) → 2HF(g)
 - (b) C₇H₁₆(l) + 11O₂(g) → 7CO₂(g) + 8H₂O(l)
 - (c) 2NH₃(g) + 6NO(g) → 3H₂O₂(l) + 4N₂(g)
- 2.13** Gasoline used as motor fuel consists of a mixture of the hydrocarbons heptane (C₇H₁₆), octane (C₈H₁₈) and nonane (C₉H₂₀). Using the bond energies in Table 2.4, estimate the enthalpy of combustion of 1 g of each of these fluids. (In a combustion reaction, an organic compound reacts with O₂(g) to produce CO₂(g) and H₂O(g).)

- 2.14** Calculate the amount of energy released in the combustion of 1 g of sucrose and compare it with the mechanical energy needed to lift 100 kg through 1 m. (Combustion of sucrose: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + 12\text{O}_2 \rightarrow 11\text{H}_2\text{O} + 12\text{CO}_2$.)
- 2.15** Consider the reaction $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$. Assume that initially there are 3.0 mol CH_4 and 2.0 mol O_2 and that the extent of reaction $\xi = 0$. When the extent of reaction $\xi = 0.25$ mol, what are the amounts of the reactants and the products? How much heat is released at this point? What is the value of ξ when all the O_2 has reacted?
- 2.16** The sun radiates energy approximately at a rate of $3.9 \times 10^{26} \text{ J s}^{-1}$. What will be the change in its mass in 1 million years if it radiates at this rate?
- 2.17** Calculate the energy released in the reaction



given the following masses: mass of $^1\text{H} = 1.0078 \text{ amu}$, mass of $\text{n} = 1.0087 \text{ amu}$, mass of $^4\text{He} = 4.0026 \text{ amu}$ ($1 \text{ amu} = 1.6605 \times 10^{-27} \text{ kg}$).

- 2.18** O_2 is flowing into a nozzle with a velocity $v_i = 50.0 \text{ m s}^{-1}$ at $T = 300.0 \text{ K}$. The temperature of the gas flowing out of the nozzle is 270.0 K. (a) Assume the ideal gas law for the flowing gas and calculate the velocity of the gas flowing out of the nozzle. (b) If the inlet diameter is 5.0 cm, what is the outlet diameter?
- 2.19** A steam turbine has the following specifications: inlet diameter 5.0 cm; steam inflow is at $p = 4.0 \text{ MPa}$, at $T = 450.0 \text{ }^\circ\text{C}$ at a velocity of $v_i = 150 \text{ m s}^{-1}$. The outlet pipe has a diameter of 25.0 cm and the steam flows out at $p = 0.08 \text{ MPa}$, $T = 93.0 \text{ }^\circ\text{C}$. (a) Assuming steady-state conditions, calculate the output power using the data given below from steam tables. (b) Show that the change in kinetic energy between the inflow and the outflow is negligible compared with the change in the specific enthalpy.

Data from steam tables:

At $p = 4.0 \text{ MPa}$, $T = 450.0 \text{ }^\circ\text{C}$, the specific volume $1/\rho = 0.080 \text{ m}^3 \text{ kg}^{-1}$ and $h/\rho = 3330.1 \text{ kJ kg}^{-1}$. At $p = 0.08 \text{ MPa}$, $T = 93.0 \text{ }^\circ\text{C}$, the specific volume $1/\rho = 2.087 \text{ m}^3 \text{ kg}^{-1}$ and $h/\rho = 2665.4 \text{ kJ kg}^{-1}$.

- 2.20** The amount of solar energy driving the water cycle is approximately $12.5 \times 10^{20} \text{ kJ year}^{-1}$. Estimate the amount of water, in moles and liters, evaporated per day in the water cycle.
- 2.21** (a) Find out how much solar energy reaches the surface of the Earth per square meter per second. (This is called the ‘solar constant’. Maps of average solar energy per day per m^2 can be found at <http://www.nrel.gov/gis/solar.html>.)
 (b) The present cost of electricity in the United States is in the range $\$0.12\text{--}0.18 \text{ kW h}^{-1}$ ($1 \text{ kW hour} = 10^3 \times 3600 \text{ J}$). Assume that the efficiency of commercial solar cells is only about 10%, that they can last 30 years and that they can produce power for 5 h day^{-1} on average. How much should 1 m^2 of solar cells cost so that the total energy it can produce amounts to about $\$0.15 \text{ kW h}^{-1}$. (Make reasonable estimates of quantities not specified.)
- 2.22** Consider a region in which the average wind speed is 9 km h^{-1} . Assume wind turbines whose diameter is 20.0 m, capable of generating electric power with an efficiency of 40%. How many wind turbines are needed in a wind farm that can produce 1.0 MW of average power? (Air density = 1.2 kg/m^3 .) Assume that these turbines are arranged in a square array, with a turbine-to-turbine distance of 5 diameters. Calculate the amount of power that can be obtained per m^2 in such a wind farm.

- 2.23** Show that the power extracted by a wind turbine given by Equation (2.7.11) reaches its maximum when $b = 1/3$.
- 2.24** Using the energy flow charts in Appendix 2.2 calculate the per capita (per person) consumption of energy in kW h and the average flow rate in kW in the United States.
- 2.25**
- (a) Calculate the residential **electrical energy** (kW h) per person per day consumed in the United States using the electricity flow chart in Appendix 2.2. If the cost of electricity is \$0.12 kW h⁻¹, what is the yearly cost of electricity per person.
 - (b) The average solar power in a city in the United States is 200 W m⁻² (this is a 24-hour, 365-day average in Miami). Assume solar panels with 12% efficiency. How many m² of solar panels are needed per person in this city? If the cost of installing and maintaining solar panels is approximately⁴ \$700/m², what is the cost of the solar panels per person. Assume that, once installed, a solar panel will produce power for a period of 20 years. What is the cost per year?

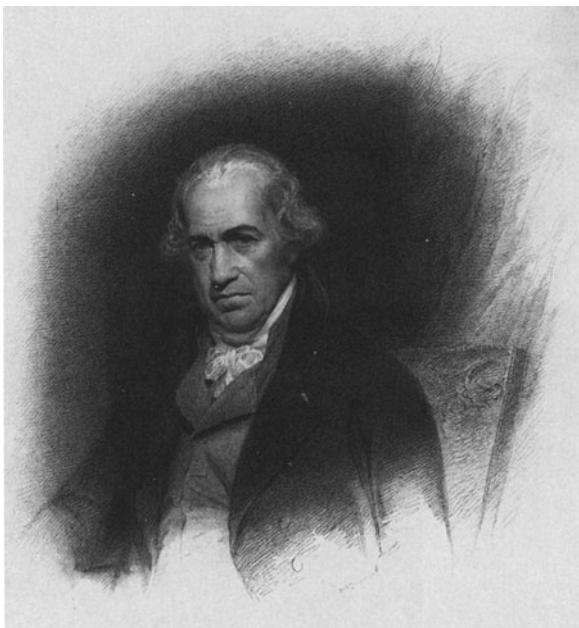
⁴Using a solar calculator: <http://www.findsolar.com/index.php?page=rightforme> gives 14 m² cost about \$10K.

3

The Second Law of Thermodynamics and the Arrow of Time

3.1 The Birth of the Second Law

James Watt (1736–1819), the most famous of Joseph Black’s pupils, obtained a patent for his modifications of Thomas Newcomen’s steam engine in the year 1769. Soon, this invention brought unimagined power and speed to everything: mining of coal, transportation, agriculture and industry. This revolutionary generation of motion from heat that began in the British Isles quickly crossed the English Channel and spread throughout Europe.



James Watt (1736–1819).

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Nicolas Léonard Sadi Carnot (1796–1832), a brilliant French military engineer, lived in this rapidly industrializing Europe. ‘Everyone knows,’ he wrote in his memoirs, ‘that heat can produce motion. That it possesses vast motive-power no one can doubt, in these days when the steam-engine is everywhere so well known’ [1, p. 3]. The name Carnot is well known in France. Sadi Carnot’s father, Lazare Carnot (1753–1823), held many high positions during and after the French Revolution and was known for his contributions to mechanics and mathematics. Lazare Carnot had a strong influence on his son Sadi. Both had their scientific roots in engineering, and both had a deep interest in general principles in the tradition of the French Encyclopedists. It was his interest in general principles that led Sadi Carnot to his abstract analysis of heat engines. Carnot pondered over the principles that governed the working of the steam engine and identified the *flow of heat* as the fundamental process required for the generation of ‘motive power’ – ‘work’ in today’s terminology. He analyzed the fundamental processes that underlie **heat engines**, engines that performed mechanical work through the flow of heat, and realized that there was a fundamental limit to the amount of work generated from the flow of a given amount of heat. Carnot’s great insight was that this limit was *independent* of the machine and the manner in which work was obtained: it depended only on the temperatures that caused the flow of heat. As explained in the following sections, further development of this principle resulted in the formulation of the Second Law of thermodynamics.



Sadi Carnot (1796–1832).

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Carnot described his general analysis of heat engines in his only scientific publication, *Réflexions sur la Puissance Motrice du Feu, et sur les Machines Propres à Développer cette Puissance* (*Reflections on the*

Motive Force of Fire and on the Machines Fitted to Develop that Power) [1]. Six hundred copies of this work were published in 1824, at Carnot's own expense. At that time, Carnot was a well-known name in the French scientific community due to the fame of Sadi's father, Lazare Carnot. Still, Sadi Carnot's book did not attract much attention at the time of its publication. Eight years after the publication of his *Reflexions*, Sadi Carnot died of cholera. A year later, Émile Clapeyron (1799–1864) was to come across Carnot's book and realize its fundamental importance and make it known to the scientific community.

Carnot's analysis proceeded as follows. First, Carnot observed, 'Wherever there exists a difference of temperature, motive force can be produced' [1, p. 9]. Every heat engine that produced work from the flow of heat operated between two heat reservoirs of unequal temperatures. In the processes of transferring heat from a hot to a cold reservoir, the engine performed mechanical work (see Figure 3.1). Carnot then specified the following condition for the production of maximum work [1, p. 13]:

The necessary condition of the maximum (work) is that in the bodies employed to realize the motive power of heat there should not occur any change of temperature which may not be due to a change of volume. Reciprocally, every time that this condition is fulfilled the maximum will be attained. This principle should never be lost sight of in the construction of a heat engine; it is its fundamental basis. If it cannot be strictly observed, it should at least be departed from as little as possible.

Thus, for maximum work generation, all changes in volume – such as the expansion of a gas (steam) that pushes a piston – should occur with minimal temperature gradients so that changes in temperature are almost all due to volume expansion and not due to the flow of heat caused by temperature gradients. This is achieved in heat engines that absorb and discard heat during very slow changes in volume, keeping their internal temperature as uniform as possible.

Furthermore, in the limit of infinitely slow transfer of heat during changes of volume, with an infinitesimal temperature difference between the source of heat (the 'heat reservoir') and the engine, the operation of such an engine is a **reversible process**, which means that the series of states the engine goes through can be retraced in the exact opposite order. A reversible engine can perform mechanical work W by transferring heat from a hot to a cold reservoir or it can do the exact reverse by transferring the *same* amount of heat from a cold reservoir to a hot reservoir by using the *same* amount of work W .

The next idea Carnot introduced is that of a **cycle**: during its operation, the heat engine went through a cycle of states so that, after producing work from the flow of heat, it returned to its initial state, ready to go through the cycle once again. A modern version of Carnot's reversible cycle will be discussed later in this section.

Carnot argued that the reversible cyclic heat engine must produce the maximum work ('motive force'), but he did so using the caloric theory of heat, according to which heat was an indestructible massless substance. If any engine could produce a greater amount of work than that produced by a reversible cyclic heat engine, then it was possible to produce work endlessly by the following means. Begin by moving heat from the hot reservoir to a cold reservoir using the more efficient engine. Then move the same amount of heat back to the hot reservoir using the reversible engine. Because the forward process does more work than is needed to perform the reverse process, there is a net gain in work. In this cycle of operations, a certain amount of heat was simply moved from the hot to the cold reservoir and back to the hot reservoir, with a net gain of work. By repeating this cycle, an unlimited amount of work can be obtained simply by moving a certain amount of heat back and forth between a hot and a cold reservoir. This, Carnot asserted, was impossible:

This would be not only perpetual motion, but an unlimited creation of motive power without consumption either of caloric or of any other agent whatever. Such a creation is entirely contrary to ideas now accepted, to laws of mechanics and of sound physics. It is inadmissible [1, p. 12].

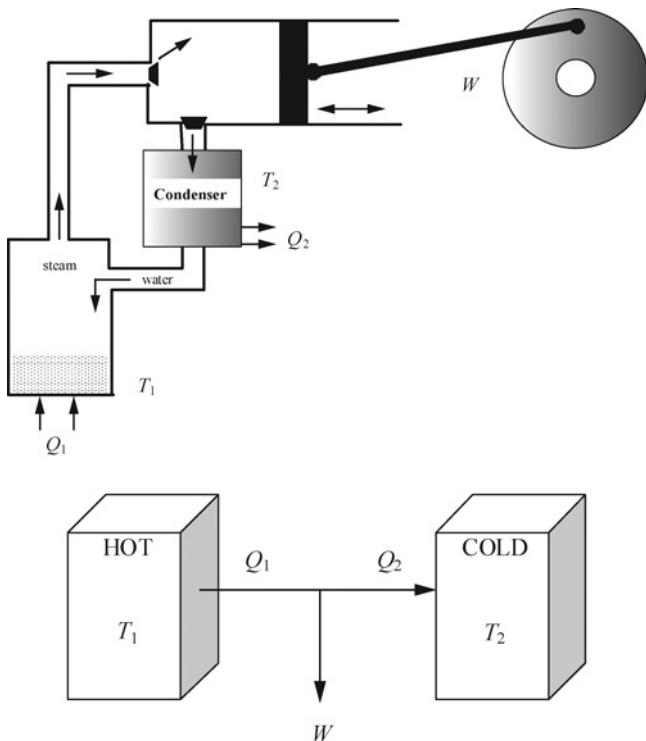


Figure 3.1 The upper figure shows a schematic of a steam engine. The lower figure shows the essential process that governs heat engines, engines that convert heat to work. It illustrates the fundamental observation made by Sadi Carnot: ‘Wherever there exists a difference of temperature, motive force can be produced’ [1, p. 9]. The heat engine absorbs heat Q_1 from a hot reservoir (heat source), converts part of it to work W and discards heat Q_2 to a cold reservoir (heat sink). The efficiency η is given by $W = \eta Q_1$ (according to the caloric theory of heat that Carnot used, $Q_1 = Q_2$, but an analysis consistent with the First Law gives $W = Q_1 - Q_2$).

Hence, *reversible cyclic engines must produce the maximum amount of work*. A corollary of this conclusion is that *all reversible cyclic engines must produce the same amount of work regardless of their construction*. Furthermore, and most importantly, since all reversible engines produce the same amount of work from a given amount of heat, the amount of work generated by a reversible heat engine is independent of the material properties of the engine: it can depend only on the temperatures of the hot and cold reservoirs. This brings us to the most important of Sadi Carnot’s conclusions [1, p. 20]:

The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of caloric.

Carnot did not derive a mathematical expression for the maximum efficiency attained by a reversible heat engine in terms of the temperatures between which it operated. This was done later by others who realized the importance of his conclusion. Carnot did, however, find a way of calculating the maximum work that can be generated. For example, he concluded that ‘1000 units of heat passing from a body maintained at the

temperature of 1 degree to another body maintained at zero would produce, in acting upon the air, 1.395 units of motive power' [1, p. 42].

Though Sadi Carnot used the caloric theory of heat to reach his conclusions, his later scientific notes reveal his realization that the caloric theory was not supported by experiments. In fact, Carnot understood that heat is converted to mechanical work and even estimated the conversion factor to be approximately 3.7 J cal^{-1} (the more accurate current value being 4.18 J cal^{-1}) [1–3]. Unfortunately, Sadi Carnot's brother, Hippolyte Carnot, who was in possession of Sadi's scientific notes after his death in 1832, did not make them known to the scientific community until 1878 [3]. That was the year in which Joule published his last paper. By then, the equivalence between heat and work and the law of conservation of energy were well known through the work of Joule, Helmholtz, von Mayer and others (1878 was also the year in which Gibbs published his famous work *On the Equilibrium of Heterogeneous Substances*).

Sadi Carnot's brilliant insight went unnoticed until Émile Clapeyron (1799–1864) came across Carnot's book in 1833. Realizing its importance, he reproduced the main ideas in an article that was published in the *Journal de l'Ecole Polytechnique* in 1834. Clapeyron represented Carnot's example of a reversible engine in terms of a *p*-*V* diagram (which is used today) and described it with mathematical detail. Clapeyron's article was later read by Lord Kelvin and others who realized the fundamental nature of Carnot's conclusions and investigated its consequences. These developments led to the formulation of the Second Law of thermodynamics as we know it today.

To obtain the efficiency of a reversible heat engine, we shall not follow Carnot's original reasoning because it considered heat as an indestructible substance. Instead, we shall modify it by incorporating the First Law. For the heat engine represented in Figure 3.1, the law of conservation of energy gives $W = Q_1 - Q_2$. This means, a fraction η of the heat Q_1 absorbed from the hot reservoir is converted into work W , i.e. $\eta = W/Q_1$. The fraction η is called *the efficiency of the heat engine*. Since $W = (Q_1 - Q_2)$ in accordance with the first law, $\eta = (Q_1 - Q_2)/Q_1 = (1 - Q_2/Q_1)$. Carnot's discovery that the reversible engine produces maximum work amounts to the statement that its efficiency is maximum. This efficiency is independent of the properties of the engine and is a function only of the temperatures of the hot and the cold reservoirs:

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - f(t_1, t_2) \quad (3.1.1)$$

in which $f(t_1, t_2)$ is a function only of the temperatures t_1 and t_2 of the hot and cold reservoirs. The scale of the temperatures t_1 and t_2 (Celsius or other) is not specified here. Equation (3.1.1) is **Carnot's theorem**. In fact, as described below, Carnot's observation enables us to define an absolute scale of temperature that is independent of the material property used to measure it.

3.1.1 Efficiency of a Reversible Engine

Now we turn to the task of obtaining the efficiency of reversible heat engines. Since the efficiency of a reversible heat engine is the maximum, all of them must have the same efficiency. Hence, obtaining the efficiency of one reversible engine will suffice. The following derivation also makes it explicit that the efficiency of Carnot's engine is only a function of temperature.

Carnot's reversible engine consists of an ideal gas that operates in a cycle between hot and cold reservoirs, at temperatures θ_1 and θ_2 respectively. Until their identity is established below, we shall use θ for the temperature that appears in the ideal gas equation and T for the absolute temperature (which, as we shall see in the next section, is defined by the efficiency of a reversible cycle). Thus, the ideal gas equation is written as $pV = NR\theta$, in which θ is the temperature measured by noting the change of some quantity such as volume or pressure. (Note that measuring temperature by volume expansion is purely empirical; each unit of temperature is simply correlated with a certain change in volume.) In the following, the work done by the

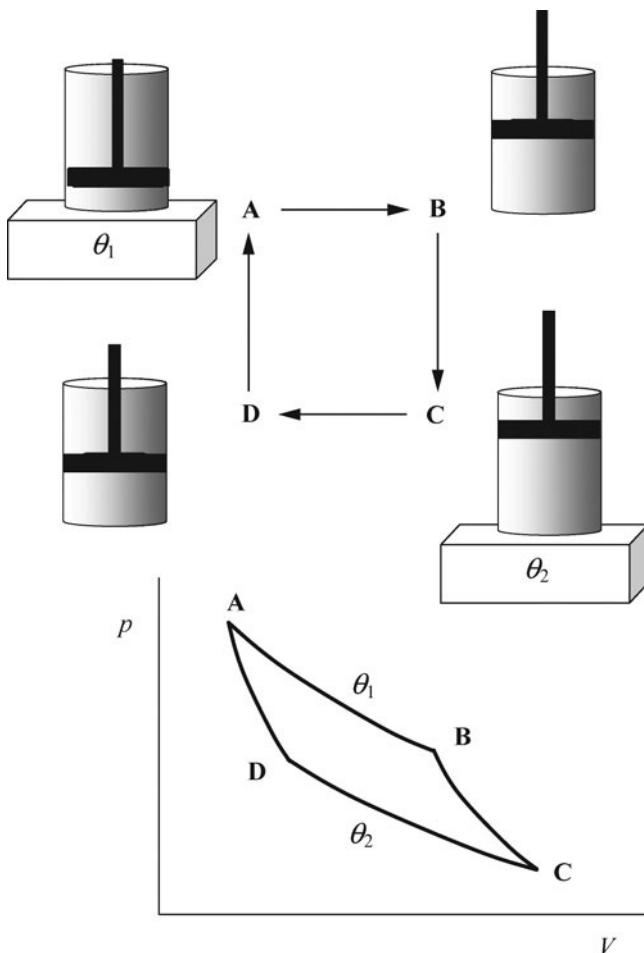


Figure 3.2 The Carnot cycle. The upper part shows the four steps of the Carnot cycle, during which the engine absorbs heat from the hot reservoir, produces work and returns heat to the cold reservoir. The lower part shows the representation of this process in a p - V diagram used by Clapeyron in his exposition of Carnot's work.

gas will be a positive quantity and the work done *on* the gas will be a negative quantity, so that the net work obtained in a cycle is positive for a net heat transfer from the hot to the cold reservoir. The reversible cycle we consider consists of the following four steps (Figure 3.2).

Step 1

The gas has an initial volume of V_A and is in contact with the hot reservoir at temperature θ_1 . At the constant temperature θ_1 due to its contact with the reservoir, the gas undergoes an infinitely slow *reversible expansion* (as Carnot specified it) to the state B, of volume V_B . The work done by the gas during this expansion is

$$W_{AB} = \int_{V_A}^{V_B} p \, dV = \int_{V_A}^{V_B} \frac{NR\theta_1}{V} \, dV = NR\theta_1 \ln \left(\frac{V_B}{V_A} \right) \quad (3.1.2)$$

During this isothermal processes, heat is absorbed from the reservoir. Since the internal energy of an ideal gas depends only on the temperature (see Equations (1.3.8) and (2.2.15)), there is no change in the energy of the gas; the heat absorbed equals the work done. Hence, the heat absorbed is

$$Q_{AB} = W_{AB} \quad (3.1.3)$$

Step 2

In the second step, the gas is thermally insulated from the reservoir and the environment and made to undergo an adiabatic expansion from state B to a state C, resulting in a decrease of temperature from θ_1 to θ_2 . During this adiabatic process, work is done by the gas. Noting that on the adiabat BC we have $pV^\gamma = p_B V_B^\gamma = P_C V_C^\gamma$, we calculate the amount of work done by the gas in this adiabatic expansion:

$$\begin{aligned} W_{BC} &= \int_{V_B}^{V_C} p \, dV = \int_{V_B}^{V_C} \frac{p_B V_B^\gamma}{V^\gamma} \, dV = \frac{p_C V_C^\gamma V_C^{1-\gamma} - p_B V_B^\gamma V_B^{1-\gamma}}{1-\gamma} \\ &= \frac{p_C V_C - p_B V_B}{1-\gamma} \end{aligned}$$

Using $pV = NR\theta$, the above equation can be further simplified to

$$W_{BC} = \frac{NR(\theta_1 - \theta_2)}{\gamma - 1} \quad (3.1.4)$$

in which θ_1 and θ_2 are the initial and final temperatures during the adiabatic expansion.

Step 3

In the third step, the gas is in contact with the reservoir of temperature θ_2 and it undergoes an isothermal compression to the point D, at which the volume V_D is such that an adiabatic compression can return it to the initial state A. (V_D can be specified by finding the point of intersection of the adiabat through the point A and the isotherm at temperature θ_2 .) During this isothermal process, the work done *on the gas* is transferred as heat Q_{CD} to the reservoir (since the energy of the ideal gas depends only on its temperature):

$$W_{CD} = \int_{V_C}^{V_D} p \, dV = \int_{V_C}^{V_D} \frac{NR\theta_2}{V} \, dV = NR\theta_2 \ln\left(\frac{V_D}{V_C}\right) = -Q_{CD} \quad (3.1.5)$$

Step 4

In the final step, an adiabatic compression takes the gas from the state D to its initial state A. Since this process is similar to step 2, we can write

$$W_{DA} = \frac{NR(\theta_2 - \theta_1)}{\gamma - 1} \quad (3.1.6)$$

The total work done in this reversible Carnot cycle in which heat Q_{AB} was absorbed from the reservoir at a temperature of θ_1 and heat Q_{CD} was transferred to the reservoir at temperature θ_2 is

$$\begin{aligned} W &= W_{AB} + W_{BC} + W_{CD} + W_{DA} = Q_{AB} - Q_{CD} \\ &= NR\theta_1 \ln\left(\frac{V_B}{V_A}\right) - NR\theta_2 \ln\left(\frac{V_C}{V_D}\right) \end{aligned} \quad (3.1.7)$$

The efficiency $\eta = W/Q_{AB}$ can now be written using Equations (3.1.2), (3.1.3) and (3.1.7):

$$\eta = \frac{W}{Q_{AB}} = 1 - \frac{NR\theta_2 \ln(V_C/V_D)}{NR\theta_1 \ln(V_B/V_A)} \quad (3.1.8)$$

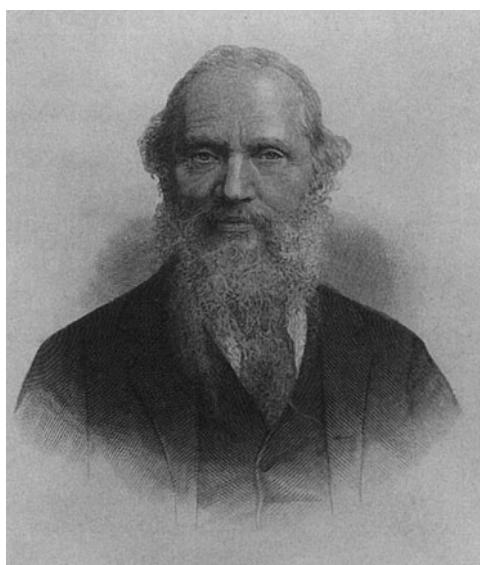
For the two isothermal processes, we have $p_A V_A = p_B V_B$ and $p_C V_C = p_D V_D$ and for the two adiabatic processes, we have $p_B V_B^\gamma = p_C V_C^\gamma$ and $p_A V_A^\gamma = p_D V_D^\gamma$. Using these relations, it can easily be seen that $(V_C/V_D) = (V_B/V_A)$. Using this relation in Equation (3.1.8), we arrive at a simple expression for the efficiency:

$$\eta = \frac{W}{Q_{AB}} = 1 - \frac{\theta_2}{\theta_1} \quad (3.1.9)$$

In this expression for the efficiency, θ is the temperature defined by one particular property (such as volume at a constant pressure) and we assume that it is the temperature in the ideal gas equation. The temperature t measured by any other empirical means, such as measuring the volume of mercury, is related to θ ; that is, θ can be expressed as a function of t , i.e. $\theta(t)$. Thus, the temperature t measured by one means corresponds to $\theta = \theta(t)$, measured by another means. In terms of any other temperature t , the efficiency may take a more complex form. In terms of the temperature θ that obeys the ideal gas equation, however, the efficiency of the reversible heat engine takes a particularly simple form shown in Equation (3.1.9).

3.2 The Absolute Scale of Temperature

The fact that the efficiency of a reversible heat engine is independent of the physical and chemical nature of the engine has an important consequence, which was noted by Lord Kelvin (William Thomson (1824–1907)). Following Carnot's work, Lord Kelvin introduced the *absolute scale of temperature*. The efficiency of a reversible heat engine is a function only of the temperatures of the hot and cold reservoirs, independent of the material properties of the engine. Furthermore, the efficiency cannot exceed unity, in accordance with the First Law. These two facts can be used to define an *absolute scale of temperature that is independent of any material properties*.



William Thomson/Lord Kelvin (1824–1907).

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First, by considering two successive Carnot engines, one operating between t_1 and t' and the other operating between t' and t_2 , we can see that the function $f(t_2, t_1)$ in Equation (3.1.1) is a ratio of a functions of t_1 and t_2 : if Q' is the heat exchanged at temperature t' , then we can write

$$f(t_2, t_1) = \frac{Q_2}{Q_1} = \frac{Q_2}{Q'} \frac{Q'}{Q_1} = f(t_2, t')f(t', t_1) \quad (3.2.1)$$

This relation, along with $f(t, t) = 1$, implies that we can write the function $f(t_2, t_1)$ as the ratio $f(t_2)/f(t_1)$. Hence, the efficiency of a reversible Carnot engine can be written as

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{f(t_2)}{f(t_1)} \quad (3.2.2)$$

One can now define a temperature $T \equiv f(t)$ based solely on the efficiencies of reversible heat engines. In terms of this temperature scale, the efficiency of a reversible engine is given by

$$\boxed{\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}} \quad (3.2.3)$$

in which T_1 and T_2 are the absolute temperatures of the cold and hot reservoirs respectively. An efficiency of unity defines the absolute zero of this scale. **Carnot's theorem** is the statement that reversible engines have the maximum efficiency given by Equation (3.2.3).

Comparing expression (3.2.3) with (3.1.9), we see that the ideal gas temperature coincides with the absolute temperature and, hence, we can use the same symbol, i.e. T , for both.¹

In summary, for an idealized, *reversible heat engine* that absorbs heat Q_1 from a hot reservoir at absolute temperature T_1 and discards heat Q_2 to a cold reservoir at absolute temperature T_2 , we have, from Equation (3.2.3),

$$\boxed{\frac{Q_1}{T_1} = \frac{Q_2}{T_2}} \quad (3.2.4)$$

All *real* heat engines that go through a cycle in finite time must involve irreversible processes such as flow of heat due to a temperature gradient. They are less efficient. Their efficiency η' is less than the efficiency of a reversible heat engine, i.e. $\eta' = 1 - (Q_2/Q_1) < 1 - (T_2/T_1)$. This implies $T_2/T_1 < Q_2/Q_1$ whenever irreversible processes are involved. Therefore, while the equality (3.2.4) is valid for a reversible cycle, for the operation of an *irreversible cycle* that we encounter in reality we have the *inequality*

$$\frac{Q_1}{T_1} < \frac{Q_2}{T_2} \quad (3.2.5)$$

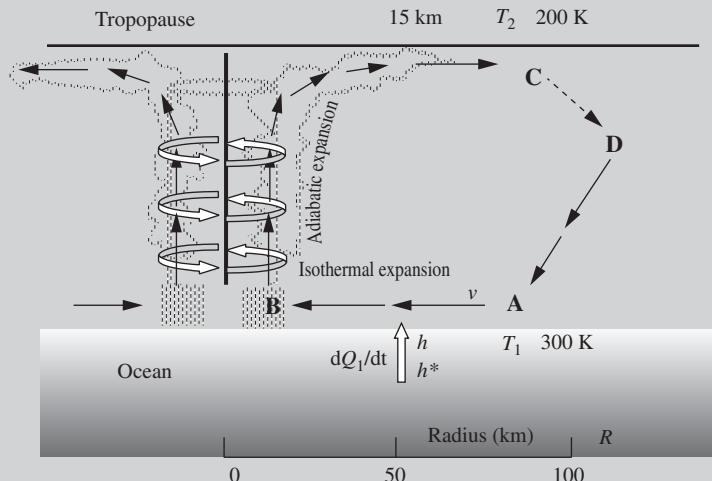
As we shall see below, irreversibility in Nature, or a sense of an ‘arrow of time’, is manifest in this inequality.

A spectacular example of a ‘heat engine’ in Nature is the hurricane. In a hurricane, heat is converted to kinetic energy of the hurricane wind. As summarized in Box 3.1 and described in more detail in Appendix 3.1, by using Carnot’s theorem one can obtain an upper bound to the velocity of the hurricane wind.

¹The empirical temperature t of a gas thermometer is defined through the increase in volume at constant pressure (see Equation (1.4.9)): $V = V_0(1 + \alpha t)$. Gay-Lussac found that $\alpha \approx (1/273) \text{ } ^\circ\text{C}^{-1}$. From this equation it follows that $dV/V = \alpha dt/(1 + \alpha t)$. On the other hand, from the ideal gas equation $pV = NRT$, we have, at constant p , $dV/V = dT/T$. This enables us to relate the absolute temperature T to the empirical temperature t by $T = (1 + \alpha t)/\alpha = (273 + t)$ in which t is in Celsius.

Box 3.1 The hurricane as a heat engine

The mechanism of a hurricane is essentially that of a heat engine, as shown in the figure below in the cycle ABCD. The maximum intensity of a hurricane, i.e. the maximum hurricane wind speed, can be predicted using Carnot's theorem for the efficiency of a heat engine.



In a hurricane, as the wind spirals inwards towards the eye at low pressure, enthalpy (heat) is absorbed at the warm ocean-air interface in an essentially isothermal process: water vaporizes and mixes with the air, carrying with it the enthalpy of vaporization (segment AB). When this moist air reaches the hurricane's eyewall, it rises rapidly to about 15 km along the eyewall. Since the pressure decreases with altitude, it expands adiabatically and cools (segment BC). As the rising moist air's temperature drops, the water vapor in it condenses as rain, releasing the enthalpy of vaporization (latent heat), part of which is radiated into outer space. In a real hurricane, the air at the higher altitude flows out into the weather system. Theoretically, in order to close the Carnot cycle, it could be assumed that the enthalpy of vaporization is lost in an isothermal process (segment CD). The last step (segment DA) of the cycle is an adiabatic compression of dry air. During the cycle, part of the enthalpy absorbed from the ocean is converted into mechanical energy of the hurricane wind.

The 'hurricane heat engine' operates between the ocean surface temperature T_1 (about 300 K) and the lower temperature T_2 (about 200 K) at the higher altitude, close to the upper boundary of the troposphere (tropopause). The conversion of the heat of vaporization to mechanical energy of the hurricane wind can now be analyzed. In a time dt , if dQ_1 is the heat absorbed at the ocean surface, dQ_2 is the heat radiated at the higher altitude and dW is the amount of heat converted to mechanical energy of the hurricane wind, then, according to Carnot's theorem:

$$\frac{dW}{dt} \leq \left(1 - \frac{T_2}{T_1}\right) \frac{dQ_1}{dt}$$

Appendix 3.1 shows that the use of this expression in an analysis of the energetics of a hurricane leads to the following estimate for the maximum hurricane wind speed $|v_{\max}|$:

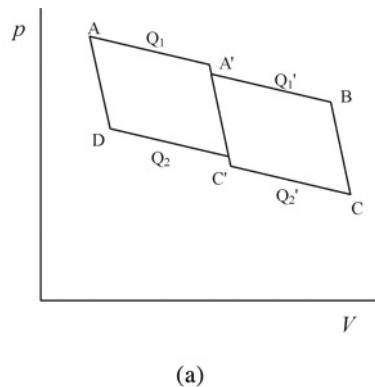
$$|v_{\max}|^2 \approx \left(\frac{T_1 - T_2}{T_2}\right) \frac{C_h}{C_D} (h^* - h)$$

Here, C_h and C_D are constants, h^* is the specific enthalpy (enthalpy per unit mass) of the air saturated with moisture close to the ocean surface and h is the specific enthalpy of dry wind above the ocean surface (see the figure above). All the terms on the right-hand side are experimentally measured or theoretically estimated. The ratio $C_h/C_D \approx 1$. Kerry Emanuel, the originator of the above theory, has demonstrated that the above expression for v_{\max} leads to remarkably good estimates of the hurricane wind speeds [4]. More details can be found in Appendix 3.1 and in the cited articles.

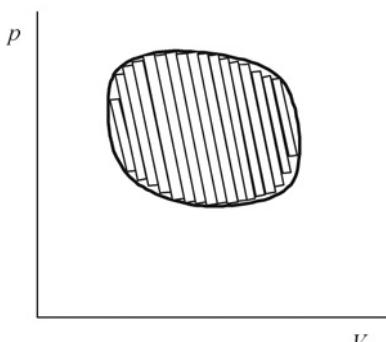
3.3 The Second Law and the Concept of Entropy

The far-reaching import of the concepts originating in Carnot's *Reflexions on the Motive Force of Fire* was realized in the generalizations made by Rudolf Clausius (1822–1888), who introduced the concept of *entropy*, a new physical quantity as fundamental and universal as energy.

Clausius began by generalizing expression (3.2.4) that follows from Carnot's theorem to an arbitrary cycle. This was done by considering composites of Carnot cycles in which the corresponding isotherms differ by an infinitesimal amount ΔT , as shown in Figure 3.3a. Let Q_1 be the heat absorbed during the transformation



(a)



(b)

Figure 3.3 Clausius's generalization of Carnot cycle. (a) Two Carnot cycles can be combined to obtain a larger cycle. (b) Any closed path can be thought of as a combination of a large number of infinitesimal Carnot cycles.

from A to A', at temperature T_1 , and let Q'_1 be the heat absorbed during the transformation A'B at temperature $(T_1 + \Delta T)$. Similarly, we define Q'_2 and Q_2 for the transformations CC' and C'D occurring at temperatures $T_2 + \Delta T$ and T_2 respectively. Then the reversible cycle AA'BCC'DA can be thought of as a sum of the two reversible cycles AA'C'DA and A'BCC'A' because the adiabatic work A'C' in one cycle cancels that of the second cycle, C'A'. For the reversible cycle AA'BCC'D, we can therefore write

$$\frac{Q_1}{T_1} + \frac{Q'_1}{T_1 + \Delta T} - \frac{Q_2}{T_2} - \frac{Q'_2}{T_2 + \Delta T} = 0 \quad (3.3.1)$$

The above composition of cycles can be extended to an arbitrary closed path (as shown in Figure 3.3b) by considering it as a combination of a large number of infinitesimal Carnot cycles. With the notation $dQ > 0$ if heat is absorbed by the system and $dQ < 0$ if it is discarded, the generalization of Equation (3.3.1) of an arbitrary closed path gives

$$\oint \frac{dQ}{T} = 0 \quad (3.3.2)$$



Rudolf Clausius (1822–1888).

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This equation has an important consequence: it means that the integral of the quantity dQ/T along a path representing a reversible process from a state A to a state B depends only on the states A and B and is independent of the path, as described in Figure 3.4. Thus, Clausius saw that one can define a function S that

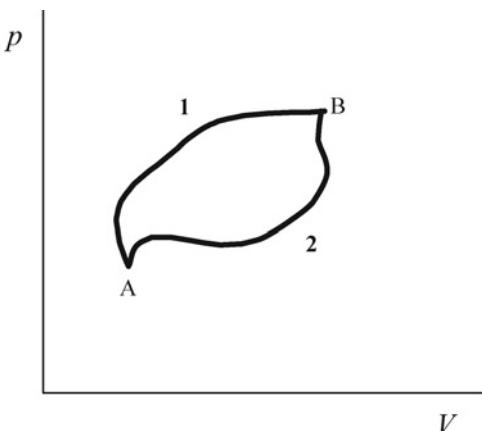


Figure 3.4 Any differential, such as dQ/T in Equation (3.3.2), whose integral over any closed path is zero can be used to define a function of state can be seen as follows. Since the total integral for a closed path from A to B along 1 and from B to A along 2 is zero, it follows that $\oint dQ/T = \int_{A,\text{path}1}^B dQ/T + \int_{B,\text{path}2}^A dQ/T = 0$. Now we note that $\int_A^B dQ/T = -\int_B^A dQ/T$ along paths 1 or 2. Hence, $\int_{A,\text{path}1}^B dQ/T = \int_{A,\text{path}2}^B dQ/T$, i.e. the integral of dQ/T from point A to point B is independent of the path; it depends only on the points A and B. Hence, if the initial reference state is fixed, the integral, which is a function only of the final state, is a state function.

depends only on the initial and final states of a reversible process (Figure 3.4). If S_A and S_B are the values of this function in the states A and B, then we can write

$$S_B - S_A = \int_A^B \frac{dQ}{T} \quad \text{or} \quad dS = \frac{dQ}{T} \quad (3.3.3)$$

By defining a reference state ‘O’, the new function of state S could be defined for any state X as the integral of dQ/T for a *reversible process* transforming the state O to the state X.

Clausius introduced this new quantity S in 1865, stating ‘I propose to call the magnitude S the *entropy* of the body, from the Greek word $\tau\rho\sigma\pi\eta$, *transformation*.’ [5, p. 357]. The usefulness of the above definition depends on the assumption that any two states can be connected by a reversible transformation.

If the temperature remains fixed, then it follows from (3.3.3) that, for a reversible flow of heat Q , the change in entropy is Q/T . In terms of entropy, Carnot’s theorem (3.2.3) is equivalent to the statement that the sum of the *entropy changes in a reversible cycle is zero*:

$$\boxed{\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0} \quad (3.3.4)$$

In a reversible process, since the temperatures of the system and the reservoirs are the same when heat is exchanged, the change of entropy of the reservoir in any part of the cyclic process is the negative of the entropy change of the system.

In a less efficient *irreversible cycle*, a smaller fraction of Q_1 (the heat absorbed from the hot reservoir) is converted into work. This means that the amount of heat delivered to the cold reservoir by an irreversible cycle Q_2^{irr} is greater than Q_2 . Therefore, we have

$$\frac{Q_1}{T_1} - \frac{Q_2^{\text{irr}}}{T_2} < 0 \quad (3.3.5)$$

Since the cyclic engine returns to its initial state whether the process is reversible or irreversible, there is no change in its entropy. On the other hand, since the heats transferred to the reservoirs and to the irreversible engine have opposite sign, the *total change of entropy of the reservoirs* is

$$\frac{-Q_1}{T_1} - \frac{-Q_2^{\text{irr}}}{T_2} > 0 \quad (3.3.6)$$

if the reservoir temperatures can be assumed to be the same as the temperatures at which the engine operates. In fact, for heat to flow at a nonzero rate, the reservoir temperatures T'_1 and T'_2 must be such that $T'_1 > T_1$ and $T'_2 < T_2$. In this case, the increase in entropy is even larger than (3.3.6).

Generalizing the above result, for a system that goes through an arbitrary cycle, with the equalities holding for a reversible process, we have

$$\oint \frac{dQ}{T} \leq 0 \text{ (system)} \quad (3.3.7)$$

For the ‘exterior’ with which the system exchanges heat, since dQ has the opposite sign, we then have

$$\oint \frac{dQ}{T} \geq 0 \text{ (exterior)} \quad (3.3.8)$$

At the end of the cycle, be it reversible or irreversible, there is no change in the system’s entropy because it has returned to its original state. For irreversible cycles this means that the system expels more heat to the exterior. This is generally a conversion of mechanical energy into heat through irreversible processes. Consequently, the entropy of the exterior increases. Thus, the entropy changes in a cyclic process may be summarized as follows:

$$\text{Reversible cycle: } dS = \frac{dQ}{T}, \quad \oint dS = \oint \frac{dQ}{T} = 0 \quad (3.3.9)$$

$$\text{Irreversible cycle: } dS > \frac{dQ}{T}, \quad \oint dS = 0, \quad \oint \frac{dQ}{T} = < 0 \quad (3.3.10)$$

As we shall see in the following section, this statement can be made more precise by expressing the entropy change dS as a sum of two parts:

$$dS = d_e S + d_i S \quad (3.3.11)$$

Here, $d_e S$ is the change of the system’s entropy due to exchange of energy and matter and $d_i S$ is the change in entropy due to irreversible processes within the system. For a closed system that does not exchange matter, $d_e S = dQ/T$. The quantity $d_e S$ could be positive or negative, but $d_i S$ can only be equal to or greater than zero. In a cyclic process that returns the system to its initial state, since the net change in entropy must be zero, we have

$$\oint dS = \oint d_e S + \oint d_i S = 0 \quad (3.3.12)$$

Since $d_i S \geq 0$, we must have $\oint d_i S \geq 0$. For a closed system, from Equation (3.3.12) we immediately obtain the previous result (3.3.10):

$$\oint d_e S = \oint \frac{dQ}{T} < 0$$

This means that, for the system to return to its initial state, the entropy $\oint d_i S$ generated by the irreversible processes within the system has to be discarded through the expulsion of heat to the exterior. There is no real system in nature that can go through a cycle of operations and return to its initial state without increasing the entropy of the exterior, or more generally the ‘universe’. Every process in Nature increases the entropy, thus establishing a distinction between the past and future. *The Second Law establishes an arrow of time: the increase of entropy distinguishes the future from the past.*

3.3.1 Statements of the Second Law

The limitation to the convertibility of heat to work that Carnot discovered is one manifestation of a fundamental limitation in all natural processes: it is the Second Law of thermodynamics. The Second Law can be formulated in many equivalent ways. For example, it can be a statement about a macroscopic impossibility, without any reference to the microscopic nature of matter:

It is impossible to construct an engine which will work in a complete cycle, and convert *all* the heat it absorbs from a reservoir into mechanical work.

This is a statement perfectly comprehensible in macroscopic, operational terms. A cyclic engine that converts all heat to work is shown in Figure 3.5. Since the reservoir or the ‘exterior’, at temperature T , only loses heat, inequality (3.3.8) is clearly violated. Such an engine is sometimes called a *perpetual motion machine of the second kind* and the Second Law is the statement that such a machine is impossible. The equivalence between this statement and Carnot’s theorem can be seen easily and is left as an exercise for the reader.

Another way of stating the Second Law is due to Rudolf Clausius (1822–1888):

Heat cannot by itself pass from a colder to a hotter body.

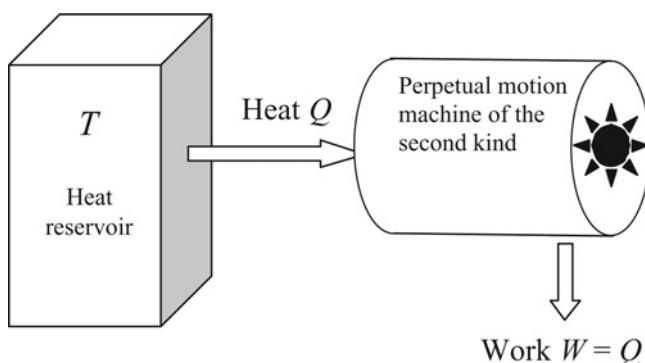


Figure 3.5 A perpetual motion machine of the second kind absorbs heat Q and converts all of it to work W . Such a machine, though consistent with the First Law, is impossible according to the Second Law. The existence of such a machine would violate the inequalities (3.3.7) and (3.3.8).

If heat could pass spontaneously from a colder body to a hotter body, then a perpetual motion machine of the second kind can be realized by simply making the heat Q_2 expelled by a cyclic heat engine to the colder reservoir pass by itself to the hotter reservoir. The result would be the complete conversion of the heat ($Q_1 - Q_2$) to work.

As we have seen above, any real system that goes through a cycle of operations and returns to its initial state does so only by *increasing* the entropy of its exterior with which it is interacting. This also means that in no part of the cycle can the *sum* of entropy changes of the system and its exterior be negative because, if it were so, we could complete the rest of the cycle through a reversible transformation, which does not contribute to the change of entropy. The net result is a *decrease* of entropy in a cyclic process. Thus, the Second Law may also be stated as:

The sum of the entropy changes of a system and its exterior can never decrease.

Thus, the universe as a whole can never return to its initial state. Remarkably, Carnot's analysis of heat engines has led to the formulation of a cosmological principle. The two laws of thermodynamics are best summarized by Rudolf Clausius thus:

The energy of the universe is a constant.

The entropy of the universe approaches a maximum.

3.4 Modern Formulation of the Second Law

The usefulness of the concept of entropy and the Second Law depends on our ability to define entropy for a physical system in a calculable way. Using Equation (3.3.3), if the entropy S_o of a *reference or standard state is defined*, then the entropy of an arbitrary state S_x can be obtained through a *reversible process* that transforms the state O to the state X (see Figure 3.6):

$$S_x = S_o + \int_o^x \frac{dQ}{T} \quad (3.4.1)$$

(In practice dQ is measured with the knowledge of the heat capacity using $dQ = C dT$.) In a real system, the transformation from the state O to the state X occurs in a finite time and involves irreversible processes along the path I. In this process, the entropy of the system, and hence the universe, increases. *In classical thermodynamics it is assumed that every irreversible transformation that a system undergoes can also be achieved through a reversible transformation for which Equation (3.4.1) is valid.* In other words, it is assumed that every irreversible transformation that results in a certain change in the entropy of the system can be exactly reproduced through a reversible process in which the entropy change is solely due to the exchange of heat. Since the change in entropy of the system depends only on the initial and final states, the change in entropy calculated using a reversible path will be equal to the entropy change produced by the irreversible processes. However, it must be noted that a reversible transformation from an initial state O to the final state X (Figure 3.6) may give the right value for the change in entropy of the system, but it leaves the entropy of the universe unchanged; in a reversible process, the change in entropy of the system is compensated by the opposite change in the entropy of the exterior, leaving the entropy of the universe unchanged. On the other hand, the naturally occurring irreversible transformation from O to X increases the entropy of the universe. Some authors restrict the above assumption to transformations between equilibrium states; this restriction excludes

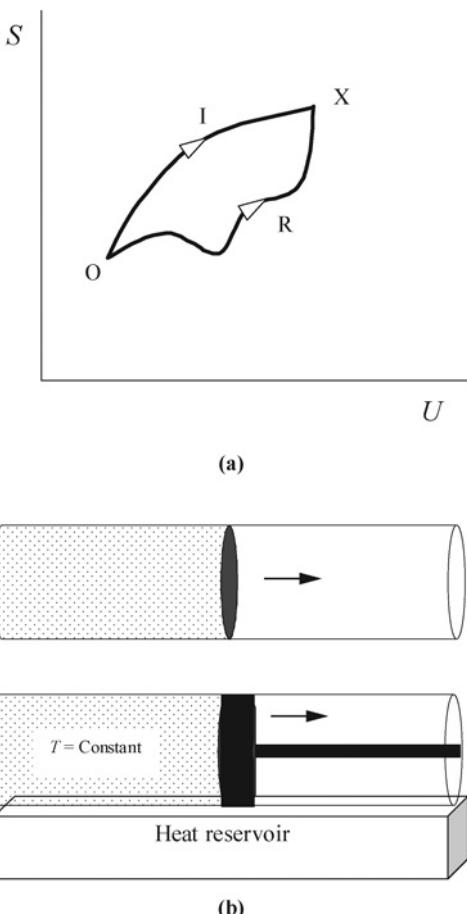


Figure 3.6 Reversible and irreversible processes. (a) The system reaches the state X from the standard state O through a path I involving irreversible processes. It is assumed that the same transformation can be achieved through a reversible transformation R . (b) An example of an irreversible process is the spontaneous expansion of a gas into a vacuum, as shown in the upper part. The same change can be achieved reversibly through an isothermal expansion of a gas that occurs infinitely slowly so that the heat absorbed from the reservoir equals the work done on the piston. In the latter case, the change in entropy can be calculated using $dS = dQ/T$.

chemical reactions, in which the transformations are often from a nonequilibrium state to an equilibrium state (see Chapters 4 and 7).

A process is reversible only in the limit of infinite slowness: as perfect reversibility is approached, the speed of the process approaches zero. As Max Planck notes in his treatise [6, p. 86], ‘Whether reversible processes exist in nature or not, is not *a priori* evident or demonstrable.’ However, irreversibility, if it exists, has to be universal because a spontaneous decrease of entropy in one system could be utilized to decrease the entropy of any other system through appropriate interaction; a spontaneous decrease of entropy of one system implies a spontaneous decrease of entropy of all systems. *Hence, either all systems are irreversible, or none are*, as Max Planck emphasized [6].

The notion of an idealized reversible path provides a convenient way for calculating entropy changes. However, it is also lacking in providing the real connection between physical processes and entropy. Addressing this issue in his 1943 monograph *The Nature of Thermodynamics*, P.W. Bridgman wrote [7, p. 133]:

It is almost always emphasized that thermodynamics is concerned with reversible processes and equilibrium states and that it can have nothing to do with irreversible processes or systems out of equilibrium in which changes are progressing at a finite rate. The reason for the importance of equilibrium states is obvious enough when one reflects that temperature itself is defined in terms of equilibrium states. But the admission of general impotence in the presence of irreversible processes appears on reflection to be a surprising thing. Physics does not usually adopt such an attitude of defeatism.

Today, in most texts on thermodynamics, an irreversible transformation is usually identified by the **Clausius inequality**:

$$\boxed{dS \geq \frac{dQ}{T}} \quad (3.4.2)$$

which we saw in the last section. However, the fact that Clausius considered irreversible processes as an integral part of formulating the Second Law is generally not mentioned. In his ninth memoir, Clausius included irreversible processes explicitly into the formalism of entropy and replaced the inequality (3.4.2) by an equality [8, p. 363, eq. (71)]:

$$N = S - S_o - \int \frac{dQ}{T} \quad (3.4.3)$$

in which S is the entropy of the final state and S_o is the entropy of the initial state. He identified the change in entropy due to the exchange of heat with the exterior by the term dQ/T (which is compensated by equal gain or loss of heat by the exterior). Clausius wrote: ‘The magnitude N thus determines the *uncompensated transformation*’ (*uncompensirte Verwandlung*) [8, p. 363]. It is the entropy produced by irreversible processes within the system. While dQ can be positive or negative, the Clausius inequality (3.4.2) implies that the change in entropy due to irreversible processes can only be positive:

$$N = S - S_o - \int \frac{dQ}{T} > 0 \quad (3.4.4)$$

Clausius also stated the Second Law as: ‘Uncompensated transformations can only be positive’ [8, p. 247].

Perhaps Clausius hoped to, but did not, provide a means of computing the entropy N associated with irreversible processes. Nineteenth century thermodynamics remained in the restricted domain of idealized reversible transformation and without a theory that related entropy explicitly to irreversible processes. Some expressed the view that entropy is a physical quantity that is spatially distributed and transported (e.g. see Reference [9]), but still no theory relating irreversible processes to entropy was formulated in the nineteenth century.

Noticing the importance of relating entropy to irreversible processes, Pierre Duhem (1861–1916) began to develop a formalism. In his extensive and difficult two-volume work titled *Energétique* [10], Duhem explicitly obtained expressions for the entropy produced in processes involving heat conductivity and viscosity [11]. Some of these ideas of calculating the ‘uncompensated heat’ also appeared in the work of the Polish researcher L. Natanson [12] and the Viennese school led by G. Jaumann [13–15], where the notions of entropy flow and entropy production were developed.

Formulation of a theory of entropy along these lines continued during the twentieth century, and today we do have a theory in which the entropy change can be calculated in terms of the variables that characterize the

irreversible processes. It is a theory applicable to all systems in which the temperature is well defined at every location. For example, the modern theory relates the rate of change of entropy to the rate of heat conduction or the rates of chemical reaction. *To obtain the change in entropy, it is not necessary to use infinitely slow reversible processes.*

With reference to Figure 3.6, in the classical formulation of entropy it is often stated that, along the irreversible path I, the entropy may not be a function of the total energy and the total volume and hence it is not defined. However, for a large class of systems, the notion of *local equilibrium* makes entropy a well-defined quantity, even if it is not a function of the total energy and volume. We shall discuss the foundations of this and other approaches in Chapter 15. For such systems, entropy, which represents irreversibility in nature, can be related directly to irreversible processes.

In his pioneering work on the thermodynamics of chemical processes, Théophile De Donder (1872–1957) [16–18] incorporated the ‘uncompensated transformation’ or ‘uncompensated heat’ of Clausius into the formalism of the Second Law through the concept of affinity (which is presented in Chapter 4). Unifying all these developments, Ilya Prigogine (1917–2003) formulated the ‘modern approach’ incorporating irreversibility into the formalism of the Second Law by providing general expressions for computing entropy produced by irreversible processes [19–21], thus giving the ‘uncompensated heat’ of Clausius a sound theoretical basis. Thus, thermodynamics evolved into a theory of irreversible processes in contrast to classical thermodynamics, which is a theory of equilibrium states. We shall follow this more general approach in which, along with thermodynamic *states*, irreversible *processes* appear explicitly in the formalism.

The basis of the modern approach is the notion of *local equilibrium*. For a very large class of systems that are not in thermodynamic equilibrium, thermodynamic quantities such as temperature, concentration, pressure and internal energy remain well-defined concepts locally, i.e. one could meaningfully formulate a thermodynamic description of a system in which intensive variables such as temperature and pressure are well defined in each elemental volume, and extensive variables such as entropy and internal energy are replaced by their corresponding *densities*. Thermodynamic variables can thus be functions of position and time. This is the assumption of *local equilibrium*. There are, of course, systems in which this assumption is not a good approximation, but such systems are exceptional. In most hydrodynamic and chemical systems, local equilibrium is an excellent approximation. Modern computer simulations of molecular dynamics have shown that if initially the system is in such a state that temperature is not well defined, then in a very short time (few molecular collisions) the system relaxes to a state in which temperature is a well-defined quantity [22].

The modern formalism begins by expressing the changes in entropy as a sum of two parts [19]:

$$dS = d_e S + d_i S \quad (3.4.5)$$

in which $d_e S$ is the entropy change due to the exchange of matter and energy with the exterior and $d_i S$ is the entropy change due to ‘uncompensated transformation’, the entropy produced by the irreversible processes in the interior of the system (Figure 3.7).

The task now is to obtain explicit expressions for $d_e S$ and $d_i S$ in terms of experimentally measurable quantities. Irreversible processes can in general be thought of as **thermodynamic forces** driving **thermodynamic flows**. The thermodynamic flows are a consequence of the thermodynamic forces. For example, the temperature gradient is the thermodynamic *force* that causes an irreversible *flow* of heat; similarly, a concentration gradient is the thermodynamic force that causes the flow of matter (Figure 3.8). In general, the irreversible change $d_i S$ is associated with a flow dX of a quantity, such as heat or matter, that has occurred in a time dt . For the flow of heat, $dX = dQ$, the amount of heat that flowed in time dt ; for the case of matter flow, $dX = dN$, moles of the substance that flowed in time dt . In each case, the change in entropy can be written in the form

$$d_i S = F dX \quad (3.4.6)$$

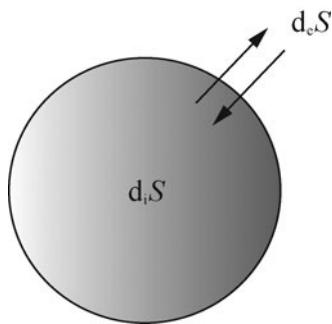


Figure 3.7 Entropy changes in a system consist of two parts: d_iS due to irreversible processes and d_eS due to the exchange of energy and matter. According to the Second Law, the change d_iS can only be positive. The entropy change d_eS can be positive or negative.

in which F is the thermodynamic force. The thermodynamic forces are expressed as functions of thermodynamic variables such as temperature and concentrations. In the following section we shall see that, for the flow of heat shown in Figure 3.8, the thermodynamic force takes the form $F = (1/T_{\text{cold}} - 1/T_{\text{hot}})$. For a continuous variation of T ,

$$F = \frac{\partial}{\partial x} \left(\frac{1}{T(x)} \right)$$

For the flow of matter, the corresponding thermodynamic force is expressed in terms of **affinity**, which, as noted above, is a concept developed in Chapter 4. All irreversible processes can be described in terms of thermodynamic forces and thermodynamic flows. In general, the irreversible increase in entropy d_iS is the sum of all the increases due to irreversible flows dX_k . We then have the general expression

$$d_iS = \sum_k F_k dX_k \geq 0 \quad \text{or} \quad \frac{d_iS}{dt} = \sum_k F_k \frac{dX_k}{dt} \geq 0 \quad (3.4.7)$$

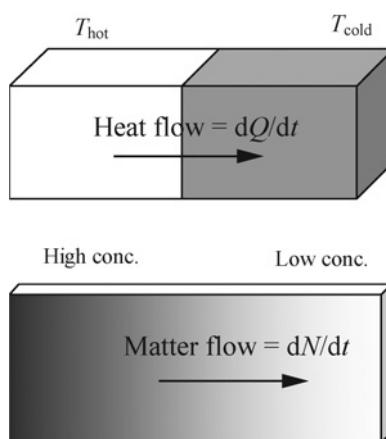


Figure 3.8 Flow of heat and diffusion of matter are examples of irreversible processes.

Equation (3.4.7) is a modern statement of the Second Law of thermodynamics. The rate of entropy production due to each irreversible process is a product of the corresponding thermodynamic force F_k and the flow $J_k = dX_k/dt$ and can only be positive.

The entropy exchange with the exterior $d_e S$ is expressed in terms of the flow of heat and matter. For **isolated systems**, since there is no exchange of energy or matter,

$$d_e S = 0 \quad \text{and} \quad d_i S \geq 0 \quad (3.4.8)$$

For **closed systems**, which exchange energy but not matter,

$$d_e S = \frac{dQ}{T} = \frac{dU + p dV}{T} \quad \text{and} \quad d_i S \geq 0 \quad (3.4.9)$$

In this expression, dQ is the amount of heat exchanged by the system in a time dt . (By defining dQ in this way, we avoid the ‘imperfect differentials’ used in classical thermodynamics.)

For **open systems**, which exchange both matter and energy:

$$d_e S = \frac{dU + p dV}{T} + (d_e S)_{\text{matter}} \quad \text{and} \quad d_i S \geq 0 \quad (3.4.10)$$

where $(d_e S)_{\text{matter}}$ is the exchange of entropy due to matter flow. This term can be written in terms of *chemical potential*, a concept that will be developed Chapter 4. When there is a flow of matter, as discussed in Section 2.7, $dU + p dV \neq dQ$, because the internal and kinetic energies of the matter flowing through the system must be included.

Whether we consider isolated, closed or open systems, $d_i S \geq 0$. It is the statement of the Second Law in its most general form. There is another important aspect to this statement: it is valid for all subsystems, not just for the entire system. For example, if we assume that the entire system is divided into two subsystems, we not only have

$$d_i S = d_i S^1 + d_i S^2 \geq 0 \quad (3.4.11)$$

in which $d_i S^1$ and $d_i S^2$ are the entropy productions in each of the subsystems, but we also have

$$d_i S^1 \geq 0 \quad d_i S^2 \geq 0 \quad (3.4.12)$$

We cannot have, for example,

$$d_i S^1 > 0, \quad d_i S^2 < 0 \quad \text{but} \quad d_i S = d_i S^1 + d_i S^2 \geq 0 \quad (3.4.13)$$

This statement is stronger and more general than the classical statement that the entropy of an isolated system can only increase.

In summary, for closed systems, the First and the Second Laws can be stated as

$$dU = dQ + dW \quad (3.4.14)$$

$$dS = d_i S + d_e S \quad \text{in which} \quad d_i S \geq 0, \quad d_e S \geq dQ/T \quad (3.4.15)$$

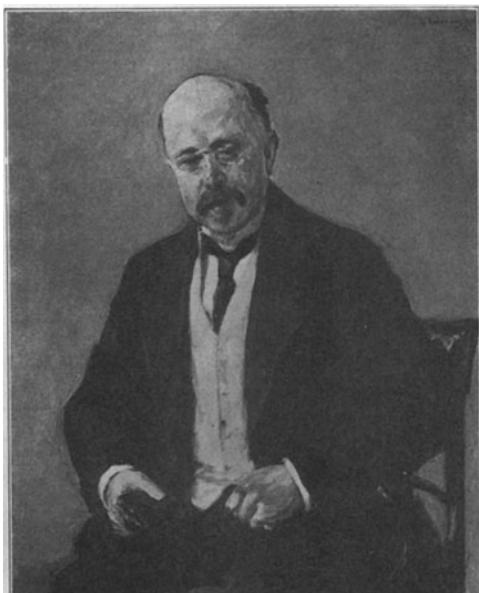
If a transformation of the state is assumed to take place through a reversible process, $d_i S = 0$ and the entropy change is solely due to the flow of heat. We then obtain the equation

$$\boxed{dU = T dS + dW = T dS - p dV} \quad (3.4.16)$$

which is found in texts that confine the formulation of thermodynamics to idealized reversible processes. For open systems, the changes in energy and entropy have additional contributions due to the flow of matter. In this case, though the definition of heat and work needs careful consideration, there is no fundamental difficulty in obtaining dU and $d_e S$.

Finally, we must note that the above formulation enables us to calculate only the *changes* of entropy. It does not give us a way to obtain the absolute value of entropy. In this formalism, entropy can be known only up to an additive constant. However, in 1906, Walther Nernst (1864–1941) formulated a law that stated that *the entropy of all systems approaches zero as the temperature approaches zero* [23]:

$$S \rightarrow 0 \text{ as } T \rightarrow 0 \quad (3.4.17)$$



Walther Nernst (1864–1941).

(Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library.)

This law is often referred to as the **Third Law** of thermodynamics or the **Nernst heat theorem**. Its validity has been well verified by experiment.

The Third Law enables us to give the absolute value for the entropy. The physical basis of this law lies in the behavior of matter at low temperatures that can only be explained by quantum theory. It is remarkable that the theory of relativity gave us means to define absolute values of energy and quantum theory enables us to define absolute values of entropy.

The concept of entropy has its foundation in macroscopic processes. No mention has been made about its meaning at a molecular level. In order to explain what entropy is at a molecular level, Ludwig Boltzmann (1844–1906) introduced the statistical interpretation of entropy. Box 3.2 gives an introduction to this topic; a more detailed discussion of this topic is given in Chapter 20.

Box 3.2 Statistical interpretation of entropy

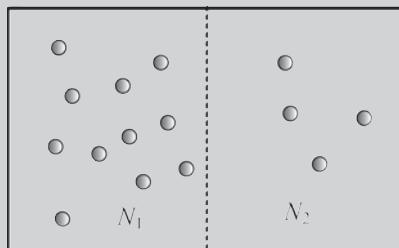
As we have seen in this chapter, the foundation of the concept of entropy as a state function is entirely macroscopic. The validity of the Second Law is rooted in the reality of irreversible processes. In stark contrast to the irreversibility of processes we see all around us, the laws of both classical and quantum mechanics possess no such irreversibility. Classical and quantum laws of motion are time symmetric: if

a system can evolve from a state A to a state B then its time-reversed evolution, from B to A, is also admissible. The laws of mechanics make no distinction between evolution into the future and evolution into the past. For example, the spontaneous flow of gas molecules from a location at higher concentration to a location at lower concentration and its reverse (which violates the Second Law) are both in accord with the laws of mechanics. Processes that are ruled impossible by the Second Law of thermodynamics do not violate the laws of mechanics. Yet all irreversible macroscopic processes, such as the flow of heat, are the consequence of motion of atoms and molecules that are governed by the laws of mechanics; the flow of heat is a consequence of molecular collisions that transfer energy. How can irreversible macroscopic processes emerge from the reversible motion of molecules? What is the relation between entropy and the microscopic constituents of matter? The energy of a macroscopic system is the sum of the energies of its microscopic constituents. What about entropy? Addressing these questions, Ludwig Boltzmann (1844–1906) proposed an extraordinary relation; entropy is a logarithmic measure of the number of microscopic states that correspond to the macroscopic state:

$$S = k_B \ln W$$

in which W is the number of microstates corresponding to the macrostate whose entropy is S . (We shall discuss this relation in detail in Chapter 20.) The constant k_B is now called the Boltzmann constant;^{*} $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$. The gas constant $R = k_B N_A$, in which N_A is the Avogadro number. The following example will illustrate the meaning of W . Consider the macrostate of a box containing a gas with N_1 molecules in one half and N_2 in the other (see the figure below). Each molecule can be in one half or the other. The total number of ways in which the $(N_1 + N_2)$ molecules can be distributed between the two halves such that N_1 molecules are in one and N_2 molecules in the other is equal to W . The number of distinct ‘microstates’ with N_1 molecules in one half and N_2 in the other is

$$W = \frac{(N_1 + N_2)!}{N_1! N_2!}$$



According to Boltzmann, macrostates with larger W are more probable. The irreversible increase of entropy then corresponds to the evolution to states of higher probability in the future. Equilibrium states are those for which W is a maximum. In the above example, it can be shown that W reaches a maximum when $N_1 = N_2$.

*Ter Harr notes that it was Max Planck who introduced k_B in the above form; Planck also determined its numerical value (D. ter Haar, *The Old Quantum Theory*, 1967, Pergamon Press: London, p. 12.)

3.5 Examples of Entropy Changes due to Irreversible Processes

To illustrate how entropy changes are related to irreversible processes, we shall consider some simple examples. The examples we consider are ‘discrete systems’ in which the system consists of two parts that are not mutually in equilibrium. An example of a continuous system is presented in Appendix 3.2.

3.5.1 Heat Conduction

Consider an *isolated* system, which we assume (for simplicity) consists of two parts, each part having a well-defined temperature, i.e. each part is locally in equilibrium. Let the temperatures of the two parts be T_1 and T_2 (as shown in Figure 3.9), with T_1 being greater than T_2 . Let dQ be the amount of heat flow from the hotter part to the colder part in a time dt . Since this isolated system does not exchange entropy with the exterior, $d_eS = 0$. Also, since the volume of each part is a constant, $dW = 0$. The energy change in each part is due solely to the flow of heat: $dU_i = dQ_i$, $i = 1, 2$. In accordance with the First Law, the heat gained by one part is equal to the heat lost by the other. Therefore, $-dQ_1 = dQ_2 = dQ$. Both parts are locally in equilibrium with a well-defined temperature and entropy. The total change in entropy d_iS of the system is the sum of the changes of entropy in each part due to the flow of heat:

$$d_iS = -\frac{dQ}{T_1} + \frac{dQ}{T_2} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) dQ \quad (3.5.1)$$

Since the heat flows irreversibly from the hotter to the colder part, dQ is positive if $T_1 > T_2$. Hence, $d_iS > 0$. In expression (3.5.1), dQ and $(1/T_1 - 1/T_2)$ correspond to dX and F respectively in Equation (3.4.6). In terms of the *rate* of flow of heat dQ/dt , the rate of entropy production can be written as

$$\frac{d_iS}{dt} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \frac{dQ}{dt} \quad (3.5.2)$$

Now the rate of flow of heat or the heat current $J_Q \equiv dQ/dt$ is given by the laws of heat conduction. For example, according to the Fourier law of heat conduction, $J_Q = \alpha(T_1 - T_2)$, in which α is the coefficient of heat flow (it can be expressed in terms of the coefficient of heat conductivity and the area of cross-section). Note that the ‘thermodynamic flow’ J_Q is driven by the ‘thermodynamic force’ $F = (1/T_2 - 1/T_1)$. For the rate of entropy production we have, from Equation (3.5.2),

$$\frac{d_iS}{dt} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \alpha(T_1 - T_2) = \frac{\alpha(T_1 - T_2)^2}{T_1 T_2} \geq 0 \quad (3.5.3)$$

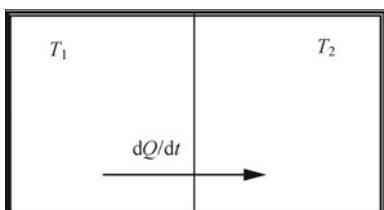


Figure 3.9 Entropy production due to heat flow. The irreversible flow of heat between parts of unequal temperature results in an increase in entropy. The rate at which entropy is produced, d_iS/dt , is given by Equation (3.5.3).

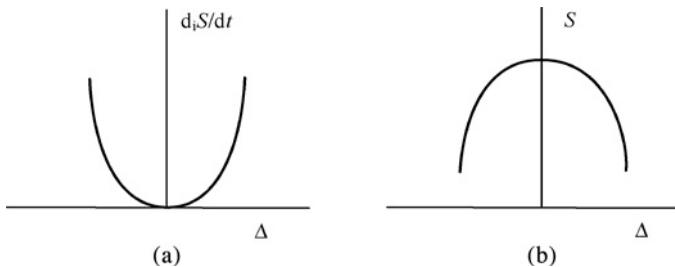


Figure 3.10 Two equivalent properties that characterize the state of equilibrium. (a) The entropy production rate d_iS/dt as a function of the difference in temperatures $\Delta \equiv (T_1 - T_2)$ of the two parts of the system shown in Figure 3.9. At equilibrium, the entropy production rate is zero. (b) At equilibrium the entropy reaches its maximum value. Both properties can be used to identify a system in equilibrium.

Owing to the flow of heat, the two temperatures eventually become equal and the entropy production ceases. This is the state of equilibrium. *Entropy production must vanish in the state of equilibrium*, which implies that the force F and the corresponding flux J_Q both vanish. In fact, we can deduce the properties of the equilibrium state by stipulating that all entropy production must vanish in that state.

From Equation (3.5.3) we see that the entropy production rate d_iS/dt is a quadratic function of the deviation $\Delta \equiv (T_1 - T_2)$. In the state of equilibrium, the entropy production rate takes its minimum value equal to zero. This is indicated graphically in Figure 3.10a.

A nonequilibrium state in which $T_1 \neq T_2$ evolves to the equilibrium state in which $T_1 = T_2 = T$ through a continuous increase of entropy. Therefore, the entropy of the equilibrium state must be larger than the entropy of any nonequilibrium state. In Chapters 12 and 14, we will see explicitly that for a small deviation $\Delta = (T_1 - T_2)$ from the state of equilibrium the corresponding change ΔS is a quadratic function of Δ , attaining a maximum at $\Delta = 0$ (see Figure 3.10b).

This example illustrates the general assertion that the state of equilibrium can be characterized either by the principle of the minimum (equal to zero) rate of entropy production or the principle of maximum entropy.

3.5.2 Irreversible Expansion of a Gas

In a reversible expansion of a gas, the pressure of the gas and that on the piston are assumed to be the same. If we consider an isothermal expansion of a gas that has a constant temperature T by virtue of its contact with a heat reservoir, the change in entropy of the gas $d_eS = dQ/T$, in which dQ is the heat flow from the reservoir to the gas that is necessary to maintain the temperature constant. This is an ideal situation. In any real expansion of a gas that takes place in a finite time, the pressure of the gas is greater than that on the piston. If p_{gas} is the pressure of the gas and p_{piston} that the pressure on the piston, the difference $(p_{\text{gas}} - p_{\text{piston}})$ is the force per unit area that moves the piston. The irreversible increase in entropy in this case is given by

$$d_iS = \frac{p_{\text{gas}} - p_{\text{piston}}}{T} dV > 0 \quad (3.5.4)$$

In this case, the term $(p_{\text{gas}} - p_{\text{piston}})/T$ corresponds to the ‘thermodynamic force’ and dV/dt the corresponding ‘flow’. The term $(p_{\text{gas}} - p_{\text{piston}}) dV$ may be identified as the ‘uncompensated heat’ of Clausius. Since the change in the volume and $(p_{\text{gas}} - p_{\text{piston}})$ have the same sign, d_iS is always positive. In this case, $dS = d_eS + d_iS = dQ/T + (p_{\text{gas}} - p_{\text{piston}}) dV/T$. In the case of an ideal gas, since the energy is only a function of T , the

initial and final energies of the gas remain the same; the heat absorbed is equal to the work done in moving the piston $p_{\text{piston}} dV$. For a given change in volume, the maximum work is obtained for a reversible process in which $p_{\text{gas}} = p_{\text{piston}}$.

3.6 Entropy Changes Associated with Phase Transformations

In this section we will consider a simple example of an entropy exchange $d_e S$. Changes in the phase of a system, from a solid to a liquid or a liquid to vapor (as shown in Figure 1.3), provide a convenient situation because, at the melting or boiling point, the temperature remains constant even when heat is being exchanged. Hence, in the expression for the entropy change associated with the heat exchange, $d_e S = dQ/T$, the temperature T remains constant. The total entropy change ΔS due to the exchange of heat ΔQ is now easy to determine. In a solid-to-liquid transition, for example, if the melting temperature is T_m , we have

$$\Delta S = \int_0^{\Delta Q} \frac{dQ}{T_m} = \frac{\Delta Q}{T_m} \quad (3.6.1)$$

As discovered by Joseph Black, the heat absorbed, ‘the latent heat’, converts the solid to a liquid at a fixed temperature. Generally, this change happens at a fixed pressure and, hence, we may equate ΔQ to ΔH , the enthalpy change associated with melting. The enthalpy associated with the conversion of 1 mol of the solid to liquid is called the **molar enthalpy of fusion** ΔH_{fus} . The corresponding change in entropy, the **molar entropy of fusion** ΔS_{fus} , can now be written as

$$\boxed{\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m}} \quad (3.6.2)$$

Water, for example, has a heat of fusion of $6.008 \text{ kJ mol}^{-1}$ and a melting temperature of 273.15 K at a pressure of 1.0 atm . When 1 mol of ice turns to water, the entropy change $\Delta S_{\text{fus}} = 21.99 \text{ J K}^{-1} \text{ mol}^{-1}$.

Similarly, if the conversion of a liquid to vapor occurs at a constant pressure at its boiling point T_b , then the **molar entropy of vaporization** ΔS_{vap} and the **molar enthalpy of vaporization** ΔH_{vap} are related by

$$\boxed{\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}} \quad (3.6.3)$$

The heat of vaporization of water is $40.65 \text{ kJ mol}^{-1}$. Since the boiling point is 373.15 K at a pressure of 1.0 atm , from the above equation it follows that the molar entropy change $\Delta S_{\text{vap}} = 108.96 \text{ J K}^{-1} \text{ mol}^{-1}$, about five times the entropy change associated with the melting of ice. Since entropy increases with volume, the large increase in volume from about 18 mL (volume of 1 mol of water) to about 30 L (volume of 1 mol of steam at $p = 1 \text{ atm}$) is partly responsible for this larger change. The molar enthalpies of fusion and vaporization of some compounds are given in Table 3.1. (Thermodynamic data may be accessed using the NIST Chemistry WebBook at <http://webbook.nist.gov/chemistry>.)

Table 3.1 Enthalpies of fusion and vaporization at $p = 101.325 \text{ kPa} = 1.0 \text{ atm}$ and the corresponding transition temperatures.

Substance	T_m (K)	ΔH_{fus} (kJ mol $^{-1}$)	T_b (K)	ΔH_{vap} (kJ mol $^{-1}$)
H ₂ O	273.15	6.01	373.15	40.65
CH ₃ OH	175.5	3.18	337.7	35.21
C ₂ H ₅ OH	159.0	5.02	351.4	38.56
CH ₄	90.69	0.94	111.7	8.19
CCl ₄	250.15	3.28	349.9	29.82
NH ₃	195.4	5.66	239.8	23.33
CO ₂ (sublimes)	$T_{\text{sub}} = 194.65$			$\Delta H_{\text{sub}} = 25.13$
CS ₂	161.6	4.40	319.1	26.74
N ₂	63.15	0.71	77.35	5.57
O ₂	54.36	0.44	90.19	6.82

Source: D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 75th edition, 1994, CRC Press: Ann Arbor, MI.

3.7 Entropy of an Ideal Gas

In this section we will obtain the entropy of an ideal gas. Being a state function, entropy of an ideal gas can be expressed as a function of its volume, temperature and the amount in moles. For a closed system in which the changes of entropy are only due to the flow of heat, if we assume that the changes in volume V and temperature T take place so as to make $d_i S = 0$, then we have seen that (see Equation (3.4.16)) $dU = T dS + dW$. If $dW = -p dV$, and if we express dU as a function of V and T , we obtain

$$TdS = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + pdV \quad (3.7.1)$$

For an ideal gas, $(\partial U / \partial V)_T = 0$, because the energy U is only a function of T – as was demonstrated in the experiments of Joule and Gay-Lussac and others (see Section 1.4, Equation (1.4.6)). Also, by definition $(\partial U / \partial T)_V = NC_{\text{mV}}$, in which C_{mV} is the molar heat capacity at constant volume, which is found to be a constant. Hence Equation (3.7.1) may be written as

$$dS = \frac{p}{T} dV + NC_{\text{mV}} \frac{dT}{T} \quad (3.7.2)$$

Using the ideal gas law, $pV = NRT$, (3.7.2) can be integrated to obtain

$$S(V, T, N) = S_0(V_0, T_0, N) + NR \ln(V/V_0) + NC_{\text{mV}} \ln(T/T_0) \quad (3.7.3)$$

in which S_0 is the entropy of the initial state (V_0, T_0) . Since $U = C_{\text{mV}}NT + U_0$ for an ideal gas, entropy can also be written as a function of V , N and U . As described in Box 3.3, entropy is an extensive function. In expression (3.7.3), the extensivity of S as a function of V and N is not explicit because $S_0(V_0, T_0, N)$ contains terms that make S extensive. The requirement that entropy is extensive, i.e. $\lambda S(V, T, N) = S(\lambda V, T, \lambda N)$, can be used to show (Exercise 3.10) that the entropy of an ideal gas has the form

$$S(V, T, N) = N[s_0 + R \ln(V/N) + C_{\text{mV}} \ln(T)] \quad (3.7.4)$$

in which s_0 is a constant. In this form, the extensivity of S is explicit and it is easy to verify that $\lambda S(U, T, N) = S(\lambda U, T, \lambda N)$.

Box 3.3 Extensivity of energy and entropy

At a fixed pressure and temperature, if the amount of substance N is changed by a factor λ , the volume V also changes by the same factor. In many cases, the system's entropy S and energy U also change by the same factor λ . This property is called *extensivity*. Entropy is an extensive function of U , V and N : $S = S(U, V, N)$. That entropy is an *extensive function* can be expressed mathematically as

$$\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N)$$

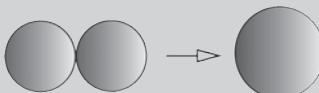
Similarly, energy is a function of S , V and N : $U = U(S, V, N)$ and

$$\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N)$$

Physically, extensivity implies that combining λ identical systems results in a larger system whose entropy is λ times the entropy of each of the systems. This means that the processes of combining λ identical systems is reversible with no entropy or energy change. Here is an example. Initially, two identical compartmentalized subsystems contain an ideal gas, both at the same p and T (see the figure below). The process of removing the wall between the two subsystems and creating a system that is twice as large requires neither work nor heat. Hence, the energy of the larger system is the sum of the energies of the subsystems.



Also, since the wall does not contribute to entropy, the process is reversible with no entropy change: $d_e S = d_i S = 0$. Therefore, we deduce that the initial entropy, which is the sum of the entropies of the two identical systems, equals the entropy of the final larger system. In this sense the entropy and energy of most systems can be assumed to be extensive functions.



On the other hand, entropy and energy are *not* extensive functions as expressed in the equations above when the process of combining identical systems to create a larger system involves a change in energy and entropy. Such is the case for very small systems, whose *surface* energy and entropy cannot be ignored as they can be for large systems. When two small drops of liquid are brought into contact, for example, they spontaneously coalesce to form a larger drop (see the figure above). Because the surface of the larger drop is not equal to the sum of the surfaces of the two initial drops, the energy of the larger drop does not equal the sum of energies of the two smaller drops. As we shall see in later chapters, $d_i S > 0$ in this process. Note also that it requires work to break the bigger drop into two smaller drops. Hence, neither entropy nor energy obey the above equations. However, there is no fundamental difficulty in taking the energy and entropy of the surface into account and formulating the thermodynamics of small systems.

3.8 Remarks about the Second Law and Irreversible Processes

As was emphasized by Planck [24], the statement of the Second Law and the concept of entropy can be made entirely macroscopic. This is perhaps why Einstein was convinced that for thermodynamics, ‘within

the framework of applicability of its basic concepts, it will never be overthrown'. Many modern expositions present the Second Law and entropy starting with their microscopic definitions based on the probability that belie their independence from microscopic theories of matter.

The Second Law is universal. In fact, its universality gives us a powerful means to understand the thermodynamic aspects of real systems through the usage of ideal systems. A classic example is Planck's analysis of radiation in thermodynamic equilibrium with matter (the 'black-body radiation') in which Planck considered idealized simple harmonic oscillators interacting with radiation. Planck considered simple harmonic oscillators, not because they are good approximations of molecules, but because the properties of radiation in thermal equilibrium with matter are universal, regardless of the particular nature of matter that it is interacting with. The conclusions one arrives at using idealized oscillators and the laws of thermodynamics must also be valid for all other forms of matter, however complex.

In the modern context, the formulation summarized in Figure 3.7 is fundamental for understanding thermodynamic aspects of self-organization, evolution of order and life that we see in Nature. When a system is isolated, $d_e S = 0$. In this case, the entropy of the system will continue to increase due to irreversible processes and reach the maximum possible value, the state of thermodynamic equilibrium. In the state of equilibrium, all irreversible processes cease. When a system begins to exchange entropy with the exterior, then, in general, it is driven away from equilibrium and the entropy-producing irreversible processes begin to operate. The exchange of entropy is due to the exchange of heat and matter. The entropy flowing out of the system is always larger than the entropy flowing into the system, the difference arising due to entropy produced by irreversible processes within the system. As we shall see in the following chapters, systems that exchange entropy with their exterior do not simply increase the entropy of the exterior, but may undergo dramatic spontaneous 'self-organization'. *The irreversible processes that produce entropy create these organized states.* Such self-organized states range from convection patterns in fluids to life. Irreversible processes are the driving force that creates this order.

Appendix 3.1 The Hurricane as a Heat Engine

The mechanism of a hurricane is essentially that of a heat engine, as shown in Figure A3.1 in the cycle ABCD. The maximum intensity of a hurricane, i.e. the maximum hurricane wind speed (Table A3.1), can be predicted using Carnot's theorem for the efficiency of a heat engine.

In a hurricane, as the wind spirals inwards towards the eye at low pressure, enthalpy (heat) is absorbed at the warm ocean-air interface in an essentially isothermal process: water vaporizes and mixes with the air, carrying with it the enthalpy of vaporization (segment AB). When this moist air reaches the hurricane's eyewall, it rises rapidly about 15 km along the eyewall. Since the pressure decreases with altitude, it expands adiabatically and cools (segment BC). As the rising moist air's temperature drops, the water vapor in it condenses as rain, releasing the enthalpy of vaporization (latent heat), a part of which is radiated into outer space. In a real hurricane, the air at the higher altitude flows out into the weather system. Theoretically, in order to close the Carnot cycle, it could be assumed that the enthalpy of vaporization is lost in an isothermal process (segment CD). The last step (segment DA) of the cycle is an adiabatic compression of dry air. During the cycle, a part of the enthalpy absorbed from the ocean is converted into mechanical energy of the hurricane wind.

The 'hurricane heat engine' operates between the ocean surface temperature T_1 (about 300 K) and the lower temperature T_2 (about 200 K) at the higher altitude, close to the upper boundary of the troposphere (tropopause). Let us look at the relationship between the heat absorbed at the ocean surface and the mechanical energy of the hurricane wind. In a time dt , if dQ_1 is the heat absorbed at the ocean surface, dQ_2 is the heat

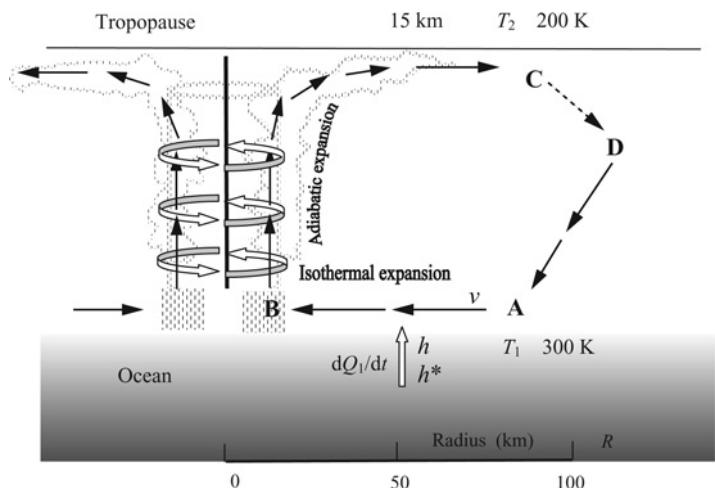


Figure A3.1 The hurricane operates as a heat engine, converting part of the heat absorbed at the ocean surface to mechanical energy of the hurricane wind.

radiated at the higher altitude and dW is the amount of heat converted to mechanical energy of the hurricane wind. Thus, according to the First Law,

$$\frac{dQ_1}{dt} = \frac{dW}{dt} + \frac{dQ_2}{dt} \quad (\text{A3.1.1})$$

Furthermore, according to Carnot's theorem:

$$\frac{dW}{dt} \leq \left(1 - \frac{T_2}{T_1}\right) \frac{dQ_1}{dt} \quad (\text{A3.1.2})$$

In a hurricane, the mechanical energy in the wind is converted to heat due to wind friction, almost all of it at the ocean surface. This heat in turn contributes to dQ_1/dt , the rate at which heat is absorbed at the ocean surface. When the hurricane is in a steady state, i.e. when all the flows are constant, all the mechanical energy entering the system as wind motion is converted to heat at the ocean surface: the rate of heat generation due

Table A3.1 The Saffir–Simpson hurricane intensity scale.

Category	Minimum central pressure (kPa)	Maximum sustained wind speed	
		m s^{-1}	mph
1	>98.0	33–42	74–95
2	97.9–96.5	43–49	96–110
3	96.4–94.5	50–58	111–130
4	94.4–92.0	59–69	131–155
5	<92.0	>70	>156

to wind friction is equal to dW/dt . Thus, the rate at which heat enters the Carnot cycle, dQ_1/dt , consists of two parts:

$$\frac{dQ_1}{dt} = \frac{dQ_{10}}{dt} + \frac{dW}{dt} \quad (\text{A3.1.3})$$

where dQ_{10}/dt is the rate at which heat enters the system in the absence of heating due to wind friction. Using Equation (A3.1.3) in Equation (A3.1.2), it is easy to see that

$$\frac{dW}{dt} \leq \left(\frac{T_1 - T_2}{T_2} \right) \frac{dQ_{10}}{dt} \quad (\text{A3.1.4})$$

A detailed study of the physics of the hurricane wind shows that the rate of heat generation per unit area of the ocean surface (i.e. vertically integrated heating) is equal to $C_D \rho |v|^3$, in which C_D is a constant, ρ is the air density and v is the wind velocity. The total amount of heat generated is obtained by integrating over the circular surface of radius R (from the center of the eye to the outer edge of the hurricane), which is the area of contact between the hurricane wind and the ocean. At steady state, since this integral equals dW/dt , we have

$$\frac{dW}{dt} = 2\pi \int_0^R C_D \rho |v|^3 r dr \quad (\text{A3.1.5})$$

The term dQ_{10}/dt is the rate at which enthalpy enters the inflowing dry air (segment AB). This energy is essentially the enthalpy of vaporization. It is proportional to the difference between specific enthalpies (enthalpies per unit mass) of the air saturated with moisture very close to the ocean surface h^* and the enthalpy of the inflowing dry air h (see Figure A3.1); it is also proportional to the wind velocity at the ocean surface. Thus, the enthalpy entering the system per unit area is $C_h \rho (h^* - h) |v|$. The total amount of enthalpy dQ_{10}/dt entering the hurricane system in this process equals the integral of this expression over the circular surface of radius R :

$$\frac{dQ_{10}}{dt} = 2\pi \int_0^R C_h \rho (h^* - h) |v| r dr \quad (\text{A3.1.6})$$

in which C_h is constant. Combining Equations (A3.1.4), (A3.1.5) and (A3.1.6) we obtain

$$\int_0^R C_D \rho |v|^3 r dr \leq \left(\frac{T_1 - T_2}{T_2} \right) \int_0^R C_h \rho (h^* - h) |v| r dr$$

If we assume that the dominant contribution to this integral comes from the region where the velocity is maximum, we can write

$$C_D \rho |v_{\max}|^3 \leq \left(\frac{T_1 - T_2}{T_2} \right) C_h \rho (h^* - h) |v_{\max}|$$

Thus, we arrive at the result

$$|v_{\max}|^2 \approx \left(\frac{T_1 - T_2}{T_2} \right) \frac{C_h}{C_D} (h^* - h) \quad (\text{A3.1.7})$$

Bister and Emanuel [25] have shown that the above result can be obtained through a more rigorous calculation. All the terms on the right-hand side are experimentally measured or theoretically estimated. A comparison of theory and experimental data suggests that the ratio C_h/C_D is in the range 0.75–1.5 [26]. Kerry Emanuel,

the originator of the above theory, has demonstrated that (A3.1.7) leads to remarkably good estimates of the hurricane wind speeds [4, 27].

When the system is in a steady state, the heat converted into mechanical energy of the hurricane wind balances the conversion of the wind energy back to heat. Under these conditions, if expression (A3.1.3) is used in (A3.1.1) we obtain $dQ_{10}/dt = dQ_2/dt$, which implies that heat of vaporization absorbed by the hurricane wind at the ocean surface is released at higher altitudes where the water condenses. This heat is ultimately radiated out of Earth's atmosphere. Thus, the vaporization and condensation of water vapor is a mechanism that transports heat from the oceans to higher altitudes where it is radiated into outer space. If this mechanism did not exist, the heat would be transported entirely through air currents, currents that would be very intense.

Appendix 3.2 Entropy Production in Continuous Systems

We consider a nonequilibrium situation in which a heat-conducting material is in contact with a hot reservoir on one side and a cold reservoir on the other (see Figure A3.2). We further assume that the conductor is insulated in such a way that it exchanges heat only with the heat reservoirs. After going through an initial transient change in temperature, such a system will settle into a steady state in which there is a uniform temperature gradient and a steady flow of heat. We will calculate the rate of entropy production at this steady state.

As each elemental quantity of heat dQ flows through the system the entropy increases. At a steady state, there is a steady flow of heat J_Q , which is the amount of heat flowing per unit area per second ($\text{J m}^{-2} \text{ s}^{-1}$). Since only one space direction is involved in this problem, we shall ignore the vectorial aspect of J_Q . For simplicity, we shall assume that the conductor has a unit area of cross-section. In this case the rate of flow of heat $dQ/dt = J_Q$. For continuous systems, the entropy production due to the flow of heat given by Equation (3.5.2) should be replaced by the entropy production due to the flow of heat through each infinitesimal segment of the heat conductor of width dx . The corresponding *entropy production per unit volume* at the point x is denoted by $\sigma(x)$. The quantity $(1/T_1 - 1/T_2)$ is now replaced by the change of the quantity $1/T$ over the length dx , namely $(\partial/\partial x)(1/T)dx$. Combining all these terms, we can now write the entropy production for flow of heat across a segment dx :

$$\sigma(x)dx = J_Q \left(\frac{\partial}{\partial x} \frac{1}{T} \right) dx \quad (\text{A3.2.1})$$

According to the Fourier law of heat conduction, $J_Q = -\kappa(\partial T/\partial x)$, in which κ is the heat conductivity.

Substituting this expression into Equation (A3.2.1) we can obtain

$$\sigma(x)dx = \alpha \frac{1}{T^2} \left(\frac{\partial T}{\partial x} \right)^2 dx \geq 0 \quad (\text{A3.2.2})$$

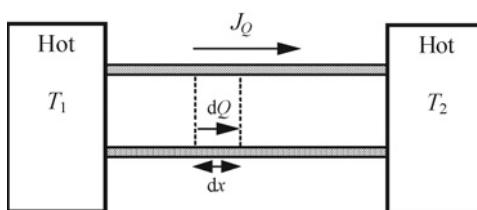


Figure A3.2 The continuous flow of heat is associated with entropy production.

The above expression gives the entropy production at each location x , i.e. the local entropy production. It is the entropy produced per unit time due to the flow of heat through the segment of width dx at the location x . As required by the Second Law, it is positive. At steady state, the temperature of the segment is constant. Hence, the entropy of the segment itself is not increasing; the entropy increase is due to the flow of heat down a temperature difference dT across the segment.

To obtain the total rate of entropy production due to the flow of heat from one end of the conductor to the other, we integrate the expression (A3.2.1) over the length l of the conductor:

$$\frac{d_i S}{dt} = \int_0^l \sigma(x) dx = \int_0^l J_Q \left(\frac{\partial}{\partial x} \frac{1}{T} \right) dx \quad (\text{A3.2.3})$$

When the system has reached steady state, since J_Q is constant, we can integrate this expression and rearrange terms to obtain

$$\frac{J_Q}{T_2} = \frac{J_Q}{T_1} + \frac{d_i S}{dt} \quad (\text{A3.2.4})$$

This result shows that the outflow of entropy equals the sum of entropy entering the system and the entropy produced due to the heat flow.

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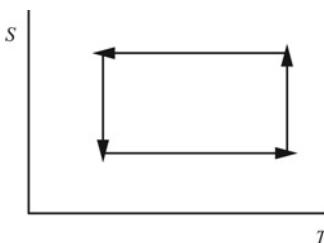
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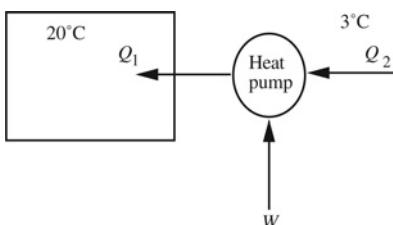
Examples

Example 3.1 Draw the S versus T diagram for the Carnot cycle.

Solution During the reversible adiabatic changes the change in entropy is zero. Hence, the S - T graph is as shown:



Example 3.2 A heat pump is used to maintain the inside temperature of a house at $20.0\text{ }^{\circ}\text{C}$ when the outside temperature is $3.0\text{ }^{\circ}\text{C}$. What is the minimum amount of work necessary to transfer 100.0 J of heat to the inside of the house?



Solution The ideal heat pump is the Carnot's engine running in reverse, i.e. it uses work to pump heat from a lower temperature to a higher temperature. For an ideal pump, $Q_1/T_1 = Q_2/T_2$. Thus, if $Q_1 = 100.0\text{ J}$ and $T_2 = 293.0\text{ K}$, we have $T_1 = 276.0\text{ K}$:

$$Q_2 = 276.0\text{ K}(100.0\text{ J}/293.0\text{ K}) = 94.0\text{ J}$$

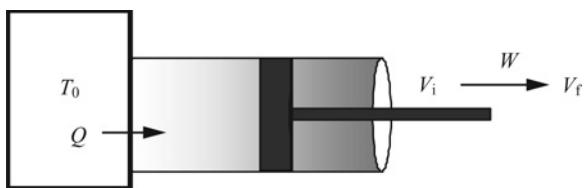
Thus, the heat pump absorbs 94.0 J from the outside and delivers 100.0 J to the inside. From the First Law it follows that the necessary work $W = Q_1 - Q_2 = 100.0\text{ J} - 94.0\text{ J} = 6.0\text{ J}$.

Example 3.3 The heat capacity of a solid is $C_p = 125.48\text{ J K}^{-1}$. What is the change in its entropy if it is heated from 273.0 K to 373.0 K ?

Solution This is a simple case of heat transfer, where $d_e S = dQ/T$. Hence:

$$\begin{aligned} S_{\text{final}} - S_{\text{initial}} &= \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln \left(\frac{T_f}{T_i} \right) \\ &= 125.48 \text{ J K}^{-1} \ln(373/273) = 39.2 \text{ J K}^{-1} \end{aligned}$$

Example 3.4 A container with N moles of ideal gas with an initial volume V_i is in contact with a heat reservoir at T_0 K. The gas expands isothermally to a volume V_f . Calculate: (a) the amount of heat absorbed by the gas in this expansion; (b) the increase in the entropy of the gas.



Solution The energy of an ideal gas depends only on its temperature. Hence, the heat absorbed Q must equal the work done W by the gas. The work done by the gas is

$$W = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{NRT_0}{V} dV = NRT_0 \ln \left(\frac{V_f}{V_i} \right) = Q$$

Since the process occurs isothermally, the change in entropy is

$$S_f - S_i = \int_{S_i}^{S_f} \frac{dQ}{T_0} = \frac{Q}{T_0} = N R \ln \left(\frac{V_f}{V_i} \right)$$

Note that the change in entropy can also be calculated using Equation (3.7.4).

Exercises

- 3.1 (a) For the Carnot cycle shown in Figure 3.2, show that $V_C/V_D = V_B/V_A$.
(b) Show the equivalence between a perpetual motion machine of the second kind and Carnot's theorem.
- 3.2 A refrigerator operating reversibly extracts 45.0 kJ of heat from a thermal reservoir and delivers 67.0 kJ as heat to a reservoir at 300 K. Calculate the temperature of the reservoir from which heat was removed.
- 3.3 What is the maximum work that can be obtained from 1000.0 J of heat supplied to a steam engine with a high-temperature reservoir at 120.0 °C if the condenser is at 25.0 °C?
- 3.4 Using the data shown in Figure 2.9, estimate the amount of entropy radiated by the Earth per hour.

- 3.5** The heat of combustion of gasoline is approximately 47 kJ g^{-1} . If a gasoline engine operated between 1500 K and 750 K, what is the maximum height that 1.0 kg of gasoline can lift a small aircraft that weighs 2000 kg?

- 3.6** The heat capacity C_p of a substance is given by

$$C_p = a + bT$$

where $a = 20.35 \text{ J K}^{-1}$ and $b = 0.2 \text{ J K}^{-2}$. Calculate the change in entropy in increasing the temperature of this substance from 298.15 K to 304.0 K.

- 3.7** When 0.5 J of heat passes between two large bodies in contact at temperatures of 70 °C and 25 °C, what is the change of entropy? If this occurs in 0.23 s, what is the rate of change of entropy $d_i S/dt$?

- 3.8** What is the entropy of 1.00 L of N₂(g) at $T = 350.0 \text{ K}$ and $p = 20.25 \text{ atm}$ given that the standard ($p = 1.00 \text{ bar}$, $T = 298.15 \text{ K}$) molar entropy $S^0_m = 191.6 \text{ J K}^{-1} \text{ mol}^{-1}$? (Calculate the molar amount of N₂ using the ideal gas equation.)

- 3.9** Which of the following are *not* extensive functions:

$$S_1 = (N/V)[S_0 + C_V \ln T + R \ln V]$$

$$S_2 = N[S_0 + C_V \ln T + R \ln(V/N)]$$

$$S_3 = N^2[S_0 + C_V \ln T + R \ln(V/N)]$$

- 3.10** Apply the condition $S(\lambda V, T, \lambda N) = \lambda S(V, T, N)$ to

$$S(V, T, N) = S_0(V_0, T_0, N) + NR \ln(V/V_0) + NC_V \ln(T/T_0)$$

differentiate it with respect to λ , set $\lambda = 1$, solve the resulting differential equation for S_0 and show that

$$S(V, T, N) = N[s_0 + R \ln(V/N) + C_{mV} \ln(T)]$$

- 3.11** In an isolated container, at a temperature T , N moles of a gas of volume V irreversibly expands into another chamber of equal volume, reaching a final volume $2V$. What is the irreversible increase in entropy?

4

Entropy in the Realm of Chemical Reactions

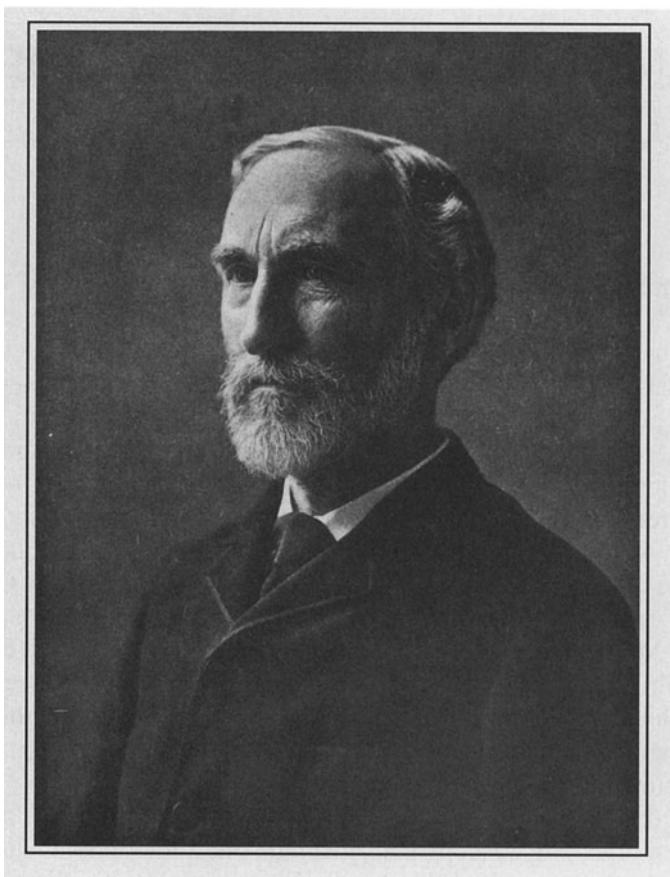
4.1 Chemical Potential and Affinity: The Thermodynamic Force for Chemical Reactions

Nineteenth century chemists did not pay much attention to the developments in thermodynamics, while experiments done by chemists – such as Gay-Lussac’s on the expansion of a gas into vacuum – were taken up and discussed by physicists for their thermodynamic implications. The interconversion of heat into other forms of energy was a matter of great interest, mostly to physicists. Among the chemists, the concept of heat as an indestructible caloric, a view supported by Lavoisier, largely prevailed [1]. As we noted in Chapter 2, the work of the Russian chemist Germain Hess on heats of reaction was an exception.

Motion is explained by the Newtonian concept of force, but what is the ‘driving force’ that was responsible for chemical change? Why do chemical reactions occur at all and why do they stop at certain points? Chemists called the ‘force’ that caused chemical reactions *affinity*, but it lacked a clear physical meaning and definition. For the chemists who sought quantitative laws, defining affinity, as precisely as Newton’s defined mechanical force, was a fundamental problem. In fact, this centuries-old concept had different interpretations at different times. ‘It was through the work of the thermochemists and the application of the principles of thermodynamics as developed by the physicists’, notes the chemistry historian Henry M. Leicester, ‘that a quantitative evaluation of affinity forces was finally obtained’ [1, p. 203]. The thermodynamic formulation of affinity as we know it today is due to Théophile De Donder (1872–1957), the founder of the Belgian school of thermodynamics.

De Donder’s formulation of chemical affinity [2,3] was founded on the concept of *chemical potential*, one of the most fundamental and far-reaching concepts in thermodynamics, which was introduced by Josiah Willard Gibbs (1839–1903). There were earlier attempts: in the nineteenth century, the French chemist Marcellin Berthelot (1827–1907) and the Danish chemist Julius Thomsen (1826–1909) attempted to quantify affinity using heats of reaction. After determining the heats of reactions for a large number of compounds, in 1875 Berthelot proposed a ‘principle of maximum work’, according to which ‘all chemical changes occurring without intervention of outside energy tend toward the production of bodies or of a system of bodies which liberate more heat’ [1, p. 205]. However, this suggestion met with criticism from Hermann Helmholtz and Walther Nernst (1864–1941), who noted that the principle could not apply to spontaneous endothermic chemical change that absorbed heat. The controversy continued until the concept of a chemical potential formulated by Gibbs (who was a professor at Yale University) became known in Europe. Later, it became clear that it was not the heat of reaction that characterized the evolution to the state of equilibrium but another

thermodynamic quantity called ‘free energy’. As we shall describe in this chapter, De Donder gave a precise definition of affinity using the concept of chemical potential and, through his definition of affinity, obtained a relation between the rate of entropy change and the chemical reaction rate. In De Donder’s formulation, the Second Law implies that chemical reactions drive the system to a state of thermodynamic equilibrium in which the affinities of the reactions equal zero.



J Willard Gibbs (1839–1903).

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4.1.1 Chemical Potential

Josiah Willard Gibbs introduced the idea of chemical potential in his famous work titled *On the Equilibrium of Heterogeneous Substances*, published in 1875 and 1878 [4–6]. Gibbs published his work in the *Transactions of the Connecticut Academy of Sciences*, a journal that was not widely read. This fundamental work of Gibbs remained in relative obscurity until it was translated into German by Wilhelm Ostwald (1853–1932) in 1892 and into French by Henri Le Châtelier (1850–1936) in 1899 [1]. Much of the present-day presentation of classical equilibrium thermodynamics can be traced back to this important work of Gibbs.

Gibbs considered a heterogeneous system (Figure 4.1) that consisted of several homogeneous parts, each part containing various substances s_1, s_2, \dots, s_n of masses m_1, m_2, \dots, m_n . His initial consideration did not

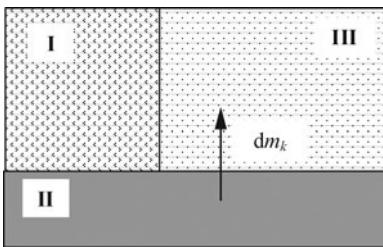


Figure 4.1 A heterogeneous system considered by Gibbs in which substances were exchanged between the parts I, II and III. The change in energy dU of any part when matter was exchanged reversibly is given by Equation (4.1.1).

include chemical reactions between these substances, but was restricted to their exchange between different homogeneous parts of a system. Arguing that the change in energy dU of a homogeneous part must be proportional to reversible changes in the masses of the substances, dm_1, dm_2, \dots, dm_n , Gibbs introduced the equation

$$dU = T dS - p dV + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n \quad (4.1.1)$$

for each homogeneous part. The coefficients μ_k are called the **chemical potentials**. The heterogeneous systems considered included different phases of a substance that exchanged matter. The considerations of Gibbs, however, were restricted to transformations between states in equilibrium. This restriction is understandable from the viewpoint of the classical definition of entropy, which required the system to be in equilibrium and the transformations between equilibrium states to be reversible so that $dQ = T dS$. In the original formulation of Gibbs, the changes in the masses dm_k in Equation (4.1.1) were due to the exchange of the substances between the homogeneous parts, a situation encountered when various phases of a substance exchange matter and reach equilibrium.

It is more convenient to describe chemical reactions by the change in the molar amounts of the reactants rather than the change in their masses, because chemical reaction rates and the laws of diffusion are most easily formulated in terms of molar amounts. Therefore, we shall rewrite Equation (4.1.1) in terms of the molar amounts N_k of the constituent substances, redefining the chemical potential accordingly:

$$dU = T dS - p dV + \mu_1 dN_1 + \mu_2 dN_2 + \dots + \mu_n dN_n$$

i.e.

$$dU = T dS - p dV + \sum_1^n \mu_k dN_k \quad (4.1.2)$$

The above equation implies that U is a function of S , V and N_k , and that the coefficients of dS , dV and dN_k are the corresponding derivatives:

$$\left(\frac{\partial U}{\partial S} \right)_{V, N_k} = T \quad \left(\frac{\partial U}{\partial V} \right)_{S, N_k} = -p \quad \left(\frac{\partial U}{\partial N_k} \right)_{S, V, N_j \neq k} = \mu_k \quad (4.1.3)$$

4.1.2 Chemical Reactions

Although Gibbs did not consider irreversible chemical reactions, Equation (4.1.1) that he introduced contained what was needed for the formulation of thermodynamics as a theory of irreversible processes in chemical systems. Using the chemical potential, the rates of entropy production due to chemical reactions can be

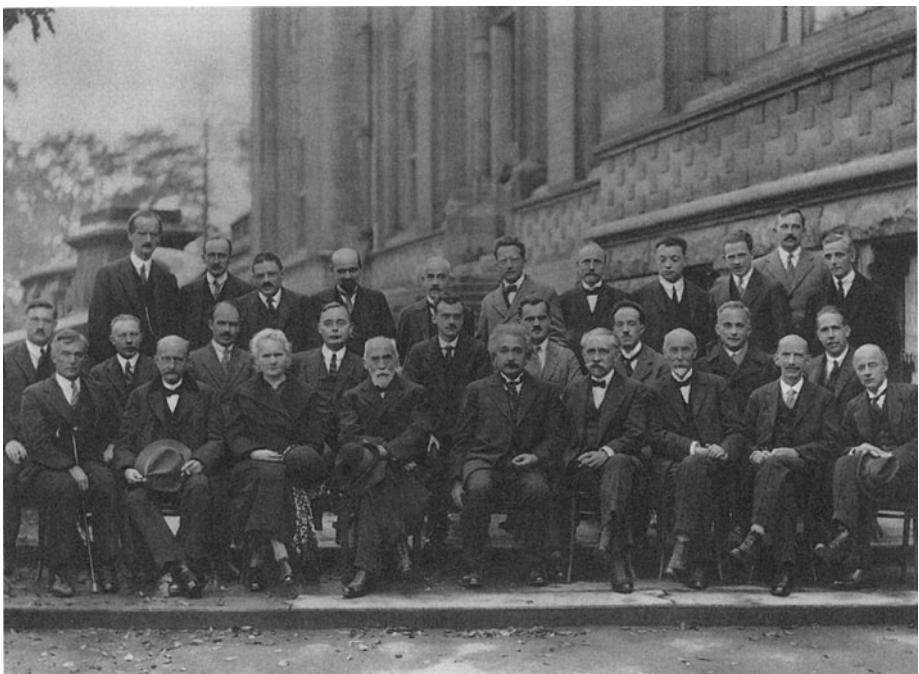
computed. By making the important distinction between the entropy change $d_e S$ due to a reversible exchange of matter and energy with the exterior and an irreversible increase of entropy $d_i S$ due to chemical reactions, De Donder formulated the thermodynamics of irreversible chemical transformations [2, 3]. Using the concept of chemical potential, De Donder took the ‘uncompensated heat’ of Clausius in the context of chemical reactions and gave it a clear expression.

Let us look at Equation (4.1.2) from the point of view of reversible entropy flow $d_e S$ and irreversible entropy production $d_i S$ that were introduced in the previous chapter. To make a distinction between irreversible chemical reactions and reversible exchange with the exterior, we express the change in the molar amounts dN_k as a sum of two parts:

$$dN_k = d_i N_k + d_e N_k \quad (4.1.4)$$

in which $d_i N_k$ is the change due to irreversible chemical reactions and $d_e N_k$ is the change due to the exchange of matter with the exterior. In Equation (4.1.2), Gibbs considered the *reversible* exchange of heat and matter. Because this corresponds to $d_e S$, we may write (see Equation (3.4.10))

$$d_e S = \frac{dU + p dV}{T} - \frac{\sum_1^n \mu_k d_e N_k}{T} \quad (4.1.5)$$



Théophile De Donder (1872–1957) (third row, fifth from the left) at the historic 1927 Solvay Conference. His book, L'Affinité was published the same year.

First row, L to R: I. Langmuir, M. Planck, Mme. Curie, H.A. Lorentz, A. Einstein, P. Langevin, Ch. E. Guye, C.T.R. Wilson, O.W. Richardson.

Second row, L to R: P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L. de Broglie, M. Born, N. Bohr.

Third row, L to R: A. Piccard, E. Henriot, P. Ehrenfest, Ed. Herzen, Th. De Donder, E. Schrödinger, E. Verschaffelt, W. Pauli, W. Heisenberg, R.H. Fowler, L. Brillouin. (Reproduced by courtesy of the International Solvay Institutes, Brussels, Belgium.)

De Donder recognized that, in a closed system, if the change of molar amounts dN_k were due to irreversible chemical reactions, then the resulting entropy production d_iS can be written as

$$d_iS = -\frac{\sum_1^n \mu_k d_i N_k}{T} \quad (4.1.6)$$

This is the ‘uncompensated heat’ of Clausius in the realm of chemical reactions. The validity of this equation lies in the fact that chemical reactions occur in such a way that d_iS is always positive in accordance with the Second Law. For the total change in entropy dS we have

$$dS = d_e S + d_i S \quad (4.1.7)$$

in which

$$d_e S = \frac{dU + p dV}{T} - \frac{1}{T} \sum_1^n \mu_k d_e N_k \quad (4.1.8)$$

and

$$d_i S = -\frac{1}{T} \sum_1^n \mu_k d_i N_k > 0 \quad (4.1.9)$$

For a closed system, which by definition does not exchange matter, $d_e N_k = 0$. Since the rates of chemical reaction specify dN_k/dt , the rate of entropy production can be written as

$$\frac{d_i S}{dt} = -\frac{1}{T} \sum_1^n \mu_k \frac{dN_k}{dt} > 0 \quad (4.1.10)$$

If we sum Equations (4.1.8) and (4.1.9) we recover (4.1.2):

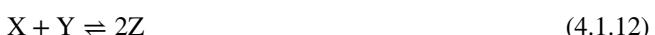
$$dU = T dS - p dV + \sum_1^n \mu_k dN_k \quad (4.1.11)$$

Further development of this theory relates chemical potential to measurable system variables such as p , T and N_k . The pioneering work of De Donder established a clear connection between entropy production and irreversible chemical reactions: the rate of entropy production d_iS/dt is related directly to the rates of chemical reactions that specify dN_k/dt . In a closed system, if initially the system is not in chemical equilibrium, then chemical reactions will take place that will irreversibly drive the system towards equilibrium. According to the Second Law of thermodynamics, this will happen in such a way that Equation (4.1.10) is satisfied.

4.1.3 Affinity

De Donder also defined the *affinity* of a chemical reaction, which enables us to write expression (4.1.10) in an elegant form, as the product of a thermodynamic force and a thermodynamic flow. The concept of affinity can be understood through the following simple example.

In a closed system, consider a chemical reaction of the form



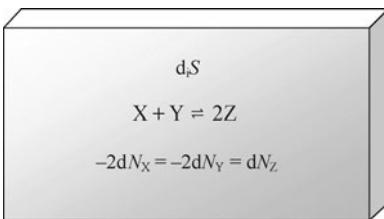


Figure 4.2 The changes in entropy d_iS due to irreversible chemical reactions is formulated using the concept of affinity. For the above reaction, the affinity $A \equiv \mu_X + \mu_Y - 2\mu_Z$, in which μ is the chemical potential.

In this case the changes in the molar amounts dN_X , dN_Y and dN_Z of the components X, Y and Z are related by the reaction stoichiometry. We can express this relation as

$$\frac{dN_X}{-1} = \frac{dN_Y}{-1} = \frac{dN_Z}{2} \equiv d\xi \quad (4.1.13)$$

in which $d\xi$ is the change in the extent of reaction ξ , which was introduced in Section 2.5. Using Equation (4.1.11), the total entropy change and the entropy change due to irreversible chemical reactions can now be written as

$$dS = \frac{dU + p dV}{T} + \frac{1}{T}(\mu_X + \mu_Y - 2\mu_Z)d\xi \quad (4.1.14)$$

$$d_iS = \frac{\mu_X + \mu_Y - 2\mu_Z}{T} d\xi > 0 \quad (4.1.15)$$

For a chemical reaction $X + Y \rightleftharpoons 2Z$, De Donder defined a new state variable called **affinity** as [1, p. 203, 2]

$$A \equiv \mu_X + \mu_Y - 2\mu_Z \quad (4.1.16)$$

This affinity is the driving force for chemical reactions (see Figure 4.2). A nonzero affinity implies that the system is not in thermodynamic equilibrium and that chemical reactions will continue to take place, driving the system towards equilibrium. In terms of affinity A , the rate of increase of entropy is written as

$$\boxed{\frac{d_iS}{dt} = \left(\frac{A}{T}\right) \frac{d\xi}{dt} > 0} \quad (4.1.17)$$

As in the case of entropy production due to heat conduction, the entropy production due to a chemical reaction is a product of a thermodynamic force A/T and a thermodynamic flow $d\xi/dt$. The flow in this case is the conversion of reactants to products (or vice versa), which is caused by the force A/T . We shall refer to the thermodynamic flow $d\xi/dt$ as the **velocity of reaction** or **rate of conversion**.

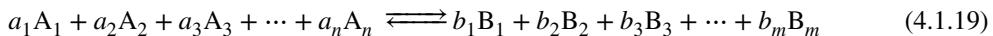
Though a nonzero affinity means that there is a driving force for chemical reactions, the velocity, $d\xi/dt$, of the chemical reactions is not specified by the value of affinity A . The velocities of chemical reactions are usually known through empirical means; there is no general relationship between the affinity and the velocity of a reaction.

At equilibrium, the thermodynamic flows and, hence, the entropy production must vanish. This implies that *in the state of equilibrium the affinity of a chemical reaction $A = 0$* . Thus, we arrive at the conclusion that, at thermodynamic equilibrium, the chemical potentials of the compounds X, Y and Z will reach values such that

$$A \equiv \mu_X + \mu_Y - 2\mu_Z = 0 \quad (4.1.18)$$

In Chapter 9, which is devoted to the thermodynamics of chemical processes, we will see how chemical potentials can be expressed in terms of experimentally measurable quantities such as concentrations and temperature. Equations such as (4.1.18) are specific predictions regarding the states of chemical equilibrium. These predictions have been amply verified by experiment and today they are routinely used in chemistry.

For a general chemical reaction of the form



the changes in the molar amounts of the reactants A_k and the products B_k are related in such a way that a change dN in molar amount of one of the species (reactants or products) completely determines the corresponding changes in all the other species. Consequently, there is only one independent variable, which can be defined as

$$\frac{dN_{A_1}}{-a_1} = \frac{dN_{A_2}}{-a_2} = \dots = \frac{dN_{A_n}}{-a_n} = \frac{dN_{B_1}}{b_1} = \frac{dN_{B_2}}{b_2} = \dots = \frac{dN_{B_m}}{b_m} = d\xi \quad (4.1.20)$$

The affinity A of the reaction (4.1.19) is defined as

$$A \equiv \sum_{k=1}^n a_k \mu_{A_k} - \sum_{k=1}^m b_k \mu_{B_k} \quad (4.1.21)$$

in which μ_{A_k} is the chemical potential of the reacting species A_k , etc. If several simultaneous reactions occur in a closed system, then an affinity A_i and a degree of advancement ξ_i can be defined for each reaction and the change of entropy is written as

$$dS = \frac{dU + pdV}{T} + \sum_i \frac{A_i}{T} d\xi_i \quad (4.1.22)$$

$$d_i S = \sum_i \frac{A_i}{T} d\xi_i \geq 0 \quad (4.1.23)$$

For the rate of entropy production we have the expression

$$\frac{d_i S}{dt} = \sum_k \frac{A_k}{T} \frac{d\xi_k}{dt} \geq 0$$

(4.1.24)

At thermodynamic equilibrium, the affinity A and the velocity $d\xi/dt$ of each reaction are zero. We will consider explicit examples of entropy production due to chemical reactions in Chapter 9.

In summary, when chemical reactions are included, the entropy is a function of the energy U , volume V and the molar amounts N_k , $S = S(U, V, N_k)$. For a closed system, following Equation (4.1.22), it can be written as a function of U , V and the extent of reaction ξ_k : $S = S(U, V, \xi_k)$.

We conclude this section with a historical remark. In Chapter 5 we will introduce a quantity called the Gibbs free energy. The Gibbs free energy of 1 mol of X can also be interpreted as the chemical potential of X. The conversion of a compound X to a compound Z causes a decrease in the Gibbs free energy of X and an increase in the Gibbs free energy of Z. Thus, the affinity of a reaction, $X + Y \rightleftharpoons 2Z$, defined as $A \equiv (\mu_X + \mu_Y - 2\mu_Z)$, can be interpreted as the negative of the change in Gibbs free energy when 1 mol of X and 1 mol of Y react to produce 2 mol of Z. This change in the Gibbs free energy, called the ‘Gibbs free energy of reaction’, is related to affinity A by a simple negative sign, but there is a fundamental conceptual difference between the two: *affinity is a concept that relates irreversible chemical reactions to entropy*, whereas *the Gibbs free energy is primarily used in connection with equilibrium states and reversible processes*. Nevertheless, in many texts the Gibbs free energy is used in the place of affinity and no mention is made about the relation between

entropy and reaction rates (for comments on this point, see Gerhartl [7]). Leicester, in his well-known book, *The Historical Background of Chemistry* [1, p. 206], traces the origin of this usage to the textbook [8] by Gilbert Newton Lewis (1875–1946) and Merle Randall (1888–1950):

The influential textbook of G.N. Lewis (1875–1946) and Merle Randall (1888–1950) which presents these ideas has led to the replacement of the term ‘affinity’ by the term ‘free energy’ in much of the English-speaking world. The older term has never been entirely replaced in thermodynamics literature, since after 1922 the Belgian school under Théophile De Donder (1872–1957) has made the concept of affinity still more precise.

De Donder’s affinity has an entirely different conceptual basis: it relates entropy to irreversible chemical processes that occur in Nature. It is clearly a more general view of entropy, one that does not restrict the idea of entropy to infinitely slow (‘quasi-static’) reversible processes and equilibrium states.

4.2 General Properties of Affinity

The affinity of a reaction is a state function, completely defined by the chemical potentials. In the following chapters we will see how the chemical potential of a substance can be expressed in terms of state variables such as pressure, temperature and concentration. Thus, affinity can be expressed as a function of p , T and N_k or it can also be expressed as a function of V , T and N_k . For a closed system, since all the changes in N_k can only be due to chemical reactions, it can be expressed in terms of V , T , ξ_k and the initial values of the molar amounts N_{k0} . We will now note some general properties of affinities that follow from the fact that chemical reactions can be interdependent when a substance is a reactant in more than one reaction.

4.2.1 Affinity and Direction of Reaction

The sign of affinity can be used to predict the direction of reaction. Consider the reaction $X + Y \rightleftharpoons 2Z$. The affinity is given by $A = \mu_X + \mu_Y - 2\mu_Z$. The sign of the velocity of reaction $d\xi/dt$ indicates the direction of reaction, i.e. whether the net conversion is from $X + Y$ to $2Z$ or from $2Z$ to $X + Y$. From the definition of ξ it follows that if $d\xi/dt > 0$ then the reaction ‘proceeds to the right’: $X + Y \rightarrow 2Z$; if $d\xi/dt < 0$ then the reaction ‘proceeds to the left’: $X + Y \leftarrow 2Z$. The Second Law requires that $A(d\xi/dt) \geq 0$. Thus, we arrive at the following relation between the sign of A and the direction of the reaction:

- If $A > 0$, the reaction proceeds to the right.
- If $A < 0$, the reaction proceeds to the left.

4.2.2 Additivity of Affinities

A chemical reaction can be the net result of two or more successive chemical reactions. For instance:



which shows that reaction (4.2.3) is the net result or ‘sum’ of the other two. By definition the affinities of the above three reactions are

$$A_1 = 2\mu_C + \mu_{O_2} - 2\mu_{CO} \quad (4.2.4)$$

$$A_2 = 2\mu_{CO} + \mu_{O_2} - 2\mu_{CO_2} \quad (4.2.5)$$

$$A_3 = \mu_C + \mu_{O_2} - \mu_{CO_2} \quad (4.2.6)$$

From these definitions it is easy to see that

$$A_1 + A_2 = 2A_3 \quad (4.2.7)$$

Clearly this result can be generalized to many reactions. We thus have the general result: *the sum of affinities of a sequence of reactions equals the affinity of the net reaction.*

The rate of entropy production for the above reactions (4.2.1) and (4.2.2) is the sum of the rates at which entropy is produced in the two reactions:

$$\frac{d_i S}{dt} = \frac{A_1}{T} \frac{d\xi_1}{dt} + \frac{A_2}{T} \frac{d\xi_2}{dt} > 0 \quad (4.2.8)$$

in which ξ_1 and ξ_2 are the corresponding extents of reactions. Note that for the net reaction (4.2.3), because the net conversion from ($C + O_2$) to CO_2 goes through the intermediate CO , $dN_C \neq dN_{CO_2}$, the loss of carbon is due to its conversion to CO and CO_2 , not just CO_2 . As a consequence, the corresponding extent of reaction $d\xi_3$ is not well defined and we cannot write $-dN_C = dN_{CO_2}$. Therefore, the rate of total entropy production cannot be written as $(A_3/T)(d\xi_3/dt)$ in general. However, if the reaction velocities $d\xi_1/dt$ and $d\xi_2/dt$ are equal, then the total rate of entropy production (4.2.8) may be written as

$$\frac{d_i S}{dt} = \frac{A_1 + A_2}{T} \frac{d\xi_1}{dt} = \frac{2A_3}{T} \frac{d\xi_1}{dt} = \frac{A_3}{T} \frac{d\xi_3}{dt} > 0 \quad (4.2.9)$$

in which $d\xi_3/dt \equiv 2(d\xi_1/dt)$, the reaction velocity of reaction (4.2.3). The condition $d\xi_1/dt = d\xi_2/dt$ means the rate of production of the intermediate CO in reaction (4.2.1) is balanced by the consumption of CO in reaction (4.2.2), i.e. N_{CO} , the amount of CO , remains constant. When the production of a substance X is exactly balanced by its consumption, it is said to be in a **steady state** (which can be expressed mathematically as $dN_X/dt = 0$). In many chemical reactions, the intermediate reactants are often in a steady state or nearly so. In a series of reactions in which intermediate compounds are produced and consumed, if all the intermediates are in a steady state, then it is possible to define an extent of reaction for the net reaction and write the rate of entropy production in terms of the affinity and the velocity of the net reaction.

4.2.3 Coupling between Affinities

In reactions coupled to each other through common reactants, it may appear as if one reaction with positive entropy production is compensating for the negative entropy production of the other in such a way that the total entropy production is positive, in accord with the Second Law. Consider the following example:



for which, as indicated, the corresponding affinity A_4 is assumed to be positive. We then expect the reaction to proceed to the right so that $d\xi_4/dt > 0$. It is possible to drive the reaction (4.2.10) effectively to the left, making $d\xi_4/dt < 0$, by ‘coupling’ it to another reaction:



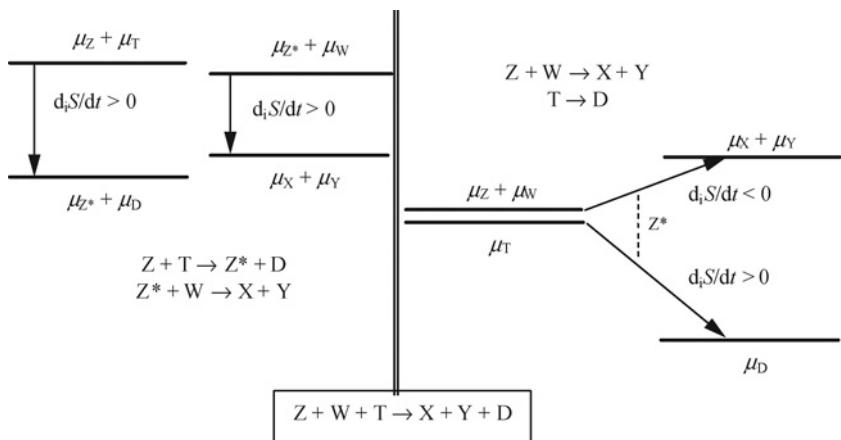
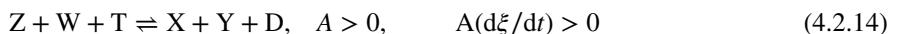
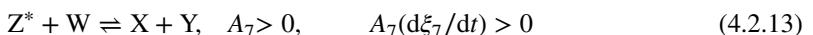
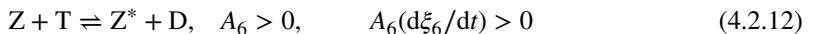


Figure 4.3 Entropy production in coupled reactions. The left and right panels show different ways of representing the same net reaction $Z + W + T \rightarrow X + Y + D$ resulting from two reaction steps. The left panel shows a reaction scheme and the corresponding chemical potentials in which entropy production of both reaction steps are positive. The right panel shows a reinterpretation of the same net reaction when the intermediate Z that couples the two reactions is in a steady state. In this case, the entropy production of one reaction is positive and the other is negative, but their sum, the total entropy production, remains positive.

The two reactions (4.2.10) and (4.2.11) could be coupled so that their total entropy production $A_4(d\xi_4/dt) + A_5(d\xi_5/dt) > 0$ but $A_4(d\xi_4/dt) < 0$. An example of a mechanism that makes such reaction reversal possible is (see Figure 4.3)



Once again, as indicated, the affinities and velocities of reactions (4.2.11) to (4.2.13) are assumed positive. The net reaction $Z + W + T \rightleftharpoons X + Y + D$ is an effective reversal of $X + Y \rightleftharpoons Z + W$ accompanied by $T \rightleftharpoons D$. This way of interpreting the net reaction can be expressed in terms of the affinities by noting that

$$A = A_6 + A_7 = -A_4 + A_5 \quad (4.2.15)$$

For the net reaction $Z + W + T \rightleftharpoons X + Y + D$, as discussed above, the corresponding velocity of reaction $d\xi/dt$ can be defined only when the intermediate Z^* is in a steady state, i.e. $d\xi_6/dt = d\xi_7/dt = d\xi/dt$. Under these steady-state conditions, we will now show that the rate of entropy production can be written as if it is due to two coupled reactions $Z + W \rightleftharpoons X + Y$ and $T \rightleftharpoons D$, each proceeding with velocity $d\xi/dt$.

The total rate of entropy production due to the two coupled reactions (4.2.12) and (4.2.13) is

$$\frac{d_i S}{dt} = \frac{A_6}{T} \frac{d\xi_6}{dt} + \frac{A_7}{T} \frac{d\xi_7}{dt} \geq 0 \quad (4.2.16)$$

Now, if $d\xi_6/dt = d\xi_7/dt = d\xi/dt$, expression (4.2.16) can be rewritten in terms of the affinities A_4 and A_5 of reactions (4.2.10) and (4.2.11) using the equality (4.2.15):

$$\frac{d_i S}{dt} = \frac{A_6 + A_7}{T} \frac{d\xi}{dt} = -\frac{A_4}{T} \frac{d\xi}{dt} + \frac{A_5}{T} \frac{d\xi}{dt} \geq 0 \quad (4.2.17)$$

In this expression, the affinities A_4 and A_5 are positive and, since we have assumed that the net reaction (4.2.14) proceeds to the right, $d\xi/dt > 0$. Thus, the first term on the right-hand side of (4.2.17) is negative but the second term is positive. It can easily be seen that the steady-state condition $d\xi_6/dt = d\xi_7/dt = d\xi/dt$ also implies that $-d\xi_4/dt = d\xi_5/dt = d\xi/dt$, which enables us to rewrite (4.2.17) as

$$\frac{d_i S}{dt} = \frac{A_4}{T} \frac{d\xi_4}{dt} + \frac{A_5}{T} \frac{d\xi_5}{dt} \geq 0 \quad \text{in which } \frac{A_4}{T} \frac{d\xi_4}{dt} < 0 \quad \text{and} \quad \frac{A_5}{T} \frac{d\xi_5}{dt} > 0 \quad (4.2.18)$$

The entropy production at every reaction step in the actual mechanism, however, is positive as indicated in (4.2.12)–(4.2.14). Such coupled reactions are common in biological systems.

4.3 Entropy Production Due to Diffusion

The concepts of chemical potential and affinity not only describe chemical reactions but also flow of matter from one region of space to another. With the concept of chemical potential, we are now in a position to obtain an expression for the entropy change due to diffusion, an example of an irreversible process we saw in Chapter 3 (see Figure 3.8). The concept of chemical potential turns out to have a wide reach. Other irreversible processes that can be described using a chemical potential will be discussed in Chapter 10. Here, we shall see how it can be used to describe diffusion.

When chemical potentials of a substance in adjacent parts of a system are unequal, diffusion of that substance takes place until the chemical potentials in the two parts equalize. The process is similar to the flow of heat due to a difference in temperature. Diffusion is another irreversible process for which we can obtain the rate of increase in entropy in terms of chemical potentials.

4.3.1 Discrete Systems

For simplicity, let us consider a system consisting of two parts of equal temperature T , one with chemical potential μ_1 and molar amount N_1 and the other with chemical potential μ_2 and molar amount N_2 , as shown in Figure 4.4. The flow of particles from one part to another can also be associated with an ‘extent of reaction’, though no real chemical reaction is taking place here:

$$-dN_1 = dN_2 = d\xi \quad (4.3.1)$$

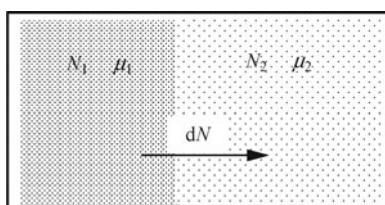


Figure 4.4 The irreversible process of diffusion can be described thermodynamically using the chemical potential. The variation of chemical potential with location corresponds to an affinity that drives a flow of matter. The corresponding entropy production is given by Equation (4.3.4).

Following Equation (4.1.14), the entropy change for this process can be written as

$$dS = \frac{dU + p dV}{T} - \frac{\mu_2 - \mu_1}{T} d\xi \quad (4.3.2)$$

$$= \frac{dU + p dV}{T} + \frac{A}{T} d\xi \quad (4.3.3)$$

in which the corresponding affinity $A = \mu_1 - \mu_2$. If $dU = dV = 0$, then the transport of particles results in the change of entropy given by

$$d_i S = \frac{\mu_1 - \mu_2}{T} d\xi > 0 \quad (4.3.4)$$

The positivity of this quantity required by the Second Law implies that particle transport is from a region of high chemical potential to a region of low chemical potential. This is, of course, the process of diffusion of particles from a region of higher concentration to a region of lower concentration in many cases, but it must be emphasized that the *driving force for diffusion is the gradient of chemical potential*, not the gradient of concentration as is often stated (see Appendix 4.1).

4.4 General Properties of Entropy

Entropy, as formulated in this and the previous chapter, encompasses all aspects of transformations of matter: changes in energy, volume and composition. Thus, every system in Nature, be it a gas, an aqueous solution, a living cell or a neutron star, is associated with a certain entropy, just as we associate an energy. We shall obtain explicit expressions for entropies of various systems in the following chapters and study how entropy production is related to irreversible processes. At this stage, however, we shall note some general properties of entropy as a function of state.

The entropy of a system is a function of its total energy U , volume V and molar amounts N_k of its constituents:

$$S = S(U, V, N_1, N_2, \dots, N_n) \quad (4.4.1)$$

As a function of variables U , V and N_k , the differential dS can be written as

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V, N_k} dU + \left(\frac{\partial S}{\partial V} \right)_{U, N_k} dV + \left(\frac{\partial S}{\partial N_k} \right)_{U, V, N_{j \neq k}} dN_k \quad (4.4.2)$$

Furthermore, from the general relation (4.1.2)

$$dU = T dS - p dV + \sum_{k=1}^n \mu_k dN_k$$

it follows that

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_k \frac{\mu_k}{T} dN_k \quad (4.4.3)$$

(Here we have combined the change in N_k due to chemical reactions and the change due to exchange with the exterior.) Comparing Equations (4.4.2) and (4.4.3) we immediately see that

$$\left(\frac{\partial S}{\partial U} \right)_{V, N_k} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V} \right)_{U, N_k} = \frac{p}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial N_k} \right)_{U, V, N_{j \neq k}} = -\frac{\mu_k}{T} \quad (4.4.4)$$

If the change in molar amounts N_k is only due to a chemical reaction, then the entropy can also be expressed as a function of U , V and ξ (see Example 4.1). Then one can show that

$$\left(\frac{\partial S}{\partial \xi}\right)_{U,V} = \frac{A}{T} \quad (4.4.5)$$

In addition, for any function of many variables, the ‘cross-derivatives’ must be equal, i.e. we must have equalities of the type

$$\frac{\partial^2 S}{\partial V \partial U} = \frac{\partial^2 S}{\partial U \partial V} \quad (4.4.6)$$

Relations (4.4.4) then imply that

$$\left(\frac{\partial}{\partial V} \frac{1}{T}\right)_U = \left(\frac{\partial}{\partial U} \frac{p}{T}\right)_V \quad (4.4.7)$$

Many such relations can be similarly derived because entropy is a function of state.

For homogeneous systems, we have seen in Chapter 3 (Box 3.3) that *entropy is an extensive variable*. Mathematically, this means that entropy S is a homogeneous function of the variables U , V and N_k , i.e. it has the following property:

$$S(\lambda U, \lambda V, \lambda N_1, \lambda N_2, \dots, \lambda N_s) = \lambda S(U, V, N_1, N_2, \dots, N_s) \quad (4.4.8)$$

Differentiating (4.4.8) with respect to λ and setting $\lambda = 1$, we obtain the well-known **Euler's theorem** for homogeneous functions:

$$S = \left(\frac{\partial S}{\partial U}\right)_{V,N_k} U + \left(\frac{\partial S}{\partial V}\right)_{U,N_k} V + \sum_k \left(\frac{\partial S}{\partial N_k}\right)_{U,V,N_{j \neq k}} N_k \quad (4.4.9)$$

Using relations (4.4.4) we can write this relation as

$$S = \frac{U}{T} + \frac{pV}{T} - \sum_k \frac{\mu_k N_k}{T} \quad (4.4.10)$$

In Equations (4.4.9) and (4.4.10), we have expressed entropy as a function of U , V and N_k . Since U can be expressed as a function of T , V and N_k , entropy can also be expressed as a function of T , V and N_k : $S = S(T, V, N_k)$. (The temperature and volume dependence of the energy U and enthalpy H of each component is obtained by using the empirical values of the heat capacity as described in Chapter 2.) Since T , V and N_k are directly measurable state variables, it is often more convenient to express thermodynamic quantities such as entropy and energy as functions of these state variables.

As a function of T , V and N_k , the derivatives of entropy can be obtained by expressing dU in relation (4.4.3) as a function of V , T and N_k :

$$\begin{aligned} TdS &= dU + p dV - \sum_k \mu_k dN_k \\ &= \left(\frac{\partial U}{\partial T}\right)_{V,N_k} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N_k} dV + \sum_k \left(\frac{\partial U}{\partial N_k}\right)_{V,T,N_{j \neq k}} N_k + p dV - \sum_k \mu_k dN_k \end{aligned}$$

i.e.

$$dS = \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_{T,N_k} + p \right] dV + \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_{V,N_k} dT - \sum_k \left(\frac{\mu_k}{T}\right) dN_k + \frac{1}{T} \sum_k \left(\frac{\partial U}{\partial N_k}\right)_{V,T,N_{j \neq k}} dN_k \quad (4.4.11)$$

In Equation (4.4.11), since the coefficient of dV must equal $(\partial S/\partial V)_{T,N_k}$, etc., we can make the following identification:

$$\left(\frac{\partial S}{\partial V}\right)_{T,N_k} = \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_{T,N_k} + \frac{p}{T} \quad (4.4.12)$$

$$\left(\frac{\partial S}{\partial T}\right)_{V,N_k} = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_{V,N_k} = \frac{C_V}{T} \quad (4.4.13)$$

$$\left(\frac{\partial S}{\partial N_k}\right)_{V,T,N_{j\neq k}} = -\frac{\mu_k}{T} + \frac{1}{T} \left(\frac{\partial U}{\partial N_k}\right)_{V,T,N_{j\neq k}} \quad (4.4.14)$$

Similar relations can be derived for U as a function of T , V and N_k .

The above relations are valid for homogeneous systems with uniform temperature and pressure. These relations can be extended to inhomogeneous systems as long as one can associate a well-defined temperature to every location. The thermodynamics of an inhomogeneous system can be formulated in terms of entropy density $s(T(\mathbf{x}), n_k(\mathbf{x}))$, which is a function of the temperature and the molar densities $n_k(\mathbf{x})$ (mol m^{-3}) at the point \mathbf{x} . If $u(\mathbf{x})$ is the energy density, then following (4.4.4) we have the relations

$$\left(\frac{\partial s}{\partial u}\right)_{n_k} = \frac{1}{T(x)}, \quad \left(\frac{\partial s}{\partial n_k}\right)_u = -\frac{\mu(x)}{T(x)} \quad (4.4.15)$$

in which the positional dependence of the variables is explicitly shown.

An empirically more convenient way is to express both entropy and energy densities as functions of the local temperature $T(\mathbf{x})$ and molar density $n_k(\mathbf{x})$, both of which can be directly measured:

$$u = u(T(x), n_k(x)) \text{ and } s = s(T(x), n_k(x)) \quad (4.4.16)$$

The total entropy and energy of the system are obtained by integrating the corresponding densities over the volume of the system:

$$S = \int_V s(T(x), n_k(x)) dV, \quad U = \int_V u(T(x), n_k(x)) dV \quad (4.4.17)$$

Since the system as a whole is not in thermodynamic equilibrium, the total entropy S in general is not a function of the total energy U and the total volume V . Nevertheless, a thermodynamic description is still possible as long as the temperature is well defined at each location \mathbf{x} .

Appendix 4.1 Thermodynamics Description of Diffusion

Expression (4.3.4) can be generalized to describe a continuous system in which μ and T are functions of the position vector \mathbf{r} and S is replaced by the entropy density s (the entropy per unit volume):

$$d_i s(r) = -\nabla \left(\frac{\mu(r)}{T(r)} \right) \cdot d\xi(r) \quad (A4.1.1)$$

in which the direction of the flow of particles (dN per unit area) is indicated by the vector $d\xi$. From Equation (A4.1.1), the *rate* of entropy production per unit volume due to diffusion can be written in terms of the particle current $\mathbf{J}_N \equiv d\xi/dt$ as

$$\frac{d_i s(r)}{dt} = -\nabla \left(\frac{\mu(r)}{T(r)} \right) \cdot \mathbf{J}_N \quad (\text{A4.1.2})$$

The particle current \mathbf{J}_N is a response to the gradient $\nabla(\mu(\mathbf{r})/T(\mathbf{r}))$. As we saw in Section 3.4, the entropy production due to each irreversible process in general has the above form of a product of a current or ‘flow’ \mathbf{J}_N and a ‘force’, such as the gradient $\nabla(\mu(\mathbf{r})/T(\mathbf{r}))$.

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Example

Example 4.1 If the change in molar amounts is entirely due to one reaction, show that entropy is a function of V , U and ξ and that

$$\left(\frac{\partial S}{\partial \xi} \right)_{U,V} = \frac{A}{T}$$

Solution Entropy is a function of U , V and N_k : $S(U, V, N_k)$. As shown in Section 4.4 (see Equation (4.4.3)), for the change in entropy dS we have

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_k \frac{\mu_k}{T} dN_k$$

If ξ is the extent of reaction of the single reaction that causes changes in N_k , then

$$dN_k = v_k d\xi, \quad k = 1, 2, \dots, s$$

in which v_k is the stoichiometric coefficient of the s species that participate in the reaction; v_k is negative for the reactants and positive for the products. For the species that do not participate in the reaction $v_k = 0$. The change in entropy dS can now be written as

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_{k=1}^s \frac{\mu_k v_k}{T} d\xi$$

Now, the affinity of the reaction $A = - \sum_{k=1}^s \mu_k v_k$ (note that v_k is negative for the reactants and positive for the products). Hence:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV + \frac{A}{T} d\xi$$

This shows that S is a function of U , V and ξ and that

$$\left(\frac{\partial S}{\partial \xi} \right)_{U,V} = \frac{A}{T}$$

If N_{10} is the molar amount of the reactant k at time $t = 0$, etc., and if we assume $\xi = 0$ at $t = 0$, then the molar amounts at any time t are $N_{10} + v_k \xi(t)$, $N_{20} + v_2 \xi(t)$, ..., $N_{s0} + v_s \xi(t)$, with all the other molar amounts being constant. Thus, $S = S(U, V, N_{10} + v_1 \xi(t), N_{20} + v_2 \xi(t), \dots, N_{s0} + v_s \xi(t))$. Thus, for a given initial molar amount N_{k0} , the entropy of a closed system with a chemical reaction is a function of U , V and ξ .

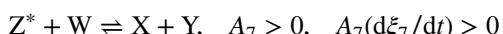
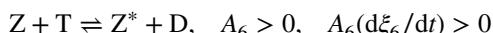
Exercises

- 4.1** In a living cell, which is an open system that exchanges energy and matter with the exterior, the entropy can decrease, i.e. $dS < 0$. Explain how this is possible in terms of $d_e S$ and $d_i S$. How is the Second Law valid in this case?
- 4.2** In SI units, what are the units of entropy, chemical potential and affinity?
- 4.3** Consider a reaction $A \rightarrow 2B$ in the gas phase (i.e. A and B are gases) occurring in a fixed volume V at a fixed temperature T . In the ideal gas approximation, at any time t , if N_A and N_B are molar amounts:
- (a) Write an expression for the total entropy.
 - (b) Assume that at time $t = 0$, $N_A(0) = N_{A0}$, $N_B(0) = 0$ and the extent of reaction $\xi(0) = 0$. At any time t , express the concentrations $N_A(t)$ and $N_B(t)$ in terms of $\xi(t)$.
 - (c) At any time t , write the total entropy as a function of T , V and $\xi(t)$ (and N_{A0} , which is a constant).
- 4.4** Consider the series of reactions:



Determine the conditions under which the rate of entropy production can be written in terms of the net reaction, i.e. $d_i S/dt = (A_3/T)(d\xi_3/dt)$ in which A_3 and ξ_3 are the affinity and the extent of reaction of the net reaction (3).

- 4.5** For the reaction scheme



- (a) Express dN_k/dt for each of the reactants and products, Z , T , Z^* , D , etc., in terms of the extents of reaction velocities $d\xi_6/dt$ and $d\xi_7/dt$.
- (b) For the steady state of Z^* , i.e. $dN_{Z^*}/dt = 0$, show that $d\xi_6/dt = d\xi_7/dt$ and that
- (c) the total entropy production $d_i S/dt$ can be written as

$$\frac{d_i S}{dt} = \frac{A_4}{T} \frac{d\xi_4}{dt} + \frac{A_5}{T} \frac{d\xi_5}{dt} \geq 0$$

in which quantities with subscripts 4 and 5 refer to the affinities and extents of reaction of the reactions $X + Y \rightleftharpoons Z + W$ and $T \rightleftharpoons D$ respectively.

- 4.6 (a)** Using the fact that S is a function of U , V and N_k , derive the relation

$$\left(\frac{\partial}{\partial V} \frac{\mu_k}{T} \right)_{U,N_k} + \left(\frac{\partial}{\partial N_k} \frac{p}{T} \right)_{V,U} = 0$$

- (b)** For an ideal gas, show that

$$\left(\frac{\partial}{\partial V} \frac{\mu_k}{T} \right)_{U,N_k} = -\frac{R}{V}$$

- (c)** For an ideal gas, show that $(\partial S / \partial V)_{T,N} = nR$ in which n is molar density (moles per unit volume).

Part II

Equilibrium Thermodynamics

5

Extremum Principles and General Thermodynamic Relations

Extremum Principles in Nature

For centuries we have been motivated by the belief that the laws of Nature are simple, and have been rewarded amply in our search for such laws. The laws of mechanics, gravitation, electromagnetism and thermodynamics can all be stated simply and expressed precisely with a few equations. The current search for a theory that unifies all the known fundamental forces between elementary particles is very much motivated by such a belief. In addition to simplicity, Nature also seems to ‘optimize’ or ‘economize’: natural phenomena occur in such a way that some physical quantity is minimized or maximized – or to use one word for both, ‘extremized’. The French mathematician Pierre Fermat (1601–1665) noticed that the change of direction of rays of light as they propagate through different media can all be precisely described using one simple principle: *light travels from one point to another along a path that minimizes the time of travel*. Later it was discovered that all the equations of motion in mechanics can be obtained by invoking the *principle of least action*, which states that if a body is at a point x_1 at a time t_1 and at a point x_2 at time t_2 , then the motion occurs so as to minimize a quantity called the *action*. (An engaging exposition of these topics can be found in Feynman’s *Lectures on Physics* [1].)

Equilibrium thermodynamics, too, has its extremum principles. In this chapter we will see that the approach to equilibrium under different conditions is such that a **thermodynamic potential** is extremized. Following this, in preparation for the applications of thermodynamics in the subsequent chapters, we will obtain general thermodynamic relations that are valid for all systems.

5.1 Extremum Principles Associated with the Second Law

We have already seen that all isolated systems evolve to the state of equilibrium in which the entropy reaches its maximum value or, equivalently, the rate of entropy production is zero. This is the basic extremum principle of equilibrium thermodynamics. However, we do not always deal with isolated systems. In many practical situations, the physical or chemical system under consideration is subject to constant pressure or temperature or both. In these situations, the positivity of entropy change due to irreversible processes, i.e. $d_i S > 0$, implies

the evolution of certain thermodynamic functions to their minimum values. Under each *constraint*, such as constant pressure, constant temperature or both, the evolution of the system to the state of equilibrium corresponds to the extremization of a thermodynamic quantity. These quantities are the *Gibbs energy*, the *Helmholtz energy* and *enthalpy* (which was introduced in Chapter 2), which, as we shall see in this chapter, are functions of state. They are also called **thermodynamic potentials**, in analogy with the potentials associated with forces in mechanics, whose minima are also points of stable mechanical equilibrium. *The systems we consider are either isolated or closed.*

5.1.1 Maximum Entropy

As we have seen in Chapter 4, owing to irreversible processes the entropy of an isolated system continues to increase ($d_iS > 0$) until it reaches the maximum possible value. The state thus reached is the state of equilibrium. Therefore, it may be stated that, *when U and V are constant, every system evolves to a state of maximum entropy*.

An equivalent statement is that, when U and V are constant, every system evolves to a state such that rate of entropy production d_iS/dt approaches zero. The latter statement refers to irreversible processes, whereas the former refers to the state. When processes are extremely slow, as may be the case for some chemical transformations, the system could be considered to be in ‘equilibrium’ with respect to all the irreversible processes whose rates have reduced to zero.

5.1.2 Minimum Energy

The Second Law also implies that, *at constant S and V, every system evolves to a state of minimum energy*. This can be seen as follows. We have seen that, for closed systems, $dU = dQ - p dV = T d_eS - p dV$. Because the total entropy change $dS = d_eS + d_iS$ we may write $dU = T dS - p dV - T d_iS$. Since S and V are constant, $dS = dV = 0$. Therefore, we have

$$dU = -T d_iS \leq 0 \quad (5.1.1)$$

Thus, in systems whose entropy is maintained at a fixed value, driven by irreversible processes, the energy evolves to the minimum possible value.

To keep the entropy constant, the entropy d_iS produced by irreversible processes has to be removed from the system. If a system is maintained at a constant T , V and N_k , the entropy remains constant. The decrease in energy $dU = -T d_iS$ is generally due to irreversible conversion of mechanical energy to heat that is removed from the system to keep the entropy (temperature) constant. A simple example is the falling of an object to the bottom of a fluid (Figure 5.1). Here, $dU = -T d_iS$ is the heat produced as a result of fluid friction or viscosity. If this heat is removed rapidly so as to keep the temperature constant, the system will evolve to a state of minimum energy. Note that, during the approach to equilibrium, $dU = -T d_iS < 0$ for every time interval dt . This represents a continuous conversion of mechanical energy (kinetic energy plus potential energy) into heat; at no time does the conversion occur in the opposite direction.

5.1.3 Minimum Helmholtz Energy

In closed systems maintained at constant T and V , a thermodynamic quantity called the **Helmholtz energy** or **Helmholtz free energy** evolves to its minimum value. The term ‘free energy’ has been in use because

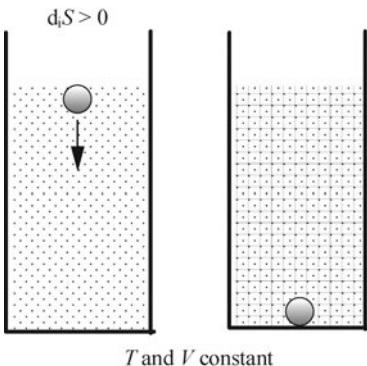


Figure 5.1 A simple illustration of the principle of minimum energy. In this example, if T and V are constant, then the entropy S is constant. At constant S and V the system evolves to a state of minimum energy.

the Helmholtz energy is the energy that is ‘free’, available to do work in an idealized reversible process (see Example 5.1). Helmholtz energy, denoted by F , is defined as

$$F \equiv U - TS \quad (5.1.2)$$

At constant T we have

$$\begin{aligned} dF &= dU - T dS = dU - T d_e S - T d_i S \\ &= dQ - p dV - T d_e S - T d_i S \end{aligned}$$

If V is also kept constant, then $dV = 0$, and for closed systems, $T d_e S = dQ$. Thus, at *constant T and V* , we obtain the inequality

$$dF = -T d_i S \leq 0 \quad (5.1.3)$$

as a direct consequence of the Second Law. This tells us that a system whose temperature and volume are maintained constant evolves such that the Helmholtz energy is minimized.

An example of the minimization of F is a chemical reaction, such as $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$, that takes place at a fixed value of T and V (see Figure 5.2a). To keep T constant, the heat generated by the reaction has to be removed. In this case, following De Donder’s identification of the entropy production in an irreversible chemical reaction (4.1.6), we have $T d_i S = -\sum_k \mu_k d_i N_k = -dF \geq 0$.

Another example is the natural evolution of the shape of a bubble (Figure 5.2b) enclosed in a box of fixed V and T . In the absence of gravity (or if the bubble is small enough that the gravitational energy is insignificant compared with other energies of the system), regardless of its initial shape, a bubble finally assumes the shape of a sphere of minimal size. The bubble’s size decreases irreversibly until the excess pressure inside the bubble balances the contracting force of the surface. During this process, the Helmholtz energy decreases with decreasing surface area. As the area of the bubble decreases irreversibly, the surface energy is transformed into heat which escapes to the surroundings (thus T is maintained constant). The entropy production in this irreversible process is given by $T d_i S = -dF$. Generally, Helmholtz energy increases with an increase in surface area (but not always) because molecules at the surface have higher energy than those below the surface. This excess surface energy γ is usually small, of the order of 10^{-2} J m^{-2} . For water, $\gamma = 7.275 \times 10^{-2} \text{ J m}^{-2}$. The thermodynamic drive to minimize the Helmholtz energy can be seen in the tendency of the surface to shrink, resulting in a ‘surface tension’ (force per unit length) whose numerical value equals γ . We will consider surface energy in more detail at the end of the chapter.

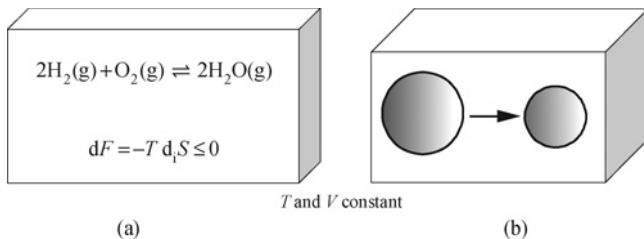


Figure 5.2 Examples of minimization of the Helmholtz free energy F . (a) If V and T are kept at a fixed value, then a chemical reaction will progress to a state of minimum F (but S is not a constant). In this case the irreversible production of entropy $T d_i S = -\sum_k \mu_k dN_k = -dF \geq 0$. (b) Similarly, the contraction of a bubble enclosed in a box of fixed V and T is an example. The contracting force on the bubble's surface decreases the bubble's radius until it reaches a point at which the excess pressure in the bubble balances the contracting force of the surface. In this case, we can identify $dF = -T d_i S \leq 0$ and determine the excess pressure in the bubble at equilibrium (see Section 5.6).

The minimization of Helmholtz energy is a very useful principle. Many interesting features, such as phase transitions and the formation of complex patterns in equilibrium systems [2], can be understood using this principle.

That Helmholtz free energy is a state function follows from its definition (5.1.2). We can show that F is function of T , V and N_k and obtain its derivatives with respect to these variables. From Equation (5.1.2) it follows that $dF = dU - T dS - S dT$. For the change of entropy due to the exchange of energy and matter we have $T d_e S = dU + p dV - \sum_k \mu_k d_e N_k$. For the change of entropy due to an irreversible chemical reaction we have $T d_i S = -\sum_k \mu_k d_i N_k$. For the total change in entropy, we have $T dS = T d_e S + T d_i S$. Substituting these expressions for dS in the expression for dF we obtain

$$\begin{aligned} dF &= dU - T \left[\frac{dU + p dV}{T} - \frac{1}{T} \sum_k \mu_k d_e N_k \right] - T \frac{\sum_k \mu_k d_i N_k}{T} - S dT \\ &= -p dV - S dT + \sum_k \mu_k (d_e N_k + d_i N_k) \end{aligned} \quad (5.1.4)$$

Since $dN_k = d_e N_k + d_i N_k$ we may write Equation (5.1.4) as

$$dF = -p dV - S dT + \sum_k \mu_k dN_k \quad (5.1.5)$$

This shows that F is a function of V , T and N_k . It also leads to the following identification of the derivatives of $F(V, T, N_k)$ with respect to V , T and N_k .¹

$$\left(\frac{\partial F}{\partial V} \right)_{T, N_k} = -p, \quad \left(\frac{\partial F}{\partial T} \right)_{V, N_k} = -S, \quad \left(\frac{\partial F}{\partial N_k} \right)_{T, V} = \mu_k \quad (5.1.6)$$

It is straightforward to include surface or other contributions to the energy (see Equations (2.2.10) and (2.2.11)) into the expression for F and obtain similar derivatives.

¹In this and the following chapters, for derivatives with respect to N_k , we assume the subscript $N_i \neq k$ is understood and drop its explicit use.

If the changes in N_k are only due to a chemical reaction, then F is a function of T , V and the extent of reaction ξ . Then it can easily be shown that (Exercise 5.2)

$$\left(\frac{\partial F}{\partial \xi} \right)_{T,V} = -A \quad (5.1.7)$$

5.1.4 Minimum Gibbs Energy

If both the pressure and temperature of a closed system are maintained constant, then the quantity that is minimized at equilibrium is the **Gibbs energy**, also called **Gibbs free energy**. We shall denote this quantity by G . As in the case of Helmholtz free energy, the term ‘free energy’ is used to note the fact that G is the maximum energy available for doing work (through an idealized reversible process). Gibbs energy is defined as the state function

$$G \equiv U + pV - TS = H - TS \quad (5.1.8)$$

where we have used the definition of enthalpy $H = U + pV$. Just as F evolves to a minimum when T and V are maintained constant, G evolves to a minimum when the pressure p and temperature T are maintained constant. When p and T are constant, $dp = dT = 0$ and we can relate dG to $d_i S$ as follows:

$$\begin{aligned} dG &= dU + p dV + V dp - T dS - S dT \\ &= dQ - p dV + p dV + V dp - T d_e S - T d_i S - S dT \\ &= -T d_i S \leq 0 \end{aligned} \quad (5.1.9)$$

where we have used the fact that $T d_e S = dQ$ for closed systems and $dp = dT = 0$.

The Gibbs energy is mostly used to describe chemical processes because the usual laboratory situation corresponds to constant p and T . The irreversible evolution of G to its minimum value can be related to the affinities A_k of the reactions and the reaction velocities $d\xi_k/dt$ (in which the index k identifies different reactions) using Equation (4.1.23):

$$\frac{dG}{dt} = -T \frac{d_i S}{dt} = - \sum_k A_k \frac{d\xi_k}{dt} \leq 0 \quad (5.1.10)$$

or

$$dG = - \sum_k A_k d\xi_k \leq 0 \quad (5.1.11)$$

in which the equality on the right-hand side holds at equilibrium. Equation (5.1.11) shows that, at constant p and T , G is a function of the state variables $d\xi_k$, the extent of reaction for reaction k . It also follows that

$$-A_k = \left(\frac{\partial G}{\partial \xi_k} \right)_{p,T} \quad (5.1.12)$$

In view of this relation, calling the affinity, which is a derivative of Gibbs energy, the ‘Gibbs free energy of reaction’, as is commonly done in many texts, is inappropriate. For a chemical reaction shown in Figure 5.3a, as shown in Figure 5.3b, at constant p and T , the extent of reactions $d\xi_k$ will evolve to a value that minimizes $G(\xi_k, p, T)$.

Note that G evolves to its minimum value monotonically in accordance with the Second Law. Thus, ξ cannot reach its equilibrium value, as a pendulum does, in an oscillatory manner. For this reason, an

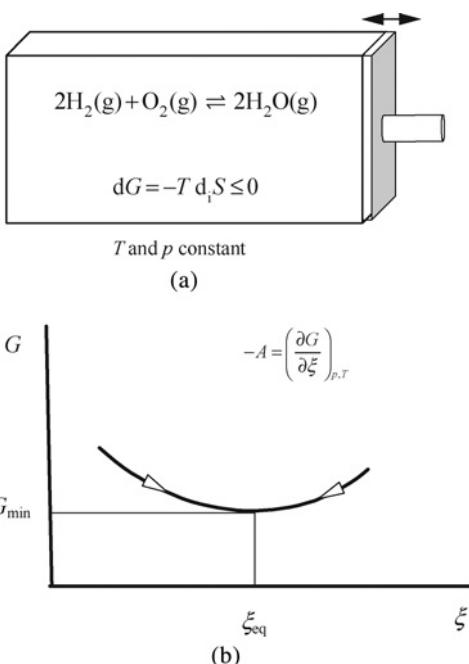


Figure 5.3 Minimization of the Gibbs energy G . (a) Under conditions of constant p and temperature T , irreversible chemical reactions will drive the system to a state of minimum G . (b) The extent of reaction ξ evolves to ξ_{eq} , which minimizes G .

oscillatory approach to equilibrium in a chemical reaction is impossible. This does not mean that concentration oscillations in chemical systems are not possible, as it was once widely thought. As we will see in later chapters, in systems that are far from equilibrium, concentration oscillations *can* occur without violating the second law; in fact these oscillations are accompanied by continuous entropy production.

We showed above that F is function of V , T and N_k . In a similar manner, it is straightforward to show that (Excercise 5.3)

$$\boxed{\mathrm{d}G = V \mathrm{d}p - S \mathrm{d}T + \sum_k \mu_k \mathrm{d}N_k} \quad (5.1.13)$$

This expression shows that G is function of p , T and N_k and that

$$\boxed{\left(\frac{\partial G}{\partial p}\right)_{T,N_k} = V, \quad \left(\frac{\partial G}{\partial T}\right)_{p,N_k} = -S, \quad \left(\frac{\partial G}{\partial N_k}\right)_{T,p} = \mu_k} \quad (5.1.14)$$

One very useful property of the Gibbs free energy is its relation to the chemical potential. From a homogeneous system we have shown that (Equation (4.4.10)) $U = TS - pV + \sum_k \mu_k N_k$. Substituting this into the definition of G (Equation (5.1.8)) we obtain

$$\boxed{G = \sum_k \mu_k N_k} \quad (5.1.15)$$

For a pure compound, $G = \mu N$. Therefore, one might think of the chemical potential μ as the Gibbs energy per mole of a pure compound. For a multicomponent system, dividing Equation (5.1.15) by N , the total molar amount, we see that the molar Gibbs energy

$$G_m \equiv \frac{G}{N} = \sum_k \mu_k x_k \quad (5.1.16)$$

in which x_k are the mole fractions. Since G must be an extensive function, we see that $G(p, T, N_k) = G(p, T, x_k N) = NG_m(p, T, x_k)$, that is G_m is a function of p, T and the mole fractions x_k . From Equation (5.1.16) it then follows that *in a multicomponent system the chemical potential is a function of p, T and the mole fractions x_k : $\mu_k = \mu_k(p, T, x_k)$.* (When we apply these general concepts to particular systems, we will obtain explicit expressions for Gibbs energies and chemical potentials. For example, in Chapter 8 we will see that for mixtures of compounds that interact very weakly with each other, what are called **ideal mixtures**, the chemical potential of a component can be written in the form $\mu_k(p, T, x_k) = \mu_k^*(p, T) + RT \ln x_k$, in which $\mu_k^*(p, T)$ is the chemical potential of the pure compound.)

Furthermore, as shown in Example 5.3, at constant p and T , we have the differential relation

$$(dG_m)_{p,T} = \sum_k \mu_k dx_k \quad (5.1.17)$$

In this relation the dx_k are not all independent because $\sum_k x_k = 1$ for mole fractions x_k .

5.1.5 Minimum Enthalpy

In Chapter 2 we introduced the enthalpy

$$H \equiv U + pV \quad (5.1.18)$$

Like the Helmholtz energy F and the Gibbs energy G , the enthalpy is also associated with an extremum principle: *at fixed entropy S and pressure p , the enthalpy H evolves to its minimum value.* This can be seen as before by relating the enthalpy change dH to $d_i S$. Since we assume that p is constant, we have

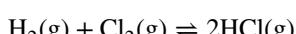
$$dH = dU + p dV = dQ \quad (5.1.19)$$

For a closed system, $dQ = T d_e S = T(dS - d_i S)$. Hence, $dH = T dS - T d_i S$. However, because the total entropy S is fixed, $dS = 0$. Therefore, we have the relation

$$dH = -T d_i S \leq 0 \quad (5.1.20)$$

in accordance with the Second Law. When irreversible chemical reactions take place, we normally do not encounter situations in which the total entropy remains constant. For illustrative purposes, however, it is possible to give an example.

Consider the reaction



In this reaction, the total number of molecules does not change. As we have seen in Section 3.7, the entropy of an ideal gas $S(V, T, N) = N[s_0 + R \ln(V/N) + C_V \ln(T)]$. Although there is a considerable difference in the heat capacity of molecules with different numbers of atoms, the difference in the heat capacity of two diatomic molecules is relatively small. The difference in the term s_0 is also small for two diatomic molecules. If we ignore these small differences in the entropy between the three species of diatomic molecules, then the entropy, which depends on N_k, V and T , will essentially remain constant if T and V are maintained constant. At the same time, since the number of molecules does not change, the pressure p remains constant

(assuming ideal gas behavior). Since this reaction is exothermic, the removal of heat produced by the reaction is necessary to keep T constant. Under these conditions, both p and S remain constant as the reaction proceeds and the enthalpy reaches its minimum possible value when the system reaches the state of equilibrium. For an arbitrary chemical reaction, V and T have to be adjusted simultaneously so as to keep p and S constant, which is not a simple task.

Just as we derived $dF = -p \, dV - S \, dT + \sum_k \mu_k \, dN_k$, it can easily be shown that (Exercise 5.4)

$$dH = T \, dS + V \, dp + \sum_k \mu_k \, dN_k \quad (5.1.21)$$

This equation shows that H can be expressed as a function of S , p and N_k . The derivatives of H with respect to these variables are

$$\left(\frac{\partial H}{\partial p} \right)_{S,N_k} = V, \quad \left(\frac{\partial H}{\partial S} \right)_{p,N_k} = T, \quad \left(\frac{\partial H}{\partial N_k} \right)_{S,p} = \mu_k \quad (5.1.22)$$

Once again, if the change in N_k is only due to a chemical reaction, then H is a function of p , S and ξ , and we have

$$\boxed{\left(\frac{\partial H}{\partial \xi} \right)_{p,S} = -A} \quad (5.1.23)$$

5.1.6 Extremum Principles and Stability of the Equilibrium State

In thermodynamics, the existence of extremum principles have an important consequence for the behavior of microscopic fluctuations. Since all macroscopic systems are made of a very large number of molecules that are in constant random motion, thermodynamic quantities, such as temperature, pressure and concentration, undergo small fluctuations. Why do these fluctuations not slowly drive the thermodynamic variables from one value to another, just as small random fluctuations in the positions of an object slowly move the object from one location to another (a phenomenon called Brownian motion)? The temperature or concentration of a system in thermodynamic equilibrium fluctuates about a fixed value but does not drift randomly. This is because *the state of equilibrium is stable*. As we have seen, irreversible processes drive the system to the equilibrium state in which one of the potentials is extremized. Thus, whenever a fluctuation drives the system away from the state of equilibrium, irreversible processes restore the state of equilibrium. The tendency of the system to reach and remain at an extremum value of a thermodynamic potential keeps the system stable. In this way the stability of the equilibrium state is related to the existence of thermodynamic potentials.

The state of a system is not always stable. There are situations in which fluctuations can drive a system from one state to another. In this case the initial state is said to be thermodynamically unstable. Some homogeneous mixtures become unstable when the temperature is decreased; driven by fluctuations, they then evolve to a state in which the components separate into two distinct phases, a phenomenon called ‘phase separation’. We shall discuss thermodynamic stability more extensively in Chapters 12, 13 and 14.

In addition, when a system is far from thermodynamic equilibrium, the state to which the system will evolve is, in general, not governed by an extremum principle; there is not an identifiable thermodynamic potential that is minimized due to the Second Law. Furthermore, the irreversible processes that assure the stability of the equilibrium state may do just the contrary and make the system unstable. The consequent instability under far-from-equilibrium systems drives the system to states with a high level of organization, such as concentration oscillations and spontaneous formation of spatial patterns. We shall discuss far-from-equilibrium instability and the consequent ‘self-organization’ in Chapters 18 and 19.

Table 5.1 Legendre transforms in thermodynamics.

$U(S, V, N_k) \rightarrow F(T, V, N_k) = U - TS$	S replaced by $\left(\frac{\partial U}{\partial S}\right)_{V, N_k} = T$
$U(S, V, N_k) \rightarrow H(S, p, N_k) = U + pV$	V replaced by $\left(\frac{\partial U}{\partial V}\right)_{S, N_k} = -p$
$U(S, V, N_k) \rightarrow G(T, p, N_k) = U + pV - TS$	S replaced by $\left(\frac{\partial U}{\partial S}\right)_{V, N_k} = T$ and V replaced by $\left(\frac{\partial U}{\partial V}\right)_{S, N_k} = -p$

5.1.7 Legendre Transformations

The relations between the thermodynamic functions $F(T, V, N_k)$, $G(T, p, N_k)$ and $H(S, p, N_k)$ and the total energy $U(S, V, N_k)$, expressed as a function of S , V and N_k (which follows from Equation (4.1.2) introduced by Gibbs), are particular instances of a general class of relations called Legendre transformations. In a Legendre transformation, a function $U(S, V, N_k)$ is transformed to a function in which one or more of the independent variables S , V , and N_k are replaced by the corresponding partial derivatives of U . Thus, $F(T, V, N_k)$ is a Legendre transform of U in which S is replaced by the corresponding derivative $(\partial U / \partial S)_{V, N_k} = T$. Similarly, $G(T, p, N_k)$ is a Legendre transform of U in which S and V are replaced by their corresponding derivatives $(\partial U / \partial S)_{V, N_k} = T$ and $(\partial U / \partial V)_{S, N_k} = -p$. We thus have the general table of Legendre transforms shown in Table 5.1.

Legendre transforms show us the general mathematical structure of thermodynamics. Clearly, not only are there more Legendre transforms of $U(S, V, N_k)$ that can be defined but also of $S(U, V, N_k)$, and indeed they are used in some situations. A detailed presentation of the Legendre transforms in thermodynamics can be found in the text by Herbert Callen [3]. (Legendre transforms also appear in classical mechanics: the Hamiltonian is a Legendre transform of the Lagrangian.)

5.2 General Thermodynamic Relations

As Einstein noted (see Introduction in Chapter 1), it is remarkable that the two laws of thermodynamics are simple to state, but have a wide range of applicability; they help us understand many different phenomena in systems ranging from gases to galaxies. Thermodynamics gives us many general relations between state variables that are valid for *any system in equilibrium*. In this section, we shall present a few important general relations. We will apply these to particular systems in later chapters. As we shall see in Chapters 15 to 17, the applicability of these relations can also be extended to nonequilibrium systems that are locally in equilibrium.

5.2.1 The Gibbs–Duhem Equation

One of the important general relations is the Gibbs–Duhem equation, named after Josiah Willard Gibbs (1839–1903) and Pierre Duhem (1861–1916). It shows that the intensive variables T , p and μ_k are not all independent. The Gibbs–Duhem equation is obtained from the fundamental relation (4.1.2), through which Gibbs introduced the chemical potential

$$dU = T dS - p dV + \sum_k \mu_k dN_k \quad (5.2.1)$$

and relation (4.4.10), which can be rewritten as

$$U = TS - pV + \sum_k \mu_k N_k \quad (5.2.2)$$

We recall the latter follows from the assumption that entropy is an extensive function of U , V and N_k and the use of Euler's theorem. The differential of (5.2.2) is

$$dU = T dS + S dT - V dp - p dV + \sum_k (\mu_k dN_k + N_k d\mu_k) \quad (5.2.3)$$

This relation can be consistent with (5.2.1) only if

$$S dT - V dp + \sum_k N_k d\mu_k = 0 \quad (5.2.4)$$

This equation is called the **Gibbs–Duhem equation**. It shows that changes in the intensive variables T , p and μ_k cannot all be independent. We shall see in Chapter 7 that the Gibbs–Duhem equation can be used to understand the equilibrium between phases and the variation of boiling point with pressure as described by the Clausius–Clapeyron equation.

At constant T and p , from Equation (5.2.4) it follows that $\sum_k N_k (d\mu_k)_{p,T} = 0$. Since the change in the chemical potential is $(d\mu_k)_{p,T} = \sum_i (\partial\mu_k/\partial N_i) dN_i$, we can write this expression as

$$\sum_{k,i} N_k \left(\frac{\partial \mu_k}{\partial N_i} \right)_{p,T} dN_i = \sum_i \left[\sum_k \left(\frac{\partial \mu_k}{\partial N_i} \right)_{p,T} N_k \right] dN_i = 0 \quad (5.2.5)$$

Since dN_i are independent and arbitrary variations, Equation (5.2.5) can be valid only if the coefficient of every dN_i is equal to zero. Thus, we have $\sum_k (\partial\mu_k/\partial N_i)_{p,T} N_k = 0$. Furthermore, since

$$\left(\frac{\partial \mu_k}{\partial N_i} \right)_{p,T} = \left(\frac{\partial^2 G}{\partial N_i \partial N_k} \right)_{p,T} = \left(\frac{\partial^2 G}{\partial N_k \partial N_i} \right)_{p,T} = \left(\frac{\partial \mu_i}{\partial N_k} \right)_{p,T}$$

we can write

$$\sum_k N_k \left(\frac{\partial \mu_i}{\partial N_k} \right)_{p,T} = 0 \quad (5.2.6)$$

Equation (5.2.6) is an important general result that we will use in later chapters.

5.2.2 The Helmholtz Equation

The Helmholtz equation gives us a useful expression to understand how the total energy U changes with the volume V at constant T . We have seen that the entropy S is a state variable and that it can be expressed as a function of T , V and N_k . The Helmholtz equation follows from the fact that, for a function of many variables, the second ‘cross-derivatives’ must be equal, i.e.

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T} \quad (5.2.7)$$

For closed systems in which no chemical reactions take place, the changes in entropy can be written as

$$dS = \frac{1}{T} dU + \frac{p}{T} dV \quad (5.2.8)$$

Since U can be expressed as a function of V and T , we have

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Using this expression in Equation (5.2.8) we obtain

$$\begin{aligned} dS &= \frac{1}{T} \left(\frac{\partial U}{\partial V} \right)_T dV + \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT + \frac{p}{T} dV \\ &= \left[\frac{1}{T} \left(\frac{\partial U}{\partial V} \right)_T + \frac{p}{T} \right] dV + \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT \end{aligned} \quad (5.2.9)$$

The coefficients of dV and dT can now be identified as the derivatives $(\partial S/\partial V)_T$ and $(\partial S/\partial T)_V$ respectively. As expressed in Equation (5.2.7), since the second ‘cross-derivatives’ must be equal, we have

$$\left\{ \frac{\partial}{\partial T} \left[\frac{1}{T} \left(\frac{\partial U}{\partial V} \right)_T + \frac{p}{T} \right] \right\}_V = \left\{ \frac{\partial}{\partial V} \left[\frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V \right] \right\}_T \quad (5.2.10)$$

It is a matter of a simple calculation (Exercise 5.6) to show that (5.2.10) leads to the **Helmholtz equation**:

$$\boxed{\left(\frac{\partial U}{\partial V} \right)_T = T^2 \left(\frac{\partial}{\partial T} \frac{p}{T} \right)_V} \quad (5.2.11)$$

This equation enables us to determine the variation of the energy with volume if the equation of state is known. In particular, it can be used to conclude that, for an ideal gas, the equation $pV = NRT$ implies that, at constant T , the energy U is independent of the volume, i.e. $(\partial U/\partial V)_T = 0$.

5.2.3 The Gibbs–Helmholtz Equation

The Gibbs–Helmholtz equation relates the temperature variation of the Gibbs energy G to the enthalpy H . It is useful for understanding how the state of chemical equilibrium responds to a change in temperature; in addition, it provides us with a way to determine enthalpies of chemical reactions using data on the variation of Gibbs energy changes with temperature. The Gibbs–Helmholtz equation is obtained as follows. By definition, $G \equiv H - TS$. First, we note that $S = -(\partial G/\partial T)_{p,N_k}$ and write

$$G = H + \left(\frac{\partial G}{\partial T} \right)_{p,N_k} T \quad (5.2.12)$$

It is easy to show (Exercise 5.8) that this equation can be rewritten as

$$\boxed{\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = -\frac{H}{T^2}} \quad (5.2.13)$$

When considering a chemical reaction, this equation can be written in terms of the *changes* in G and H that accompany the conversion of reactants to products. If the total Gibbs energy and the enthalpy of the reactants are G_r and H_r respectively and those of the products are G_p and H_p respectively, then the changes due to the reactions will be $\Delta G = G_p - G_r$ and $\Delta H = H_p - H_r$. By applying Equation (5.2.13) to the reactants and the products and subtracting one equation from the other, we obtain

$$\boxed{\frac{\partial}{\partial T} \left(\frac{\Delta G}{T} \right) = -\frac{\Delta H}{T^2}} \quad (5.2.14)$$

In Chapter 9 we will see that a quantity called the ‘standard ΔG ’ of a reaction can be obtained by measuring the equilibrium concentrations of the reactants and products. If the equilibrium concentrations (and hence

ΔG) are measured at various temperatures, then the data on the variation of ΔG with T can be used to obtain ΔH , which is the enthalpy of reaction. Equations (5.2.13) and (5.2.14) are referred to as the **Gibbs–Helmholtz equations**.

5.3 Gibbs Energy of Formation and Chemical Potential

Other than heat conduction, every irreversible process – e.g. chemical reactions, diffusion, the influence of electric, magnetic and gravitational fields, ionic conduction, dielectric relaxation – can be described in terms of suitable chemical potentials. Chapter 10 is devoted to some of the processes described using the concept of a chemical potential. All these processes drive the system to the equilibrium state in which the corresponding affinity vanishes. Because of its central role in the description of irreversible processes, we will derive a general expression for the chemical potential that facilitate its application.

As already noted, μ is the molar Gibbs energy of a pure compound. In general, the Gibbs energy and the chemical potential are related by

$$\left(\frac{\partial G}{\partial N_k} \right)_{p,T} = \mu_k \quad (5.3.1)$$

This equation does not give us a means to relate the chemical potential directly to experimentally measurable quantities such as heat capacities. As we have seen in Chapter 2, enthalpy can be related to heat capacities; therefore, we seek an expression that relates chemical potential to enthalpy. To this end, we differentiate the Gibbs–Helmholtz equation (5.2.13) with respect to N_k and use Equation (5.3.1) to obtain

$$\frac{\partial}{\partial T} \left(\frac{\mu_k}{T} \right) = -\frac{H_{mk}}{T^2} \quad \text{where } H_{mk} = \left(\frac{\partial H}{\partial N_k} \right)_{p,T,N_{i \neq k}} \quad (5.3.2)$$

in which H_{mk} is called the **partial molar enthalpy** of the compound k .

If the value of the chemical potential $\mu(p_0, T_0)$ at a reference temperature T_0 and pressure p_0 is known, then by integrating Equation (5.3.2) we can obtain the chemical potential at any other temperature T if the partial molar enthalpy $H_{mk}(p_0, T)$ is known as a function of T :

$$\frac{\mu(p_0, T)}{T} = \frac{\mu(p_0, T_0)}{T_0} + \int_{T_0}^T \frac{-H_{mk}(p_0, T')}{T'^2} dT' \quad (5.3.3)$$

As was shown in Chapter 2 (see Equations (2.4.10) and (2.4.11)), the molar enthalpy of a pure compound $H_{mk}(T)$ can be obtained using the tabulated values of $C_{mp}(T)$, the molar heat capacity at constant pressure. For ideal mixtures, H_{mk} is the same as that of a pure compound. For nonideal mixtures, a detailed knowledge of the heat capacities of the mixture is needed to obtain H_{mk} . As noted earlier, the chemical potential of a component k is not only a function of its mole fraction, x_k , but also a function of mole fractions of other components x_j . The chemical potential of a component k depends on how it interacts with other components in the mixture.

For a pure compound, knowing $\mu(p_0, T)$ at a pressure p_0 and temperature T , the value of $\mu(p, T)$ at any other pressure p can be obtained using the expression $d\mu = -S_m dT + V_m dp$, which follows from the Gibbs–Duhem

equation (5.2.4), where the molar quantities $S_m = S/N$ and $V_m = V/N$. Since T is fixed, $dT = 0$, and we may integrate this expression with respect to p to obtain

$$\mu(p, T) = \mu(p_0, T) + \int_{p_0}^p V_m(p', T) dp' \quad (5.3.4)$$

Thus, if the value of the chemical potential $\mu(p_0, T_0)$ is known at a reference pressure p_0 and temperature T_0 , Equations (5.3.3) and (5.3.4) tell us that a knowledge of the molar volume $V_m(p, T)$ (or density) and the molar enthalpy $H_m(p, T)$ of a compound will enable us to calculate the chemical potential at any other pressure p and temperature T . An alternative and convenient way of writing Equation (5.3.4) is due to G.N. Lewis (1875–1946), who introduced the concept of **activity** a_k of a compound k [4]. The activity is defined by the expression

$$\boxed{\mu_k(p, T) = \mu_k(p_0, T) + RT \ln a_k = \mu_k^0 + RT \ln a_k} \quad (5.3.5)$$

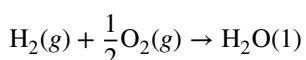
in which $\mu_k^0 = \mu_k(p_0, T)$. When we write the chemical potential in this form in terms of activity a_k , it turns out that activity has a direct relationship to experimentally measurable quantities such as concentration and pressure. As an illustration, let us apply Equation (5.3.4) to the case of an ideal gas. Since $V_m = RT/p$, we have

$$\begin{aligned} \mu(p, T) &= \mu(p_0, T) + \int_{p_0}^p \frac{RT}{p'} dp' \\ &= \mu(p_0, T) + RT \ln(p/p_0) = \mu^0 + RT \ln a \end{aligned} \quad (5.3.6)$$

which shows that the activity $a = (p/p_0)$ in the ideal gas approximation. In Chapter 6 we will obtain the expression for the activity of gases when the molecular size and molecular forces are taken into account, as in the van der Waals equation.

5.3.1 Tabulation of Gibbs Energies of Compounds

The formalism presented above does not give us a way to compute the absolute values of Gibbs energies of compounds. Hence, the convention described in Box 5.1 is usually used for tabulating Gibbs energies. Computation of Gibbs energy changes in chemical reactions are based on this convention. Here, the **molar Gibbs energy of formation** of a compound k , denoted by $\Delta G_f^0[k]$, is defined. Since chemical thermodynamics assumes that there is no interconversion between elements, the Gibbs energy of elements may be used to define the ‘zero’ with respect to which the Gibbs energies of all other compounds are measured. The Gibbs energy of formation of H_2O , written as $\Delta G_f^0[H_2O]$, for example, is the Gibbs energy *change* ΔG in the reaction



The molar Gibbs energies of formation of compounds $\Delta G_f^0[k] = \mu(p_0, T_0)$ are tabulated generally for $T_0 = 298.15$ K. We shall consider the use of ΔG_f^0 in more detail in Chapter 9, which is devoted to the thermodynamics of chemical reactions. From these values, the chemical potentials of compounds can be

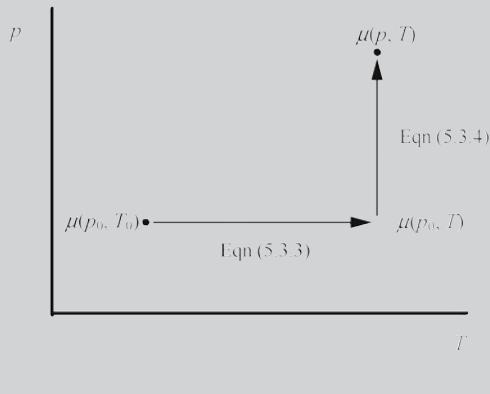
Box 5.1 Tabulation of Gibbs free energies of compounds

To compute the *changes* in the Gibbs energy in a chemical reaction, the **molar Gibbs energy** $\mu(p_0, T)$ of a compound in its **standard state** (its state at pressure $p_0 = 1$ bar) at temperature T , may be *defined* using the **Gibbs energy of formation**, $\Delta G_f^0[k, T]$, as follows:

$$\begin{aligned}\Delta G_f^0[k, T] &= 0 && \text{for all elements } k, \text{ at all temperatures } T \\ \mu_k^0(T) = \mu_k(p_0, T) = \Delta G_f^0[k, T] &= && \text{standard molar Gibbs energy of formation of compound } k \text{ at} \\ &= && \text{temperature } T \\ &= && \text{Gibbs energy of formation of 1 mol of the compound from its} \\ & && \text{constituent elements, all in their standard states, at temperature } T\end{aligned}$$

Since chemical thermodynamics assumes that there is no interconversion between the elements, the Gibbs energy of formation of elements may be used to define the ‘zero’ with respect to which the Gibbs energies of all other compounds are measured.

The molar Gibbs energy at any other p and T can be obtained using Equations (5.3.3) and (5.3.4) (or (5.3.7)), as shown in the figure below.



calculated as explained in Box 5.1. We conclude this section by noting that substitution of Equation (5.3.3) into (5.3.4) gives us a general expression for the computation of the chemical potential:

$$\mu(p, T) = \frac{T}{T_0} \mu(p_0, T_0) + \int_{p_0}^p V_m(p', T_0) dp' + T \int_{T_0}^T \frac{-H_m(p, T')}{T'^2} dT' \quad (5.3.7)$$

Thus, once the reference chemical potential $\mu(p_0, T_0)$ is defined using some convention, the chemical potential of a compound can be computed using the above formula if the molar volumes V_m and molar enthalpy H_m are known as functions of p and T . These quantities are experimentally measured and tabulated (e.g. see the *NIST Chemistry Webbook* at <http://webbook.nist.gov/chemistry>).

5.4 Maxwell Relations

The two laws of thermodynamics establish energy and entropy as functions of state, making them functions of many variables. As we have seen, $U = U(S, V, N_k)$ and $S = S(U, V, N_k)$ are functions of the indicated variables. James Clerk Maxwell (1831–1879) used the rich theory of multivariable functions to obtain a large number of relations between thermodynamic variables. The methods he employed are general, and the relations thus obtained are called the Maxwell relations.

In Appendix 1.1 we introduced the following result: if three variables x , y and z are such that each may be expressed as a function of the other two, $x = x(y, z)$, $y = y(x, z)$ and $z = z(x, y)$, then the theory of multivariable functions gives us the following fundamental relations:

$$\frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y} \quad (5.4.1)$$

$$\left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z} \quad (5.4.2)$$

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad (5.4.3)$$

Also, if we consider two functions of x and y , $z = z(x, y)$ and $w = w(x, y)$, then the partial derivative $(\partial z / \partial x)_w$, in which the derivative is evaluated at constant w , is given by

$$\left(\frac{\partial z}{\partial x} \right)_w = \left(\frac{\partial z}{\partial x} \right)_y + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_w \quad (5.4.4)$$

We have already seen how Equation (5.4.1) can be used to derive the Helmholtz equation (5.2.11) in which entropy S was considered as a function of T and V . In most cases, Equations (5.4.1) to (5.4.4) are used to write thermodynamic derivatives in a form that can easily be related to experimentally measurable quantities. For example, using the fact that the Helmholtz energy $F(V, T)$ is a function of V and T , Equation (5.4.1) can be used to derive the relation $(\partial S / \partial V)_T = (\partial p / \partial T)_V$, in which the derivative on the right-hand side is clearly more easily related to the experiment.

Some thermodynamic derivatives are directly related to properties of materials that can be measured experimentally. Other thermodynamic derivatives are expressed in terms of these quantities. The following are among the most commonly used physical properties in thermodynamics:

Isothermal compressibility: $\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (5.4.5)$

Coefficient of volume expansion: $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (5.4.6)$

Now the **pressure coefficient** $(\partial p / \partial T)_V$, for example, can be expressed in terms of κ_T and α as follows. From Equation (5.4.3), it follows that

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{-1}{\left(\frac{\partial V}{\partial p} \right)_T \left(\frac{\partial T}{\partial V} \right)_p}$$

Now, using Equation (5.4.2) and dividing the numerator and the denominator by V we obtain

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{-\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p}{\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha}{\kappa_T} \quad (5.4.7)$$

5.4.1 General Relation between C_{mp} and C_{mV}

As another example of the application of Maxwell's relations, we will derive a general relation between C_{mp} and C_{mV} in terms of α , κ_T , the molar volume V_m and T – all of which can be measured experimentally. We start with the relation we have already derived in Chapter 2, i.e. Equation (2.3.5):

$$C_{mp} - C_{mV} = \left[p + \left(\frac{\partial U_m}{\partial V_m} \right)_T \right] \left(\frac{\partial V_m}{\partial T} \right)_p \quad (5.4.8)$$

where we have used all molar quantities, as indicated by the subscript 'm'. The first step is to write the derivative $(\partial U/\partial V)_T$ in terms of the derivatives involving p , V and T , so that we can relate it to α and κ_T . From the Helmholtz equation (5.2.11), it is easy to see that $(\partial U/\partial V)_T + p = T(\partial p/\partial T)_V$. Therefore, we can write Equation (5.4.8) as

$$C_{mp} - C_{mV} = T \left(\frac{\partial p}{\partial T} \right)_V \alpha V_m \quad (5.4.9)$$

in which we have used the definition (5.4.6) for α . Now, using the Maxwell relation $(\partial p/\partial T)_V = (\alpha/\kappa_T)$ (see Equation (5.4.7)) in Equation (5.4.9) we obtain the general relation

$$C_{mp} - C_{mV} = \frac{T\alpha^2 V_m}{\kappa_T} \quad (5.4.10)$$

5.5 Extensivity with Respect to N and Partial Molar Quantities

In multicomponent systems, thermodynamic functions such as volume V , Gibbs energy G and all other thermodynamic functions that can be expressed as functions of p , T and N_k are extensive functions of N_k . This extensivity leads to general thermodynamic relations, some of which we will discuss in this section.

Consider the volume of a system as a function of p , T and N_k : $V = V(p, T, N_k)$. At constant p and T , if all the molar amounts were increased by a factor k , the volume V will also increase by the same factor. This is the property of extensivity. In mathematical terms, we have

$$V(p, T, \lambda N_k) = \lambda V(p, T, N_k) \quad (5.5.1)$$

At constant p and T , using Euler's theorem as was done in Section 4.4, we can arrive at the relation

$$V = \sum_k \left(\frac{\partial V}{\partial N_k} \right)_{p,T} N_k \quad (5.5.2)$$

It is convenient to define **partial molar volumes** as the derivatives

$$V_{mk} \equiv \left(\frac{\partial V}{\partial N_k} \right)_{p,T} \quad (5.5.3)$$

Using this definition, Equation (5.5.2) can be written as

$$V = \sum_k V_{mk} N_k \quad (5.5.4)$$

Partial molar volumes are intensive quantities. As was done in the case of the Gibbs–Duhem relation, we can derive a relation between the V_{mk} by noting that at constant p and T

$$(dV)_{p,T} = \sum_k \left(\frac{\partial V}{\partial N_k} \right)_{p,T} dN_k = \sum_k V_{mk} dN_k \quad (5.5.5)$$

in which we have explicitly noted that the change dV is at constant p and T . Comparing dV obtained from Equations (5.5.4) and (5.5.5), we see that $\sum_k N_k (dV_{mk})_{p,T} = 0$. Now $(dV_{mk})_{p,T} = \sum_i (\partial V_{mk}/\partial N_i) dN_i$, so we obtain

$$\sum_k \sum_i N_k \left(\frac{\partial V_{mk}}{\partial N_i} \right) dN_i = 0$$

In this equation, dN_i are arbitrary variations in N_i ; consequently, the above equation can be valid only when the coefficient of each dN_i equals zero, i.e. $\sum_k N_k (\partial V_{mk}/\partial N_i) = 0$. Finally, using the property $(\partial V_{mk}/\partial N_i) = (\partial^2 V/\partial N_i \partial N_k) = (\partial V_{mi}/\partial N_k)$ we arrive at the final result:

$$\sum_k N_k \left(\frac{\partial V_{mi}}{\partial N_k} \right)_{p,T} = 0 \quad (5.5.6)$$

Relations similar to Equations (5.5.4) and (5.5.6) can be obtained for all other functions that are extensive in N_k . For Gibbs energy, which is an extensive quantity, the equation corresponding to (5.5.4) is

$$G = \sum_k \left(\frac{\partial G}{\partial N_k} \right)_{p,T} N_k = \sum_k G_{mk} N_k = \sum_k \mu_k N_k \quad (5.5.7)$$

in which we recognize the **partial molar Gibbs energy** G_{mk} as the chemical potentials μ_k . The equation corresponding to (5.5.6) follows from the Gibbs–Duhem relation (5.2.4) when p and T are constant:

$$\sum_k N_k \left(\frac{\partial \mu_i}{\partial N_k} \right)_{p,T} = 0 \quad (5.5.8)$$

Similarly, for the Helmholtz energy F and the enthalpy H , we can obtain the following relations:

$$F = \sum_k F_{mk} N_k \quad \sum_k N_k \left(\frac{\partial F_{mi}}{\partial N_k} \right)_{p,T} = 0 \quad (5.5.9)$$

$$H = \sum_k H_{mk} N_k \quad \sum_k N_k \left(\frac{\partial H_{mi}}{\partial N_k} \right)_{p,T} = 0 \quad (5.5.10)$$

in which the **partial molar Helmholtz energy** $F_{mk} = (\partial F/\partial N_k)_{p,T}$ and the **partial molar enthalpy** $H_{mk} = (\partial H/\partial N_k)_{p,T}$. Similar relations can be obtained for entropy S and the total internal energy U .

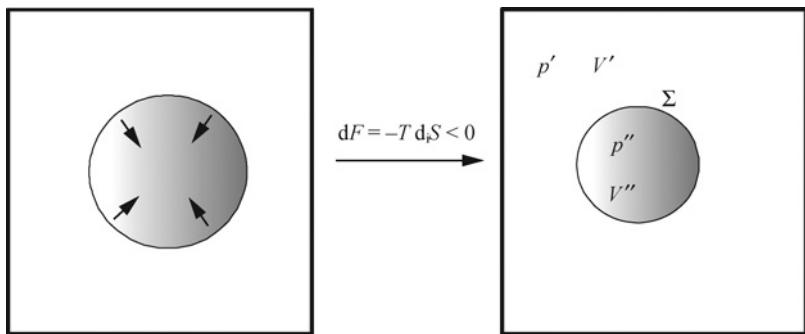


Figure 5.4 To minimize the interfacial Helmholtz energy, a liquid drop shrinks its surface area to the least possible value. As a result, the pressure p'' inside the drop is larger than the external pressure p' . The excess pressure $(p'' - p') = 2\gamma/r$.

5.6 Surface Tension

We conclude this chapter by considering some elementary thermodynamic relations involving interfaces [5]. Since molecules at an interface are in a different environment from molecules in the bulk, their energies and entropies are different. Molecules at a liquid–air interface, for example, have a larger Helmholtz energy than those in the bulk. At constant V and T , since every system minimizes its Helmholtz energy, the interfacial area shrinks to its minimum possible value, thus increasing the pressure in the liquid (Figure 5.4).

The thermodynamics of such a system can be formulated as follows. Consider a system with two parts, separated by an interface of area Σ (Figure 5.4). For this system we have

$$dU = T dS - p'' dV'' - p' dV' + \gamma d\Sigma \quad (5.6.1)$$

in which p' and V' are the pressure and the volume of one part and p'' and V'' are the pressure and the volume of the other, Σ is the interfacial area and the coefficient γ is called the surface tension. Since $dF = dU - T dS - S dT$, using Equation (5.6.1) we can write dF as

$$dF = -S dT - p'' dV'' - p' dV' + \gamma d\Sigma \quad (5.6.2)$$

From this it follows that

$$\left(\frac{\partial F}{\partial \Sigma} \right)_{T,V',V''} = \gamma \quad (5.6.3)$$

Thus, surface tension γ is the change of F per unit extension of the interfacial area at constant T , V' and V'' . This energy is small, usually of the order of 10^{-2} J m $^{-2}$.

The minimization of Helmholtz energy drives the interface to contract like an elastic sheet. The force per unit length that the interface exerts in its tendency to contract is also equal to γ . This can be seen as follows. Since enlarging an interfacial area increases its Helmholtz energy, work needs to be done. As shown in Figure 5.5, this means a force f is needed to stretch the surface by an amount dx , i.e. the interface behaves like an elastic sheet. The work done, $f dx$, equals the increase in the surface energy, $\gamma d\Sigma = (\gamma l dx)$, in which l is the width of the surface (Figure 5.5). Thus, $f dx = \gamma l dx$, or the force per unit length $f/l = \gamma$. For this reason, γ is called the ‘surface tension’.

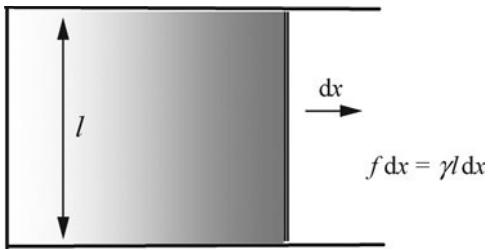


Figure 5.5 Energy is required to enlarge a surface of a liquid. The force per unit length is γ .

5.6.1 Excess Pressure in a Liquid Drop

In the case of the liquid drop in air shown in Figure 5.4, the difference in the pressures $(p'' - p') = \Delta p$ is the excess pressure inside the liquid drop. An expression for the excess pressure Δp in a spherical liquid drop can be obtained as follows. As shown in Section 5.1, if the total volume of a system and its temperature are constant, then the irreversible approach to equilibrium is described by $-T d_i S = dF \leq 0$. Now consider an irreversible contraction of the volume V'' of the liquid drop to its equilibrium value when the total volume $V = V' + V''$ and T are constant. Setting $dT = 0$ and $dV' = -dV''$ in Equation (5.6.2) we obtain

$$-T \frac{d_i S}{dt} = \frac{dF}{dt} = -(p'' - p') \frac{dV''}{dt} + \gamma \frac{d\Sigma}{dt} \quad (5.6.4)$$

For a spherical drop of radius r , $dV'' = (4\pi/3)3r^2 dr$ and $d\Sigma = 4\pi 2r dr$; hence, the above equation can be written as

$$-T \frac{d_i S}{dt} = \frac{dF}{dt} = [-(p'' - p')4\pi r^2 + \gamma 8\pi r] \frac{dr}{dt} \quad (5.6.5)$$

We see that this expression is a product of a ‘thermodynamic force’ $-(p'' - p')\pi 4r^2 + \gamma 8\pi r$ that causes the ‘flow rate’ dr/dt . At equilibrium, both must vanish. Hence, $-(p'' - p')4\pi r^2 + \gamma 8\pi r = 0$. This gives us the well-known equation for the excess pressure inside a liquid drop of radius r :

$$\boxed{\Delta p \equiv (p'' - p') = \frac{2\gamma}{r}} \quad (5.6.6)$$

This result is called the **Laplace equation** because it was first derived by the French mathematician Pierre-Simon Laplace (1749–1827).

5.6.2 Capillary Rise

Another consequence of surface tension is the phenomenon of ‘capillary rise’: in narrow tubes or capillaries, most liquids rise to a height h (Figure 5.6) that depends on the radius of the capillary. The smaller the radius, the higher the rise. The liquid rises because an increase in the area of the liquid–glass interface lowers the Helmholtz energy. The relation between the height h , the radius r and the surface tension can be derived as follows. As shown in Figure 5.6c, the force of surface tension of the liquid–air interface pulls the surface down while the force at the liquid–glass interface pulls the liquid up. Let the ‘contact angle’, i.e. the angle at which the liquid is in contact with the wall of the capillary, be θ . When these two forces balance each other along the vertical direction, the force per unit length generated by the liquid–glass interface must be $\gamma \cos \theta$. As the liquid moves up, the liquid–glass interface is increasing while the glass–air interface is decreasing; $\gamma \cos \theta$ is the net force per unit length due to these two factors. The force per unit length is equal

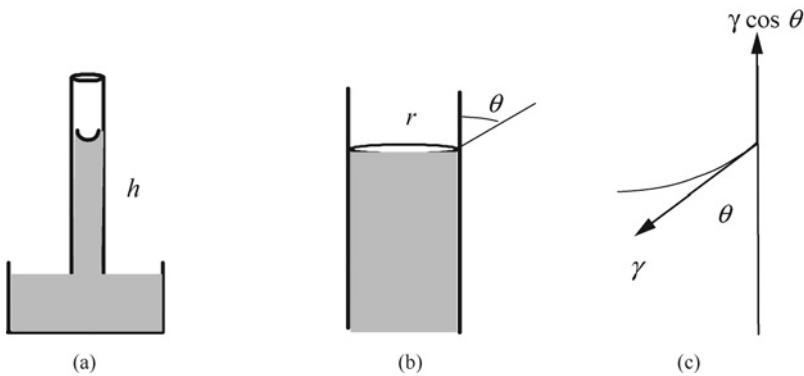


Figure 5.6 Capillary rise due to surface tension. (a) The height h to which the liquid rises depends on the contact angle θ , the surface tension γ and the radius r . (b) The contact angle θ specifies the direction in which the force due to the liquid–air interface acts. (c) The vertical component of the force due to the liquid–air interface balances the net force due to the liquid–glass and glass–air interfaces.

to the interfacial energy per unit area; thus, as the liquid moves up, the decrease in the interfacial energy is $\gamma \cos \theta$ per unit area. Hence, as the liquid moves up and increases the area of the glass–liquid interface, the decrease in Helmholtz energy is $\gamma \cos \theta$ per unit area. On the other hand, as the liquid rises in the capillary, there is an increase in the potential energy of the liquid due to gravity. A liquid layer of thickness dh and density ρ has the mass $(\rho \pi r^2 dh)$ and its potential energy at a height h is equal to $(\rho \pi r^2 dh)gh$. For the entire liquid column, this expression has to be integrated from 0 to h . The change in the Helmholtz energy ΔF as the liquid rises is the sum of the potential energy and glass–liquid interfacial energy:

$$\Delta F(h) = \int_0^h g \rho \pi r^2 dh - 2\pi r h (\gamma \cos \theta) = \frac{\pi \rho g r^2 h^2}{2} - 2\pi r h (\gamma \cos \theta) \quad (5.6.7)$$

The value of h that minimizes F is obtained by setting $\partial(\Delta F(h)/\partial h) = 0$ and solving for h . This leads to the expression

$$h = \frac{2\gamma \cos \theta}{\rho g r} \quad (5.6.8)$$

The same result can also be derived by balancing the forces of surface tension and the weight of the liquid column. As shown in Figure 5.6b, the liquid column of height h is held at the surface by the surface tension. The total force due to the surface tension of the liquid along the circumference is $2\pi r \gamma \cos \theta$. Since this force holds the weight of the liquid column, we have

$$2\pi r \gamma \cos \theta = \rho g h \pi r^2 \quad (5.6.9)$$

from which Equation (5.6.8) follows.

The contact angle θ depends on the interface (see Table 5.2). For a glass–water interface the contact angle is nearly zero, as it is for many, though not all, organic liquids. For a glass–kerosene interface, $\theta = 26^\circ$. The contact angle can be greater than 90° , as in the case of a mercury–glass interface, for which θ is about 140° , or a paraffin–water interface, for which it is about 107° . When θ is greater than 90° , the liquid surface in the capillary is lowered.

Table 5.2 Examples of surface tension and contact angles.

	$\gamma(10^{-2} \text{ J m}^{-2} \text{ or } 10^{-2} \text{ N m}^{-1})$	Interface	Contact angle ($^\circ$)
Methanol	2.26	Glass–water	0
Benzene	2.89	Glass–many organic liquids*	0
Water	7.73	Glass–kerosene	26
Mercury	47.2	Glass–mercury	140
Soap solution	2.3 (approximate)	Paraffin–water	107

*Not all organic liquids have a contact angle value of 0° , as is clear in the case of kerosene.

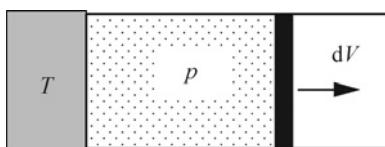
More extensive data may be found in D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 75th edition, 1994, CRC Press: Ann Arbor, MI.

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Examples

Example 5.1 Show that the change in the value of the Helmholtz free energy F corresponds to the work done when T and N_k are constant, thus justifying the name ‘free energy’ (available for doing work).



Solution As a specific example, consider a gas in contact with a thermal reservoir at temperature T . By expanding this gas, work can be done. We can show that the change of F corresponds to the work done at constant T and N_k as follows. $F = U - TS$. From this it follows that (see Equation (5.1.5))

$$dF = -p dV - S dT + \sum_k \mu_k dN_k$$

At constant T and N_k , $dF = -p dV$. Integrating both sides, we see that

$$\int_{F_1}^{F_2} dF = F_2 - F_1 = \int_{V_1}^{V_2} -p dV$$

which shows that the change in F is equal to the work done by the gas. The same will be true for any other system.

Example 5.2 For a closed system with one chemical reaction, show that $(\partial F/\partial \xi)_{T,V} = -A$.

Solution The change in F is given by (see Equation (5.1.5))

$$dF = -p dV - S dT + \sum_k \mu_k dN_k$$

Since the system is closed, the changes in N_k are due to a chemical reaction; hence, we have $dN_k = v_k d\xi$ in which v_k are the stoichiometric coefficients (which are negative for the reactants and positive for the products). Thus:

$$dF = -p dV - S dT + \sum_k v_k \mu_k d\xi$$

Since $\sum_k v_k \mu_k = -A$ we have

$$dF = -p dV - S dT - A d\xi$$

When F is considered as a function of V , T and ξ , then

$$dF = \left(\frac{\partial F}{\partial V}\right)_{T,\xi} dV + \left(\frac{\partial F}{\partial T}\right)_{V,\xi} dT + \left(\frac{\partial F}{\partial \xi}\right)_{T,V} d\xi = d\xi$$

and we see that $(\partial F/\partial \xi)_{T,V} = -A$.

Example 5.3 Using the Gibbs–Duhem relation show that, at constant p and T , $(dG_m)_{p,T} = \sum_k \mu_k dx_k$ (which is Equation (5.1.17)).

Solution The molar Gibbs free energy $G_m = \sum_k \mu_k x_k$ in which x_k is the mole fraction of component k . Hence:

$$dG_m = \sum_k dx_k \mu_k + \sum_k x_k d\mu_k$$

The Gibbs–Duhem relation is

$$S dT - V dp + \sum_k N_k d\mu_k = 0$$

Since p and T are constant, $dT = dp = 0$. Furthermore, $x_k = N_k/N$ in which N is the total number of moles. Dividing the Gibbs–Duhem equation by N and setting $dp = dT = 0$, we have $\sum_k x_k d\mu_k = 0$. Using this result in the expression for dG_m above, for constant p and T we see that

$$(dG_m)_{p,T} = \sum_k \mu_k dx_k$$

(Note that $\sum_k x_k = 1$ and, hence, x_k are not all independent. Hence, the above equation does not imply that $(\partial G_m/\partial x_k)_{p,T} = \mu_k$.)

Exercises

- 5.1** Use the expression $T d_i S = -\gamma dA$ and $T d_e S = dU + p dV$ in the general expressions for the First and the Second Laws and obtain $dU = T dS - p dV + \gamma dA$ (assuming $dN_k = 0$).

- 5.2** (a) In an isothermal expansion of a gas from a volume V_i to V_f , what is the change in the Helmholtz free energy F ? (b) For a system undergoing chemical transformation at constant V and T , prove Equation (5.1.7).

- 5.3** Use the relations $dU = dQ - p dV$, $T d_e S = dQ$ and $T d_i S = -\sum_k \mu_k dN_k$ to derive

$$dG = V dp - S dp + \sum_k \mu_k dN_k$$

which is Equation (5.1.13).

- 5.4** Use the relations $dU = dQ - p dV$, $T d_e S = dQ$ and $T d_i S = -\sum_k \mu_k dN_k$ to derive

$$dH = T dS + V dp + \sum_k \mu_k dN_k$$

which is Equation (5.1.21).

- 5.5** For an ideal gas, in an isothermal process, show that the change in the Gibbs energy of a system is equal to the amount of work done by a system in an idealized reversible process.

- 5.6** Obtain the Helmholtz equation (5.2.11) from (5.2.10).

- 5.7** (a) Use the Helmholtz equation (5.2.11) to show that, at constant T , the energy of an ideal gas is independent of volume.
 (b) Use the Helmholtz equation (5.2.11) to calculate $(\partial U / \partial V)_T$ for N moles of a gas using the van der Waals equation.

- 5.8** Obtain Equation (5.2.13) from Equation (5.2.12).

- 5.9** Derive the following general equation, which is similar to the Gibbs–Helmholtz equation:

$$\frac{\partial}{\partial T} \left(\frac{F}{T} \right) = -\frac{U}{T^2}$$

- 5.10** Assume that ΔH changes little with temperature, integrate the Gibbs–Helmholtz equation (5.2.14) and express ΔG_f at temperature T_f in terms of ΔH , the initial ΔG_i and the corresponding temperature T_i .

- 5.11** Obtain an explicit expression for the Helmholtz energy of an ideal gas as a function T , V and N .

- 5.12** The variation of Gibbs energy of a substance with temperature is given by $G = aT + b + c/T$. Determine the entropy and enthalpy of this substance as a function of temperature.

- 5.13** Show that Equation (5.4.10) reduces to $C_{mp} - C_{mV} = R$ for an ideal gas.

- 5.14** Consider a reaction $X \rightleftharpoons{2Y}$ in which X and Y are ideal gases.

- (a) Write the Gibbs energy of this system as a function of the extent of reaction ξ so that ξ is the deviation from the equilibrium amounts of X and Y, i.e. $N_X = N_{X_{eq}} - \xi$ and $N_Y = N_{Y_{eq}} + 2\xi$ in which $N_{X_{eq}}$ and $N_{Y_{eq}}$ are the equilibrium amounts of X and Y.
 (b) Through explicit evaluation, show that $(\partial G / \partial \xi)_{p,T} = -A = (2\mu_Y - \mu_X)$.

- 5.15** (a) By minimizing the free energy $\Delta F(h)$ given by Equation (5.6.1) as a function of h , obtain the expression

$$h = \frac{2\gamma \cos \theta}{\rho g r}$$

for the height h of capillary rise due to surface tension.

- (b) Assume that the contact angle θ between water and glass is nearly zero and calculate the height of water in a capillary of diameter 0.1 mm.
- 5.16** (a) Owing to surface tension, the pressure inside a bubble is higher than the outside pressure. Let this excess pressure be Δp . By equating the work done, $\Delta p dV$, due to an infinitesimal increase dr in the radius r to the increase in surface energy γdA , show that $\Delta p = 2\gamma/r$.
- (b) Calculate the excess pressures inside water bubbles of radius 1.0 mm and 1.0 μm .
- 5.17** What is the minimum energy needed to convert 1.0 mL of water to droplets of diameter 1.0 μm ?
- 5.18** When the surface energy is included we have seen that

$$dU = T dS - p dV + \mu dN + \gamma dA$$

in which γ is the surface tension and dA is the change in the surface area. For a small spherical liquid drop of a pure substance, show that the above expression can be written as $dU = T dS - p dV + \mu'(r) dN$ in which $\mu'(r) = \mu + (2\gamma/r)V_m$, a size-dependent chemical potential.

6

Basic Thermodynamics of Gases, Liquids and Solids

Introduction

The formalism and general thermodynamic relations that we have seen in the previous chapters have wide applicability. In this chapter, we will see how thermodynamic quantities can be calculated for gases, liquids, solids and solutions using general methods.

6.1 Thermodynamics of Ideal Gases

Many thermodynamic quantities, such as total internal energy, entropy, chemical potential, etc., for an ideal gas have been derived in the preceding chapters as examples. In this section, we will bring all these results together and list the thermodynamic properties of gases in the ideal gas approximation. In the following section, we will see how these quantities can be calculated for ‘real gases’ for which we take into account the molecular size and intermolecular forces.

6.1.1 The Equation of State

Our starting point is the equation of state, *the ideal gas law*:

$$pV = NRT \quad (6.1.1)$$

As we saw in Chapter 1, this approximation is valid for most gases when their densities are less than about 1 mol L^{-1} . At this density and temperature of about 300 K, for example, the pressure of $\text{N}_2(\text{g})$ obtained using the ideal gas equation is 24.76 atm, whereas that predicted using the more accurate van der Waals equation is 24.36 atm, a difference of only a few percent.

6.1.2 The Total Internal Energy

Through thermodynamics, we can see that the *ideal gas law* (6.1.1) implies that the total internal energy U is independent of the volume at fixed T , i.e. the energy of an ideal gas depends only on its temperature.

One arrives at this conclusion using the Helmholtz equation (see Equation (5.2.11)), which is valid for all thermodynamic systems:

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \left[\frac{\partial}{\partial T} \left(\frac{p}{T} \right) \right]_V \quad (6.1.2)$$

(We remind the reader that the Helmholtz equation is a consequence of the fact that entropy is a state function of V , T and N_k .) Since the ideal gas equation implies that the term $p/T = NR/V$ is independent of T , it immediately follows from Equation (6.1.2) that $(\partial U/\partial V)_T = 0$. Thus, the total internal energy $U(T, V, N)$ of N moles of an ideal gas is independent of the volume at a fixed T . We can get a more explicit expression for U . Since $C_{mV} = (\partial U_m/\partial T)_V$ is found to be independent of T , we can write

$$U_{\text{ideal}} = NU_0 + N \int_0^T C_{mV} dT = N(U_0 + C_{mV}T) \quad (6.1.3)$$

(The constant U_0 is not defined in classical thermodynamics, but, using the definition of energy that the theory of relativity gives us, we may set $NU_0 = MNc^2$, in which M is the molar mass, N is the molar amount of the substance and c is the velocity of light. In thermodynamic calculations of changes of energy, U_0 does not appear explicitly.)

6.1.3 Heat Capacities and Adiabatic Processes

We have seen earlier that there are two molar heat capacities: C_{mV} and C_{mp} , the former at constant volume and the latter at constant pressure. We have also seen in Chapter 2 that the First Law gives us the following relation between molar heat capacities:

$$C_{mp} - C_{mV} = R \quad (6.1.4)$$

For an *adiabatic process*, the First Law also gives us the relation

$$TV^{\gamma-1} = \text{constant} \quad \text{or} \quad pV^\gamma = \text{constant} \quad (6.1.5)$$

in which $\gamma = C_{mp}/C_{mV}$. In an adiabatic process, by definition $d_eS = dQ/T = 0$. If the process occurs such that $d_iS \approx 0$, then the entropy of the system remains constant because $dS = d_iS + d_eS$.

6.1.4 Entropy and Thermodynamic Potentials

We have already seen that the entropy $S(V, T, N)$ of an ideal gas is (see Equation (3.7.4))

$$S = N[s_0 + C_{mV} \ln(T) + R \ln(V/N)] \quad (6.1.6)$$

From the equation of state (6.1.1) and the expressions for U_{ideal} and S it is straightforward to obtain explicit expressions for the enthalpy $H = U + pV$, the Helmholtz energy $F = U - TS$ and the Gibbs energy $G = U - TS + pV$ of an ideal gas (Exercise 6.1).

6.1.5 Chemical Potential

For the chemical potential of an ideal gas, we obtained the following expression in Section 5.3 (see Equation (5.3.6)):

$$\mu(p, T) = \mu(p_0, T) + RT \ln(p/p_0) \quad (6.1.7)$$

For a mixture of ideal gases the total energy is the sum of the energies of all its components. The same is true for the entropy. The chemical potential of a component k can be expressed in terms of the partial pressures p_k as

$$\mu_k(p_k, T) = \mu_k(p_0, T) + RT \ln(p_k/p_0) \quad (6.1.8)$$

Alternatively, if x_k is the mole fraction of the component k , since $p_k = x_k p$, the chemical potential can be written as

$\mu_k(p, T, x_k) = \mu_k^0(p, T) + RT \ln(x_k)$

(6.1.9)

in which $\mu_k^0(p, T) = \mu_k(p_0, T) + RT \ln(p/p_0)$ is the chemical potential of a pure ideal gas. This form of the chemical potential is generally used in the thermodynamics of multicomponent systems to define an ‘ideal mixture’.

6.1.6 Entropy of Mixing and the Gibbs Paradox

Using the expression for the entropy of an ideal gas, we can calculate the increase in its entropy due to irreversible mixing of two gases. Consider two nonidentical gases in chambers of volume V separated by a wall (Figure 6.1). The entire system is isolated. Let us assume that the two chambers contain the same amount, N moles, of the two gases. The total initial entropy of the system is the sum of the entropies of the two gases:

$$S_{\text{init}} = N[s_{01} + C_{mV1} \ln(T) + R \ln(V/N)] + N[s_{02} + C_{mV2} \ln(T) + R \ln(V/N)] \quad (6.1.10)$$

Now if the wall separating the two chambers is removed, the two gases will mix irreversibly and the entropy will increase. T and p remain constant. When the two gases have completely mixed and the system has reached

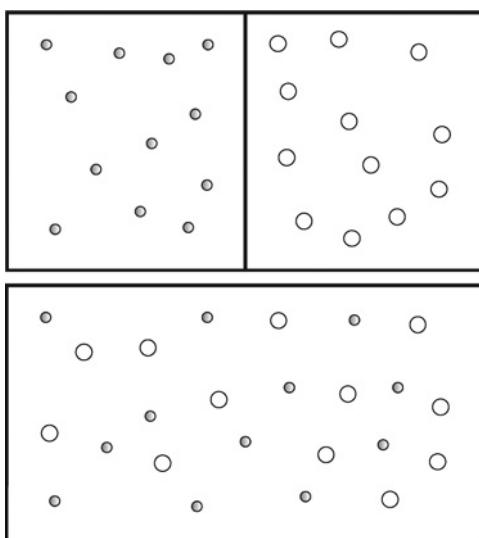


Figure 6.1 The entropy of mixing two nonidentical gases is given by Equation (6.1.12), however small the difference between the gases. If the two gases are identical, then there is no change in the entropy.

a new state of equilibrium, each gas would be occupying a volume of $2V$. Hence, the total final entropy after the mixing is

$$S_{\text{fin}} = N[s_{01} + C_{mV1} \ln(T) + R \ln(2V/N)] + N[s_{02} + C_{mV2} \ln(T) + R \ln(2V/N)] \quad (6.1.11)$$

The difference between Equations (6.1.10) and (6.1.11) is the entropy of mixing $\Delta S_{\text{mix}} = S_{\text{fin}} - S_{\text{init}}$. It is easy to see that

$$\Delta S_{\text{mix}} = 2NR \ln 2 \quad (6.1.12)$$

The generalization of this result to unequal volumes and molar amounts is left as an exercise. It can be shown that if initially the densities of the two gases are the same, i.e. $(N_1/V_1) = (N_2/V_2)$, then the entropy of mixing can be written as (Exercise 6.2)

$$\Delta S_{\text{mix}} = -RN(x_1 \ln x_1 + x_2 \ln x_2) \quad (6.1.13)$$

where x_1 and x_2 are the mole fractions and $N = N_1 + N_2$.

Gibbs noted a curious aspect of this result. If the two gases were identical, then the states of the gas before and after the removal of the wall are indistinguishable except for the wall; by replacing the wall, the initial state can be restored. This means that there is no irreversible process mixing the two gases. Hence, there is no change in entropy because the initial and final states are the same. For two nonidentical gases, however small the difference between them, the change of entropy is given by Equation (6.1.12). Generally, in most physical systems, a small change in one quantity results in a small change in another dependent quantity. Not so with the entropy of mixing; even the smallest difference between two gases leads to an entropy difference of $2NR \ln 2$. If the difference between the two gases vanishes, then S_{mix} abruptly drops to zero. This discontinuous behavior of the entropy of mixing is often called the **Gibbs paradox**.

The entropy of mixing (6.1.13) can also be obtained using the statistical formula $S = k_B \ln W$ introduced in Chapter 3 (Box 3.1). Consider a gas containing $(N_1 + N_2)$ moles or $(N_1 + N_2)N_A$ molecules (N_A is the Avogadro number). For this gas, interchange of molecules does not correspond to distinct microstates because the molecules are indistinguishable. However, if N_2 moles of the gas are replaced by another gas, then an interchange of molecules of the two different gases corresponds to a distinct microstate. Thus, the gas mixture with N_1 moles of one gas and N_2 of another gas has additional microstates in comparison with $(N_1 + N_2)$ moles of one gas. That these additional microstates when used in the formula $S = k_B \ln W$ give the entropy of mixing, Equation (6.1.13), can be seen as follows. The number of additional microstates in the mixture is

$$W_{\text{mix}} = \frac{(N_A N_1 + N_A N_2)!}{(N_A N_1)! (N_A N_2)!} \quad (6.1.14)$$

Using the Stirling approximation $\ln(N!) \approx N \ln N - N$, it can easily be shown that (Exercise 6.2)

$$\Delta S_{\text{mix}} = k_B \ln W_{\text{mix}} = -k_B N_A (N_1 + N_2)(x_1 \ln x_1 + x_2 \ln x_2) \quad (6.1.15)$$

in which x_1 and x_2 are mole fractions. Equation (6.1.15) is identical to (6.1.13) because $R = k_B N_A$ and $N = N_1 + N_2$. This derivation shows that expression (6.1.13) for the entropy of mixing is not dependent on the interactions between the gas molecules: it is entirely a consequence of distinguishability of the two components of the system.

6.2 Thermodynamics of Real Gases

Useful though it might be, the ideal gas approximation ignores the finite size of the molecules and the intermolecular forces. Consequently, as the gas becomes denser, the ideal gas equation does not predict the

relation between the volume, pressure and temperature with good accuracy: one has to use other equations of state that provide a better description. If the molecular size and forces are included in the theory, then one refers to it as a theory of a ‘real gas’.

As a result of molecular forces, the total internal energy U , the relation between the molar heat capacities C_{mp} and C_{mV} , the equation for adiabatic processes and other thermodynamic quantities will differ from those for the ideal gas. In this section, we shall see how the thermodynamic quantities of a real gas can be obtained from an equation of state that takes molecular size and forces into account.

The van der Waals equation, which takes into account the intermolecular forces and molecular size, and the critical constants p_c , V_{mc} and T_c , were introduced in Chapter 1:

$$\boxed{\left(p + \frac{a}{V_m^2} \right) (V_m - b) = RT} \quad (6.2.1)$$

$$P_c = \frac{a}{27b^2}, \quad V_{mc} = 3b, \quad T_c = \frac{8a}{27bR}$$

in which V_m is the molar volume. Since the van der Waals equation also has its limitations, other equations have been proposed for gases. Some of the other equations that have been proposed and the corresponding critical constants are as follows:

The Berthelot equation:

$$\boxed{p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}} \quad (6.2.2)$$

$$p_c = \frac{1}{12} \left(\frac{2aR}{3b^3} \right)^{1/2}, \quad V_{mc} = 3b, \quad T_c = \frac{2}{3} \left(\frac{2a}{3bR} \right)^{1/2}$$

The Dieterici equation:

$$\boxed{p = \frac{RT e^{-a/RTV_m}}{V_m - b}} \quad (6.2.3)$$

$$p_c = \frac{a}{4e^2 b^2}, \quad V_{mc} = 2b, \quad T_c = \frac{a}{4Rb}$$

The Redlich–Kwong equation:

$$\boxed{p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}} \quad (6.2.4)$$

$$a = \frac{0.42748 R^2 T_c^{2.5}}{p_c}, \quad b = \frac{0.08664 RT_c}{p_c}$$

in which a and b are constants similar to the van der Waals constants, which can be related to the critical constants as shown.

Another equation that is often used is the **virial equation**, proposed by Kamerlingh Onnes (1853–1926). It expresses the pressure as a power series in the molar density $\rho = N/V$:

$$\boxed{p = RT \frac{N}{V} \left[1 + B(T) \frac{N}{V} + C(T) \left(\frac{N}{V} \right)^2 + \dots \right]} \quad (6.2.5)$$

in which $B(T)$ and $C(T)$ are functions of temperature, called the **virial coefficients**; they are experimentally measured and tabulated. For example, it is found that experimental data for the virial coefficient can be

Table 6.1 An empirical function for the second virial coefficient $B(T) = \alpha - \beta \exp(\gamma/T)$.

Gas	α (mL mol $^{-1}$)	β (mL mol $^{-1}$)	γ (K)	Range of validity (K)
Ar	154.2	119.3	105.1	80–1024
N ₂	185.4	141.8	88.7	75–700
O ₂	152.8	117.0	108.8	90–400
CH ₄	206.4	159.5	133.0	110–600
C ₂ H ₆	267.3	191.5	256	210–500

Source: Online Kaye & Laby Tables of Physical and Chemical Constants at the National Physical Laboratory, UK (<http://www.kayelaby.npl.co.uk/chemistry>).

approximated by the function $B(T) = \alpha - \beta \exp(\gamma/T)$, in which α , β and γ are constants and T is the temperature in kelvin.¹ Values of these constants for a few gases are shown in Table 6.1.

It is also found that a better fit for experimental data can be obtained by dropping $(N/V)^3$ and higher odd powers from the virial expansion (6.2.5). As expected, Equation (6.2.5) reduces to the ideal gas equation at low densities. The van der Waals constants a and b can be related to the virial coefficients $B(T)$ and $C(T)$ (Exercise 6.4); conversely, the virial coefficients can be calculated from the van der Waals constants. Since the ideal gas equation is valid at low pressures, the virial equation may also be written as

$$p = RT \frac{N}{V} [1 + B'(T)p + C'(T)p^2 + \dots] \quad (6.2.6)$$

Comparing Equations (6.2.5) and (6.2.6), it can be shown that $B = B'RT$, to a first approximation.

6.2.1 Total Internal Energy

For real gases, due to the molecular interaction, the energy is no longer only a function of the temperature. Because the interaction energy of the molecules depends on the distance between the molecules, a change in volume (at a fixed T) causes a change in energy, i.e. the term $(\partial U/\partial V)_T$ does not vanish for a real gas. Molecular forces have a short range. At low densities, since molecules are far apart, the force of interaction is small. As the density approaches zero, the energy of real gas U_{real} approaches the energy of an ideal gas U_{ideal} . We can obtain an explicit expression for U_{real} through the Helmholtz equation, $(\partial U/\partial V)_T = T^2[\partial(p/T)/\partial T]_V$, which is valid for all systems (not only for gases). Upon integration, this equation yields

$$U_{\text{real}}(T, V, N) = U_{\text{real}}(T, V_0, N) + \int_{V_0}^V T^2 \left(\frac{\partial}{\partial T} \frac{p}{T} \right)_V dV$$

To write this expression in a convenient form, first we note that, for a fixed N , as $V_0 \rightarrow \infty$, the density approaches zero, and, as noted above, U_{real} approaches the energy of an ideal gas U_{ideal} given by Equation (6.1.3). Hence, Equation (6.2.6) can be written as

$$U_{\text{real}}(T, V, N) = U_{\text{ideal}}(T, N) + \int_{\infty}^V T^2 \left(\frac{\partial}{\partial T} \frac{p}{T} \right)_V dV \quad (6.2.7)$$

¹The values of the constants α , β and γ and the ranges of T for which the empirical formula is valid can be found at http://www.kayelaby.npl.co.uk/chemistry/3_5/3_5.html of the National Physical Laboratory, UK.

If $[\partial(p/T)/\partial T]_V$ can be calculated using an equation of state, then explicit expressions for U_{real} could be derived. As an example, let us consider the van der Waals equation of state. From (6.2.1) it is easy to see that $p/T = NR/(V - Nb) - a(N/V)^2(1/T)$. Substituting this expression into (6.2.7) we obtain the energy of a van der Waals gas U_{vw} :

$$U_{\text{vw}}(T, V, N) = U_{\text{ideal}}(T, N) + \int_{\infty}^V a \left(\frac{N}{V}\right)^2 dV$$

Evaluation of the integral gives

$$U_{\text{vw}}(V, T, N) = U_{\text{ideal}} - a \left(\frac{N}{V}\right)^2 V \quad (6.2.8)$$

Writing the energy in this form shows us that the energy due to molecular interactions is equal to $-a(N/V)^2$ per unit volume. As expected, as the volume increases, U_{vw} approaches U_{ideal} .

6.2.2 Molar Heat Capacities C_{mV} and C_{mp}

If the molar internal energy U_m of a gas is known, then the molar heat capacity at constant volume $C_{mV} = (\partial U_m / \partial T)_V$ can be calculated. For a real gas, we can use Equation (6.2.7) to obtain the following expression for the molar heat capacity C_{mV} :

$$C_{mV,\text{real}} = \left(\frac{\partial U_{m,\text{real}}}{\partial T}\right)_V = \left(\frac{\partial U_{m,\text{ideal}}}{\partial T}\right)_V + \frac{\partial}{\partial T} \int_{\infty}^V T^2 \left(\frac{\partial p}{\partial T} \frac{p}{T}\right)_V dV$$

which upon explicit evaluation of the derivatives in the integral gives

$$C_{mV,\text{real}} = C_{mV,\text{ideal}} + \int_{\infty}^V T \left(\frac{\partial^2 p}{\partial T^2}\right)_V dV \quad (6.2.9)$$

Given an equation of state, such as the van der Waals equation, the above integral can be evaluated to obtain an explicit expression for C_{mV} . Equation (6.2.9) shows that, *for any equation of state in which p is a linear function of T* , $C_{mV,\text{real}} = C_{mV,\text{ideal}}$. This is true for the case of the van der Waals equation. The energy due to the molecular interactions depends on the intermolecular distance or density N/V . Because this does not change at constant V , the value of C_{mV} is unaffected by the molecular forces. C_{mV} is the change in kinetic energy of the molecules per unit change in temperature.

Also, given the equation of state, the isothermal compressibility κ_T and the coefficient of volume expansion α (which are defined by Equations (5.4.5) and (5.4.6) respectively) can be calculated. Then, using the general relation

$$C_{mp} - C_{mV} = \frac{TV_m \alpha^2}{\kappa_T}$$

(6.2.10)

(see Equation (5.4.10)), C_{mp} can also be obtained. Thus, using Equations (6.2.9) and (6.2.10), the two molar heat capacities of a real gas can be calculated using its equation of state.

6.2.3 Adiabatic Processes

For an ideal gas, we have seen in Chapter 2 that in an adiabatic process $TV^{\gamma-1} = \text{constant}$ or $pV^\gamma = \text{constant}$ (see Equations (2.3.11) and (2.3.12)), in which $\gamma = C_{mp}/C_{mV}$. One can obtain a similar equation for a real gas. An adiabatic process is defined by $dQ = 0 = dU + p dV$. By considering U as a function of V and T , this equation can be written as

$$\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + pdV = 0 \quad (6.2.11)$$

Since $(\partial U/\partial T)_V = NC_{mV}$, where N is the molar amount of the gas, this equation becomes

$$\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV = -NC_{mV} dT \quad (6.2.12)$$

By evaluating the derivative on the right-hand side of the Helmholtz equation (5.2.11), it is easy to see that $[(\partial U/\partial V)_T + p] = T(\partial p/\partial T)_V$. Furthermore, we have also seen in Chapter 5 (see Equation (5.4.7)) that $(\partial p/\partial T)_V = \alpha/\kappa_T$. Using these two relations, Equation (6.2.12) can be written as

$$\frac{T\alpha}{\kappa_T} dV = -NC_{mV} dT \quad (6.2.13)$$

To write this expression in terms of the ratio $\gamma = C_{mp}/C_{mV}$ we use the general relation:

$$C_{mp} - C_{mV} = \frac{T\alpha^2 V_m}{\kappa_T} \quad (6.2.14)$$

in which V_m is the molar volume. Combining Equations (6.2.14) and (6.2.13) we obtain

$$N \frac{C_{mp} - C_{mV}}{V\alpha} dV = -NC_{mV} dT \quad (6.2.15)$$

where we have made the substitution $V_m = V/N$ for the molar volume. Dividing both sides of this expression by C_{mV} and using the definition $\gamma = C_{mp}/C_{mV}$ we obtain the simple expression

$$\frac{\gamma - 1}{V} dV = -\alpha dT \quad (6.2.16)$$

Generally, γ varies little with volume or temperature, so it may be treated as a constant and Equation (6.2.16) can be integrated to obtain

$$(\gamma - 1) \ln V = - \int \alpha(T) dT + C \quad (6.2.17)$$

in which we have written α as an explicit function of T . C is the integration constant. An alternative way of writing this expression is

$$\boxed{V^{\gamma-1} e^{\int \alpha(T) dT} = \text{constant}} \quad (6.2.18)$$

This relation is valid for all gases. For an ideal gas, $\alpha = (1/V)(\partial V/\partial T)_p = 1/T$. When this is substituted into Equation (6.2.18) we obtain the familiar equation $TV^{\gamma-1} = \text{constant}$. If p is a linear function of T , as is the case with the van der Waals equation, since $C_{mV,\text{real}} = C_{mV,\text{ideal}}$, from Equation (6.2.14) it follows that

$$\gamma - 1 = \frac{T\alpha^2 V_m}{C_{mV,\text{ideal}} \kappa_T} \quad (6.2.19)$$

If the equation of state of a real gas is known, then α and γ can be evaluated (numerically, if not analytically) as a function of T , and the relation (6.2.18) between V and T can be made explicit for an adiabatic process.

6.2.4 Helmholtz and Gibbs Energies

The method used to obtain a relation (6.2.7) between U_{ideal} and U_{real} can also be used to relate the corresponding Helmholtz and Gibbs energies. The main idea is that the thermodynamic quantities for a real gas approach those of an ideal gas as $p \rightarrow 0$ or $V \rightarrow \infty$. Let us consider the Helmholtz energy F . Since $(\partial F / \partial V)_T = -p$ (see Equation (5.1.6)) we have the general expression

$$F(T, V, N) = F(T, V_0, N) - \int_{V_0}^V p \, dV \quad (6.2.20)$$

The difference between the Helmholtz energy of a real and an ideal gas at any T , V and N can be obtained as follows. Writing Equation (6.2.20) for a real and an ideal gas, and subtracting one from the other, it is easy to see that

$$F_{\text{real}}(T, V, N) - F_{\text{ideal}}(T, V, N) = F_{\text{real}}(T, V_0, N) - F_{\text{ideal}}(T, V_0, N) - \int_{V_0}^V (p_{\text{real}} - p_{\text{ideal}}) \, dV \quad (6.2.21)$$

Now, since $\lim_{V_0 \rightarrow \infty} [F_{\text{real}}(V_0, T, N) - F_{\text{ideal}}(V_0, T, N)] = 0$, we can write the above expression as

$$F_{\text{real}}(T, V, N_k) - F_{\text{ideal}}(T, V, N_k) = - \int_{\infty}^V (p_{\text{real}} - p_{\text{ideal}}) \, dV \quad (6.2.22)$$

where we have explicitly indicated the fact that this expression is valid for a multicomponent system by replacing N with N_k . Similarly, we can also show that

$$G_{\text{real}}(T, p, N_k) - G_{\text{ideal}}(T, p, N_k) = \int_0^p (V_{\text{real}} - V_{\text{ideal}}) \, dp \quad (6.2.23)$$

As an example, let us calculate F using the van der Waals equation. For the van der Waals equation, we have $p_{\text{real}} = p_{\text{vw}} = [NRT/(V - bN)] - (aN^2/V^2)$. Substituting this expression for p_{real} into Equation (6.2.22) and performing the integration one can obtain (Exercise 6.10)

$$F_{\text{vw}}(T, V, N) = F_{\text{ideal}}(T, V, N) - a \left(\frac{N}{V} \right)^2 V - NRT \ln \left(\frac{V - Nb}{V} \right) \quad (6.2.24)$$

where

$$\begin{aligned} F_{\text{ideal}} &= U_{\text{ideal}} - TS_{\text{ideal}} \\ &= U_{\text{ideal}} - TN[s_0 + C_{mV} \ln(T) + R \ln(V/N)] \end{aligned} \quad (6.2.25)$$

Substituting Equation (6.2.25) into Equation (6.2.24) and simplifying we obtain

$$\begin{aligned} F_{\text{vw}} &= U_{\text{ideal}} - a(N/V)^2 V - TN[s_0 + C_{mV} \ln(T) + R \ln((V - Nb)/N)] \\ &= U_{\text{vw}} - TN[s_0 + C_{mV} \ln(T) + R \ln((V - Nb)/N)] \end{aligned} \quad (6.2.26)$$

where we have used the expression $U_{\text{vw}}(V, T, N) = U_{\text{ideal}} - a(N/V)^2 V$ for the energy of a van der Waals gas (see Equation (6.2.8)). Similarly, the Gibbs energy of a real gas can be calculated using the van der Waals equation.

6.2.5 Entropy

The entropy of a real gas can be obtained using expressions (6.2.7) and (6.2.21) for U_{real} and F_{real} because $F_{\text{real}} = U_{\text{real}} - TS_{\text{real}}$. Using the van der Waals equation, for example, the entropy S_{vw} of a real gas can be identified in Equation (6.2.26):

$$S_{\text{vw}}(T, V, N) = N \{ s_0 + C_{mV} \ln(T) + R \ln[(V - Nb)/N] \} \quad (6.2.27)$$

A comparison of Equation (6.2.27) with the entropy of an ideal gas (6.1.6) shows that, in the van der Waals entropy, the term $(V - Nb)$ takes the place of V in the ideal gas entropy.

6.2.6 Chemical Potential

The chemical potential for a real gas can be derived from the expression (6.2.23) for the Gibbs free energy. Since the chemical potential of the component k is $\mu_k = (\partial G / \partial N_k)_{p,T}$, by differentiating Equation (6.2.23) with respect to N_k we obtain

$$\mu_{k,\text{real}}(T, p) - \mu_{k,\text{ideal}}(T, p) = \int_0^p (V_{mk,\text{real}} - V_{mk,\text{ideal}}) dp \quad (6.2.28)$$

in which $V_{mk} = (\partial V / \partial N_k)_{p,T}$ is the partial molar volume of the component k by definition. For simplicity, let us consider a single gas. To compare the molar volume of the ideal gas $V_{m,\text{ideal}} = RT/p$ with that of a real gas $V_{m,\text{real}}$, a **compressibility factor** Z is defined as follows:

$$V_{m,\text{real}} = ZRT/p \quad (6.2.29)$$

For an ideal gas $Z = 1$; a deviation of the value of Z from 1 indicates nonideality. In terms of Z , the chemical potential can be written as

$$\begin{aligned} \mu_{\text{real}}(T, p) &= \mu_{\text{ideal}}(T, p) + RT \int_0^p \left(\frac{Z-1}{p} \right) dp \\ &= \mu_{\text{ideal}}(p_0, T) + RT \ln \left(\frac{p}{p_0} \right) + RT \int_0^p \left(\frac{Z-1}{p} \right) dp \end{aligned} \quad (6.2.30)$$

in which we have used expression $\mu_{\text{ideal}}(p, T) = \mu(p_0, T) + RT \ln(p/p_0)$ for the chemical potential of an ideal gas. The chemical potential is also expressed in terms of a quantity called **fugacity** f , which was introduced by G.N. Lewis, a quantity similar to pressure [1]. To keep the form of the chemical potential of a real gas similar to that of the ideal gases, G.N. Lewis introduced the fugacity f through the definition

$$\mu_{\text{real}}(p, T) = \mu_{\text{ideal}}(p, T) + RT \ln \left(\frac{f}{p} \right) \quad (6.2.31)$$

Indeed, we must have $\lim_{p \rightarrow 0} (f/p) = 1$ to recover the expression for the ideal gas at a very low pressure. Thus, the deviation of f from the pressure of an ideal gas is a measure of the ‘nonideality’ of the real gas. Comparing Equations (6.2.30) and (6.2.31), we see that

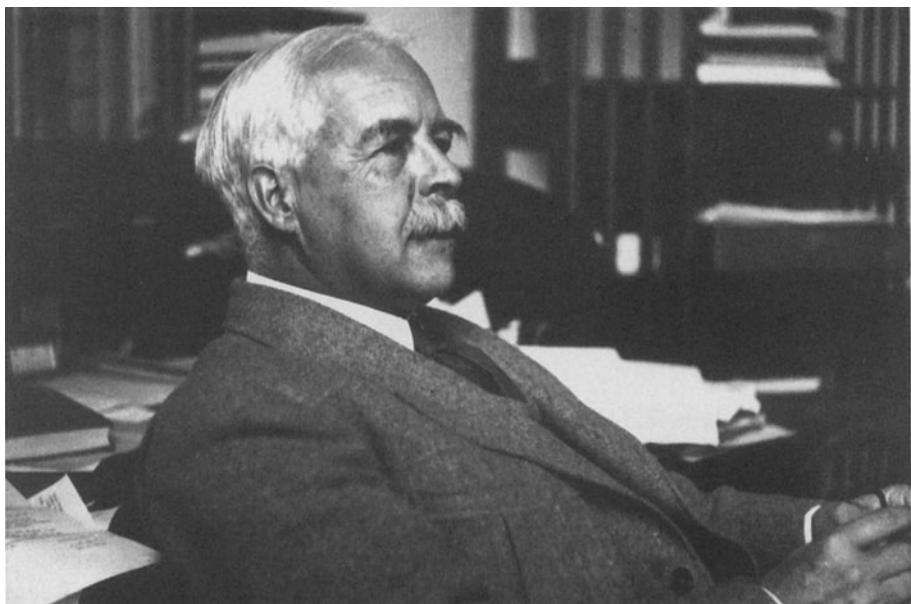
$$\boxed{\ln \left(\frac{f}{p} \right) = \int_0^p \left(\frac{Z-1}{p} \right) dp} \quad (6.2.32)$$

It is possible to obtain Z explicitly for various equations such as the van der Waals equation or the virial equation (6.2.5). For example, if we use the virial equation we have

$$\begin{aligned} Z &= \frac{pV_m}{RT} = [1 + B'(T)p + C'(T)p^2 + \dots] \\ &= \left[1 + B(T) \left(\frac{N}{V} \right) + C(T) \left(\frac{N}{V} \right)^2 + \dots \right] \end{aligned} \quad (6.2.33)$$

Substituting this expression in Equation (6.2.33) in Equation (6.2.32) we find that, to the second order in p :

$$\ln \left(\frac{f}{p} \right) = B'(T)p + \frac{C'(T)p^2}{2} + \dots \quad (6.2.34)$$



G.N. Lewis (1875–1946).

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Generally, terms of the order p^2 are small and may be ignored. Then, Equation (6.2.34) can be used for the chemical potential of a real gas μ_{real} given by Equation (6.2.31) and can be written as

$$\begin{aligned} \mu_{\text{real}}(p, T) &= \mu_{\text{ideal}}(p, T) + RT \ln \left(\frac{f}{p} \right) \\ &= \mu_{\text{ideal}}(p, T) + RT(B'(T)p + \dots) \end{aligned} \quad (6.2.35)$$

This expression can also be written in terms of the virial coefficients of Equation (6.2.5) by noting the relation $B = B'RT$, to a first approximation. Thus, the chemical potential in terms of the virial coefficients is

$$\mu_{\text{real}} = \mu_{\text{ideal}}(p, T) + Bp + \dots \quad (6.2.36)$$

Similarly, expressions for μ_{real} can be obtained using the van der Waals equation.

We can also obtain explicit expressions for μ using $(\partial F/\partial N)_{T,V} = \mu$. Using the van der Waals equation, for example, we can write the chemical potential as a function of the molar density $n = N/V$ and temperature T (Exercise 6.9):

$$\mu(n, T) = (U_0 - 2an) + \left(\frac{C_{\text{mV}}}{R} + \frac{1}{1-nb} \right) RT - T \left[s_0 + C_{\text{mV}} \ln T - R \ln \left(\frac{n}{1-bn} \right) \right] \quad (6.2.37)$$

6.2.7 Chemical Affinities

Finally, to understand the nature of chemical equilibrium of real gases it is useful to obtain affinities for chemically reacting real gases. The affinity of a reaction $A = -\sum_k v_k \mu_k$, in which v_k are the stoichiometric coefficients (which are negative for reactants and positive for products). For a real gas this can be written using the expression (6.2.28) for the chemical potential:

$$A_{\text{real}} = A_{\text{ideal}} - \sum_k v_k \int_0^p (V_{\text{m,real},k} - V_{\text{m,ideal},k}) dp \quad (6.2.38)$$

This expression can be used to calculate the equilibrium constants for reacting real gases. The partial molar volume $V_{\text{m,ideal},k}$ is RT/p . Hence, the above expression becomes

$$A_{\text{real}} = A_{\text{ideal}} - \sum_k v_k \int_0^p \left(V_{\text{m,real},k} - \frac{RT}{p} \right) dp \quad (6.2.39)$$

With the above quantities, all the thermodynamics of real gases can be described once the real gas parameters, such as the van der Waals constants or the virial coefficients, are known.

6.3 Thermodynamics Quantities for Pure Liquids and Solids

6.3.1 Equation of State

For pure solids and liquids, jointly called *condensed phases*, the volume is determined by the molecular size and molecular forces and it does not change much with a change in p and T . Since the molecular size and forces are very specific to a compound, the equation of state is specific to that compound. A relation between V , T and p is expressed in terms of the coefficient of thermal expansion α and the isothermal compressibility κ_T defined by Equations (5.4.5) and (5.4.6). If we consider V as a function of p and T , $V(p, T)$, we can write

$$dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp = \alpha V dT - \kappa_T V dp \quad (6.3.1)$$

The values of α and κ_T are small for solids and liquids. For liquids, the coefficient of thermal expansion α is in the range 10^{-3} to 10^{-4} K $^{-1}$ and isothermal compressibility κ_T is about 10^{-5} atm $^{-1}$. For solids, α is in the range 10^{-5} to 10^{-6} K $^{-1}$ and κ_T is in the range 10^{-6} to 10^{-7} atm $^{-1}$. Table 6.2 lists the values of α and κ_T for some liquids and solids. Furthermore, the values of α and κ_T are almost constant for T variations of about

Table 6.2 List of coefficient of thermal expansion α and isothermal compressibility κ_T for some liquids and solids.

Compound	α (10^{-4} K $^{-1}$)	κ_T (10^{-6} atm $^{-1}$)
Water	2.1	49.6
Benzene	12.4	92.1
Mercury	1.8	38.7
Ethanol	11.2	76.8
Carbon tetrachloride	12.4	90.5
Copper	0.501	0.735
Diamond	0.030	0.187
Iron	0.354	0.597
Lead	0.861	2.21

100 K and pressure variations of about 50 atm. Therefore, Equation (6.3.1) can be integrated to obtain the following equation of state:

$$\begin{aligned} V(p, T) &= V(p_0, T_0) \exp[\alpha(T - T_0) - \kappa_T(p - p_0)] \\ &\approx V(p_0, T_0)[1 + \alpha(T - T_0) - \kappa_T(p - p_0)] \end{aligned} \quad (6.3.2)$$

6.3.2 Thermodynamic Quantities

Thermodynamically, the characteristic feature of solids and liquids is that μ , S and H change very little with pressure and, hence, they are essentially functions of T for a given N . If entropy is considered as a function of p and T , then

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \quad (6.3.3)$$

The first term, $(\partial S/\partial T)_p = NC_{mp}/T$, which relates dS to the experimentally measurable C_{mp} . The second term can be related to α as follows:

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left[\frac{\partial}{\partial p} \left(\frac{\partial G(p, T)}{\partial T} \right)_p \right]_T = - \left[\frac{\partial}{\partial T} \left(\frac{\partial G(p, T)}{\partial p} \right)_T \right]_p = - \left(\frac{\partial V}{\partial T} \right)_p = -V\alpha \quad (6.3.4)$$

With these observations, we can now rewrite Equation (6.3.3) as

$$dS = \frac{NC_{mp}}{T} dT - \alpha V dp \quad (6.3.5)$$

Upon integration, this equation yields

$$S(p, T) = S(0, 0) + N \int_0^T \frac{C_{mp}}{T} dT - N \int_0^p \alpha V_m dp \quad (6.3.6)$$

where we have used $V = NV_m$. (That $S(0, 0)$ is well defined is guaranteed by the Nernst theorem.) Since V_m and α do not change much with p , the third term in Equation (6.3.6) can be approximated to $N\alpha V_m p$. For $p = 1-10$ atm, this term is small compared with the second term. For example, in the case of water, $V_m = 18.0 \times 10^{-6}$ m 3 mol $^{-1}$ and $\alpha = 2.1 \times 10^{-4}$ K $^{-1}$. For $p = 10$ bar = 10×10^5 Pa, the term $\alpha V_m p$ is about

$3.6 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1}$. The value of C_{mp} , on the other hand, is about $75 \text{ J K}^{-1} \text{ mol}^{-1}$. Though C_{mp} approaches zero so that S is finite as $T \rightarrow 0$, the molar entropy of water at $p = 1 \text{ bar}$ and $T = 298 \text{ K}$ is about 70 J K^{-1} . Thus, it is clear that the third term in Equation (6.3.6) that contains p is insignificant compared with the second term. Since this is generally true for solids and liquids, we may write

$$S(p, T) = S(0, 0) + N \int_0^T \frac{C_{mp}(T)}{T} dT \quad (6.3.7)$$

where we have written C_{mp} explicitly as a function of T . A knowledge of $C_{mp}(T)$ will enable us to obtain the value of entropy of a pure solid or liquid. Note that the integral in Equation (6.3.7) is $\int_0^T d_e S$ because $(NC_{mp} dT/T) = dQ/T = d_e S$.

The chemical potential of condensed phases can be obtained from the Gibbs–Duhem equation $d\mu = -S_m dT + V_m dp$ (see Equation (5.2.4)). Substituting the value of molar entropy into the Gibbs–Duhem equation and integrating, we get

$$\begin{aligned} \mu(p, T) &= \mu(0, 0) - \int_0^T S_m(T) dT + \int_0^p V_m dp \\ &= \mu^0(T) + RT \ln a \end{aligned} \quad (6.3.8)$$

where we assumed that V_m is essentially a constant. Once again, it can be shown that the term containing p is small compared with the first term, which is a function of T . For water, $V_m p = 1.8 \text{ J mol}^{-1}$ when $p = 1 \text{ atm}$, whereas the first term is of the order 280 kJ mol^{-1} . Following the definition of activity a , if we write $V_m p = RT \ln(a)$, then we see that for *liquids and solids the activity is nearly equal to unity*.

In a similar manner, one can obtain other thermodynamic quantities such as enthalpy H and the Helmholtz free energy F .

6.3.3 Heat Capacities

From the above expressions it is clear that one needs to know the molar heat capacities of a substance as a function of temperature and pressure in order to calculate the entropy and other thermodynamic quantities. A theory of heat capacities of solids, which requires statistical mechanics and quantum theory, is presented in chapter 20. Here we shall only give a brief outline of Debye's theory of molar heat capacities of solids, which provides an approximate general theory. The situation is more complex for liquids because for liquids there is neither complete molecular disorder, as in a gas, nor is there a long-range order as in the case of a solid.

According to a theory of solids formulated by Peter Debye, the molar heat capacity C_{mV} of a pure solid is of the form

$$C_{mV} = 3RD(T/\theta) \quad (6.3.9)$$

in which $D(T/\theta)$ is a function of the ratio T/θ . The parameter θ depends mainly on the chemical composition of the solid and, to a very small extent, varies with the pressure. As the ratio T/θ increases, the 'Debye function' $D(T/\theta)$ tends to unity, and molar heat capacities of all solids $C_{mV} = 3R$. The fact that the heat capacities of solids tend to have the same value had been observed long before Debye formulated a theory of

heat capacities; it is called the law of Dulong and Petit. Debye theory provided an explanation for the law of Dulong and Petit. At very low temperatures, when $T/\theta < 0.1$:

$$D \left(\frac{T}{\theta} \right) \approx \frac{4\pi^4}{5} \left(\frac{T}{\theta} \right)^3 \quad (6.3.10)$$

Thus, Debye's theory predicts that the molar heat capacities at low temperatures will be proportional to the third power of the temperature. Experimentally, this was found to be true for many solids. Quantum theory is required to explain this result.

Once C_{mV} is known, C_{mp} can be obtained using the general expression $C_{mp} - C_{mV} = TV_m\alpha^2/\kappa_T$. More detail on this subject can be found in texts on condensed matter. The thermodynamics of liquid and solid mixtures is discussed in Chapters 7 and 8.

Reference

1. Lewis, G.N., Randall, M., *Thermodynamics and Free Energy of Chemical Substances*. 1925, McGraw-Hill: New York.

Examples

Example 6.1 Show that C_{mV} for a van der Waals gas is the same as that of an ideal gas.

Solution The relation between C_{mV} for real and ideal gases is given by Equation (6.2.9):

$$C_{mV,\text{real}} = C_{mV,\text{ideal}} + \int_{\infty}^V T \left(\frac{\partial^2 p}{\partial T^2} \right)_V dV$$

For 1 mol of a van der Waals gas:

$$p = \frac{RT}{V_m - b} - a \frac{1}{V_m^2}$$

Since this is a linear function of T the derivative $(\partial^2 p / \partial T^2)_V = 0$. Hence, the integral in the expression relating $C_{mV,\text{real}}$ and $C_{mV,\text{ideal}}$ is zero. Hence, $C_{mV,\text{real}} = C_{mV,\text{ideal}}$.

Example 6.2 Calculate the total internal energy of a real gas using the Berthelot equation (6.2.2).

Solution The internal energy of a real gas can be calculated using the relation (6.2.7):

$$U_{\text{real}}(T, V, N) = U_{\text{ideal}}(T, N) + \int_{\infty}^V T^2 \left(\frac{\partial}{\partial T} \frac{p}{T} \right)_V dV$$

For the Berthelot equation:

$$p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$$

In this case, the integral

$$\int_{\infty}^V T^2 \left(\frac{\partial}{\partial T} \frac{p}{T} \right)_V dV = - \int_{\infty}^V \frac{aN^2}{V^2} T^2 \frac{\partial}{\partial T} \left(\frac{1}{T^2} \right) dV = \int_{\infty}^V \frac{2aN^2}{T} \frac{1}{V^2} dV \\ = - \frac{2aN^2}{TV}$$

Hence:

$$U_{\text{real}}(T, V, N) = U_{\text{ideal}}(T, N) - \frac{2aN^2}{TV}$$

Exercises

- 6.1** For an *ideal gas* obtain the explicit expressions for the following:

- (a) $F(V, T, N) = U - TS$ as a function of V, T and N .
- (b) $G = U - TS + pV$ as a function of p, T and N .
- (c) Use the relation $\mu = (\partial F / \partial N)_{V,T}$ to obtain an expression for μ as a function of the molar density N/V and T . Also show that $\mu = \mu^0(T) + RT \ln(p/p_0)$, in which $\mu^0(T)$ is a function of T .

- 6.2** (a) Obtain a general expression for the entropy of mixing of two nonidentical gases of equal molar densities N/V , with molar amounts N_1 and N_2 , initially occupying volumes V_1 and V_2 . Also show that the entropy of mixing can be written as $\Delta S_{\text{mix}} = -RN(x_1 \ln x_1 + x_2 \ln x_2)$, where x_1 and x_2 are the mole fractions and $N = N_1 + N_2$.
 (b) Using the Stirling approximation $N! \approx N \ln N - N$, obtain Equation (6.1.15) from Equation (6.1.14).

- 6.3** For N_2 the critical values are $p_c = 33.5$ atm, $T_c = 126.3$ K and $V_{mc} = 90.1 \times 10^{-3}$ L mol $^{-1}$. Using Equations (6.2.1) to (6.2.3), calculate the constants a and b for the van der Waals, Berthelot and Dieterici equations. Plot the p - V_m curves for the three equations at $T = 300$ K, 200 K and 100 K on the same graph in the range $V_m = 0.1$ L to 10 L and comment on the differences between the curves.

- 6.4** Using the van der Waals equation, write the pressure as a function of the molar density N/V . Assume that the quantity $b(N/V)$ is small and use the expansion $1/(1-x) = 1 + x + x^2 + x^3 + \dots$, valid for $x < 1$, to obtain an equation similar to the virial equation

$$p = RT \frac{N}{V} \left[1 + B(T) \frac{N}{V} + C(T) \left(\frac{N}{V} \right)^2 + \dots \right]$$

Comparing the two series expansions for p , show that the van der Waals constants a and b and the virial coefficients $B(T)$ and $C(T)$ are related by $B = b - (a/RT)$ and $C = b^2$.

- 6.5** The Boyle temperature is defined as the temperature at which the virial coefficient $B(T) = 0$. An empirical function used to fit experimental data is $B(T) = \alpha - \beta \exp(\gamma/T)$, in which α , β and γ are constants tabulated in Table 6.1.

- (a) Using the data in Table 6.1, determine the Boyle temperatures of N_2 , O_2 and CH_4 .
- (b) Plot $B(T)$ for N_2 , O_2 and CH_4 on one graph for an appropriate range of T .

- 6.6** (a) Assume an ideal gas energy $U_{\text{ideal}} = C_{\text{mV}}NT$, where $C_{\text{mV}} = 28.46 \text{ J K}^{-1}$ for CO₂ and calculate the difference ΔU between U_{ideal} and U_{vw} for $N = 1$, $T = 300 \text{ K}$ at $V = 0.5 \text{ L}$. What percentage of U_{ideal} is ΔU ?
 (b) Use *Maple/Mathematica* to obtain a three-dimensional plot of $\Delta U/U_{\text{ideal}}$ for 1 mol of CO₂, in the volume range $V = 22.00 \text{ L}$ to 0.50 L for $T = 200 \text{ K}$ to 500 K .
- 6.7** Obtain Equation (6.2.9) from Equation (6.2.7) and the definition $C_{\text{mV,real}} = (\partial U_{\text{real}}/\partial T)_V$.
- 6.8** For CO₂, using the van der Waals equation:
 (a) Obtain an expression for the compressibility factor Z. At $T = 300 \text{ K}$ and for $N = 1$, using *Mathematica/Maple*, plot Z as a function of V from $V = 22.0 \text{ L}$ to 0.5 L .
 (b) Obtain an explicit expression for $(F_{\text{vw}} - F_{\text{ideal}})$ for 1 mol of CO₂ as a function of T and V in which if T is in Kelvin and V is in liters, then $(F_{\text{vw}} - F_{\text{ideal}})$ is in joules.
- 6.9** Show that for a van der Waals gas:
- $$\mu_{\text{vw}}(n, T) = (U_0 - 2an) + \left(\frac{C_{\text{mV}}}{R} + \frac{1}{1-nb} \right) RT - T \left[s_0 + C_{\text{mV}} \ln T - R \ln \left(\frac{n}{1-bn} \right) \right]$$
- in which $n = N/V$. (Hint: it can be obtained from F_{vw} .)
- 6.10** Obtain Equation (6.2.24) from (6.2.22) and Equation (6.2.26) from (6.2.24) and (6.2.25).

7

Thermodynamics of Phase Change

Introduction

Transformations from a liquid to a vapor phase or from a solid to a liquid phase are caused by heat. The eighteenth century investigations of Joseph Black revealed that these transformations take place at a definite temperature: the boiling point or the melting point. At this temperature the heat absorbed by the substance does not increase its temperature but is ‘latent’ or concealed; the heat’s effect is to cause the change from one phase to another, not to increase the substance’s temperature. Joseph Black, who clarified this concept, measured the ‘latent heat’ for the transformation of ice to water.

Under suitable conditions, the phases of a compound can coexist in a state of thermal equilibrium. The nature of this state of thermal equilibrium and how it changes with pressure and temperature can be understood using the laws of thermodynamics. In addition, at the point where the phase transition takes place, some thermodynamic quantities, such as molar entropy, change discontinuously. Based on such discontinuous changes of some thermodynamic quantities, such as molar heat capacity and molar entropy, phase transitions in various materials can be classified into different ‘orders’. There are general theories that describe phase transitions of each order. The study of phase transitions has grown to be a large and interesting subject, and some very important developments occurred during the 1960s and the 1970s. In this chapter, we will only present some of the basic results. For further understanding of phase transitions, we refer the reader to books devoted to this subject [1–3].

7.1 Phase Equilibrium and Phase Diagrams

The conditions of temperature and pressure under which a substance exists in different phases, i.e. gas, liquid or solid, are summarized in a **phase diagram**. A simple phase diagram is shown in Figure 7.1. Under suitable conditions of pressure and temperature, two phases may coexist in thermodynamic equilibrium. The thermodynamic study of phase equilibrium leads to many interesting and useful results. For example, it tells us how the boiling point or freezing point of a substance changes with changes in pressure. We shall see how the thermodynamic formalism developed in the previous chapters enables us to obtain expression that relates the boiling point of a liquid to its pressure.

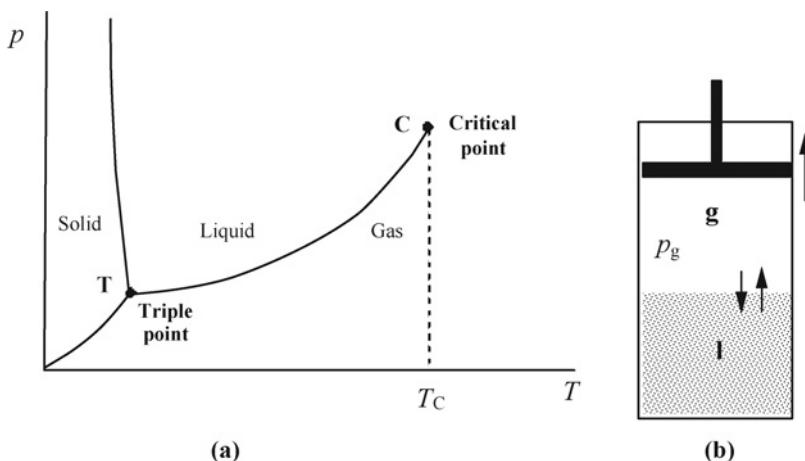


Figure 7.1 (a) Phase diagram for a one-component system showing equilibrium p - T curves (defined by the equality of the chemical potentials), the triple point T and the critical point C . T_c is the critical temperature above which the gas cannot be liquefied by increasing the pressure. (b) A liquid in equilibrium with its vapor. The affinity for the liquid–vapor transformation $A = \mu_l - \mu_g = 0$. An infinitely slow expansion in the system’s volume results in a ‘reversible’ transformation of the liquid to gas at an affinity $A \approx 0$.

We begin by looking at the equilibrium between liquid and gas phases, as shown in Figure 7.1b. When a liquid is in a closed container, a part of it will evaporate and fill the space above it until an equilibrium is reached. The system under consideration is closed and consists only of the liquid in equilibrium with its vapor at a fixed temperature. In Figure 7.2, the p - V isotherms of a vapor–liquid system are shown. The region of coexistence of the liquid and vapor phases corresponds to the flat portion XY of the isotherms. When $T > T_c$, the flat portion does not exist; there is no distinction between the gas and the liquid phases. The flat portion

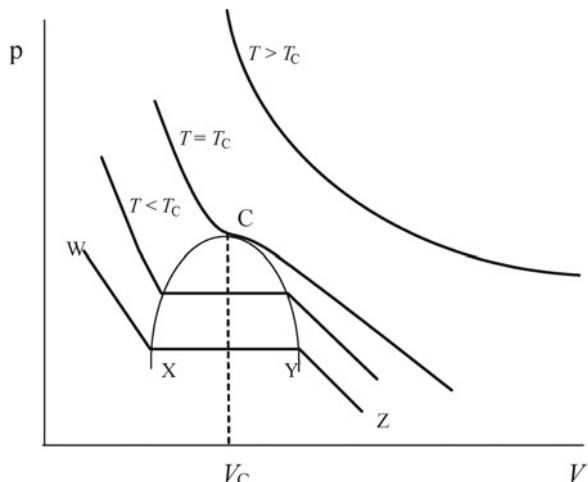


Figure 7.2 p - V isotherms of a gas showing critical behavior. T_c is the critical temperature above which the gas cannot be liquefied by increasing the pressure. In the flat region XY, the liquid and the gas phases coexist.

of each isotherm in Figure 7.2 corresponds to a point on the curve TC in Figure 7.1a; as the temperature approaches T_c , we approach the critical point C.

For a thermodynamic analysis of the equilibrium between liquid and gas phases of a substance let us consider a **heterogeneous system** in which the two phases coexist and can interconvert, thus changing the volume of each phase. Under these conditions, the liquid converts irreversibly to vapor, or vice versa, until equilibrium between the two phases is attained. The exchange of matter between the two phases may be considered a ‘chemical reaction’, which we may represent as



Let the chemical potential of the substance k in the two phases be μ_k^g and μ_k^l , with the superscripts ‘g’ for gas and ‘l’ for liquid. At equilibrium, the entropy production due to every irreversible process must vanish. This implies that the affinity corresponding to liquid–vapor conversion must vanish, i.e.

$$A = \mu_k^l(p, T) - \mu_k^g(p, T) = 0$$

i.e.

$$\mu_k^l(p, T) = \mu_k^g(p, T) \quad (7.1.2)$$

in which we have made explicit that the two chemical potentials are functions of pressure and temperature. The pressure of the vapor phase in equilibrium with the liquid phase is called the **saturated vapor pressure**. The equality of the chemical potentials implies that, when a liquid is in equilibrium with its vapor, the pressure and temperature are not independent. This relationship between p and T , as expressed in Equation (7.1.2), gives the **coexistence curve** TC in the phase diagram shown in Figure 7.1a.

A liquid in equilibrium with its vapor is a good system to illustrate the idea of a ‘reversible’ transformation for which $d_iS = 0$ (Figure 7.1b). Let us assume that initially the system is in equilibrium with $A = 0$. If the volume of the system is increased slowly, the chemical potential of the gas phase will decrease by a small amount, making the affinity for the liquid-to-gas transformation positive. This will result in the conversion of liquid to gas until a new equilibrium is established. In the limit of an ‘infinitely slow’ increase of volume such that the transformation takes place at an arbitrarily small A , i.e. $A \approx 0$, virtually no entropy is produced during this transformation because $d_iS = A d\xi \approx 0$. Therefore, it is a reversible transformation. A reversible transformation, of course, is an idealized process taking place at an infinitely slow rate. In any real process that occurs at a nonzero rate, $d_iS = A d\xi > 0$, but this change can be made arbitrarily small by slowing the rate of transformation.

Clearly, equality of chemical potentials as in Equation (7.1.2) must be valid between any two phases that are in equilibrium. If there are P phases, then we have the general equilibrium condition:

$$\mu_k^1(p, T) = \mu_k^2(p, T) = \mu_k^3(p, T) = \dots = \mu_k^P(p, T) \quad (7.1.3)$$

The phase diagram Figure 7.1a also shows another interesting feature: the **critical point** C at which the liquid–vapor coexistence curve TC terminates. If the temperature of the gas is above T_c , the gas cannot be liquefied by increasing the pressure. As the pressure increases, the density increases but there is no transition to a condensed phase – and no latent heat. In contrast, there is no critical point for the transition between solid and liquid due to the fact that a solid phase has a definite crystal structure that the liquid phase does not have. Owing to the definite change in symmetry, the transition between a solid and liquid is always well defined.

A change of phase of a solid is not necessarily a transformation to a liquid. A solid may exist in different phases. Thermodynamically, a phase change is identified by a sharp change in properties such as the heat capacity. In molecular terms, these changes correspond to different arrangements of the atoms, i.e. different crystal structures. For example, at very high pressures, ice exists in different structures, and these are the different solid phases of water. Figure 7.3 shows the phase diagram of water.

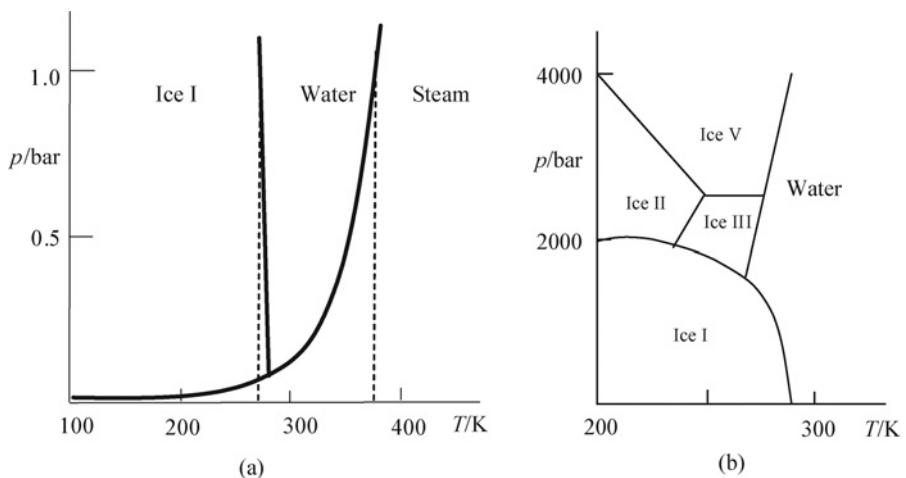


Figure 7.3 (a) The phase diagram of water at ordinary pressures (not to scale). (b) At high pressures, the solid phase (ice) can exist in different phases, as shown on the right. The triple point of water is at $p = 0.006 \text{ bar}$, $T = 273.16 \text{ K}$. The critical point is at $p_c = 218 \text{ bar}$, $T_c = 647.3 \text{ K}$.

7.1.1 The Clapeyron Equation

At a given pressure, the coexistence curve specifies the temperature at which the two phases can coexist. It is the temperature at which one phase begins to convert to the other; in the case of a liquid–vapor coexistence curve, the temperature corresponds to the boiling point at the given pressure. Thus, if we obtain an explicit relation between the pressure and the temperature that defines the coexistence curve, then we can know how the boiling point or freezing point changes with pressure. Using the condition for equilibrium (7.1.2), we can arrive at a more explicit expression for the coexistence curve. Let us consider two phases denoted by 1 and 2. Using the Gibbs–Duhem equation, $d\mu = -S_m dT + V_m dp$, one can derive a differential relation between p and T of the system as follows. From Equation (7.1.3) it is clear that, for a component k , $d\mu_k^1 = d\mu_k^2$. Therefore, we have the equality

$$-S_{m1}dT + V_{m1}dp = -S_{m2}dT + V_{m2}dp \quad (7.1.4)$$

in which the molar quantities for the two phases are indicated by the subscripts ‘m1’ and ‘m2’. From this it follows that

$$\frac{dp}{dT} = \frac{S_{m1} - S_{m2}}{V_{m1} - V_{m2}} = \frac{\Delta H_{\text{trans}}}{T(V_{m1} - V_{m2})} \quad (7.1.5)$$

in which we have expressed the difference in the molar entropy between the two phases in terms of the enthalpy of transition: $S_{m1} - S_{m2} = (\Delta H_{\text{trans}}/T)$, where ΔH_{trans} is the *molar enthalpy* of the transition (vaporization, fusion or sublimation). Molar enthalpies of vaporization and fusion of some substances are listed in Table 7.1. More generally, then, we have the equation called the **Clapeyron equation**:

$$\frac{dp}{dT} = \frac{\Delta H_{\text{trans}}}{T\Delta V_m} \quad (7.1.6)$$

Table 7.1 Enthalpies of fusion of and vaporization at $p = 1 \text{ bar} = 10^5 \text{ Pa} = 0.987 \text{ atm}$.

Substance	$T_m \text{ (K)}$	$\Delta H_{\text{fus}} \text{ (kJ mol}^{-1}\text{)}$	$T_b \text{ (K)}$	$\Delta H_{\text{vap}} \text{ (kJ mol}^{-1}\text{)}$
He	0.95*	0.021	4.22	0.082
H ₂	14.01	0.12	20.28	0.46
O ₂	54.36	0.444	90.18	6.820
N ₂	63.15	0.719	77.35	5.586
Ar	83.81	1.188	87.29	6.51
CH ₄	90.68	0.941	111.7	8.18
C ₂ H ₅ OH	156	4.60	351.4	38.56
CS ₂	161.2	4.39	319.4	26.74
CH ₃ OH	175.2	3.16	337.2	35.27
NH ₃	195.4	5.652	239.7	23.35
CO ₂	217.0	8.33	194.6	25.23
Hg	234.3	2.292	629.7	59.30
CCl ₄	250.3	2.5	350	30.0
H ₂ O	273.15	6.008	373.15	40.66
Ga	302.93	5.59	2676	270.3
Ag	1235.1	11.3	2485	257.7
Cu	1356.2	13.0	2840	306.7

Source: D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 75th edition, 1994, CRC Press: Ann Arbor, MI.

*Under high pressure.

Here, ΔV_m is the difference in the *molar volumes* of the two phases. The temperature T in this equation is the transition temperature, i.e. boiling point, melting point, etc. This equation tells us how the transition temperature changes with pressure. For example, for a transition from a solid to a liquid in which there is an increase in the molar volume ($\Delta V > 0$), the freezing point will increase ($dT > 0$) when the pressure is increased ($dp > 0$); if there is a decrease in the molar volume, then the opposite will happen – as is the case when ice melts and becomes liquid water.

7.1.2 The Clausius–Clapeyron Equation

For the case of liquid–vapor transitions, the Clapeyron equation can be further simplified. In this transition $V_{m1} \ll V_{mg}$. Therefore, we may approximate $V_{mg} - V_{m1}$ by V_{mg} . In this case the Clapeyron equation (7.1.6) simplifies to

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{TV_{mg}} \quad (7.1.7)$$

As a first approximation, we may use the ideal gas molar volume $V_{mg} = RT/p$. Substituting this expression in the place of V_{mg} , and noting that $dp/p = d(\ln p)$, we arrive at the following equation, called the **Clausius–Clapeyron equation**:

$$\frac{d(\ln p)}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} \quad (7.1.8)$$

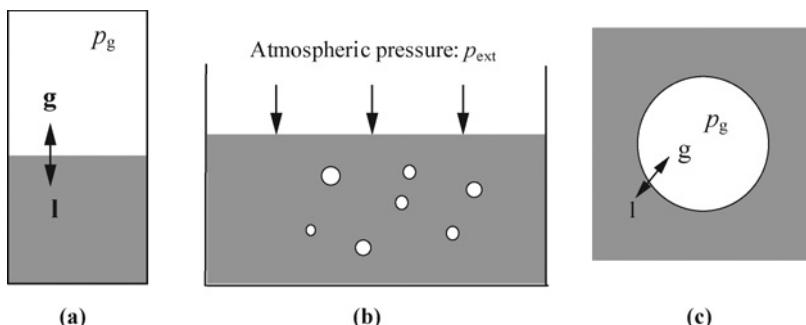


Figure 7.4 Equilibrium between liquid and vapor phases. (a) An isolated system, which contains a liquid in equilibrium with its vapor. The pressure of the vapor p_g is called the saturated vapor pressure. (b) When the liquid subject to a pressure p_{ext} (atmospheric pressure) is heated, bubbles of its vapor can form when $p_g \geq p_{\text{ext}}$ and the liquid begins to ‘boil’. (c) The vapor in the bubble is the saturated vapor in equilibrium with the liquid, as in the case of an isolated system (a).

This equation is also applicable to a solid in equilibrium with its vapor (e.g. I_2), since the molar volume of the vapor phase is much larger than that of the solid phase. For a solid in equilibrium with its vapor, ΔH_{sub} takes the place of ΔH_{vap} . At times, Equation (7.1.8) is also written in its integrated form:

$$\ln p_2 - \ln p_1 = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (7.1.9)$$

As illustrated in Figure 7.4, Equations (7.1.8) and (7.1.9) tell us how the boiling point of a liquid changes with pressure. When a liquid subjected to an external pressure, p_{ext} , is heated, bubbles containing the vapor (in equilibrium with the liquid) can form provided that the vapor pressure $p_g \geq p_{\text{ext}}$. The liquid then begins to ‘boil’. If the vapor pressure p is less than p_{ext} , then the bubbles cannot form: they ‘collapse’. The temperature at which $p = p_{\text{ext}}$ is what we call the boiling point T_b . Hence, in Equations (7.1.8) and (7.1.9) we may interpret p as the pressure to which the liquid is subjected and T is the corresponding boiling point. It tells us that the boiling point of a liquid decreases with a decrease in pressure p_{ext} .

7.2 The Gibbs Phase Rule and Duhem’s Theorem

Thus far we have considered the equilibrium between two phases of a single compound. When many compounds or components and more than two phases are in equilibrium, the chemical potential of each component should be the same in every phase in which it exists. When we have a single phase, such as a gas, its intensive variables, i.e. pressure and temperature, can be varied independently. However, when we consider equilibrium between two phases, such as a gas and liquid, p and T are no longer independent. Since the chemical potentials of the two phases must be equal, $\mu^1(p, T) = \mu^2(p, T)$, which implies that only one of the two intensive variables is independent. In the case of liquid–vapor equilibrium of a single component, p and T are related according to Equation (7.1.8). The number of independent intensive variables depends on the number of phases in equilibrium and the number of components in the system.

The *independent intensive variables* that specify a state are called its **degrees of freedom**. Gibbs observed that there is a general relationship between the number of degrees of freedom f , the number of phases P and the number of components C :

$$f = C - P + 2 \quad (7.2.1)$$

This can be seen as follows. At a given T , specifying p is equivalent to specifying the density as moles per unit volume (through the equation of state). For a given density, the mole fractions specify the composition of the system. Thus, for each phase, p , T and the C mole fractions x_k^l (in which the superscript indicates the phase and the subscript the component) are the intensive variables that specify the state. Of the C mole fractions in each phase i , there are $(C - 1)$ independent mole fractions x_k^i because $\sum_{k=1}^C x_k^i = 1$. In a system with C components and P phases, there are a total of $P(C - 1)$ independent mole fractions x_k^i . These, together with p and T , make a total of $P(C - 1) + 2$ independent variables. On the other hand, equilibrium between the P phases of a component k requires the equality of chemical potentials in all the phases:

$$\mu_k^1(p, T) = \mu_k^2(p, T) = \mu_k^3(p, T) = \dots = \mu_k^P(p, T) \quad (7.2.2)$$

in which, as before, the superscript indicates the phase and the subscript the component. These constitute $(P - 1)$ constraining equations for each component. For the C components, we then have a total of $C(P - 1)$ equations between the chemical potentials, which reduces the number of independent intensive variables by $C(P - 1)$. Thus, the total number of independent degrees of freedom is

$$f = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

If a component ‘a’ does not exist in one of the phases ‘b’, then the corresponding mole fraction $x_b^a = 0$, thus reducing the number of independent variables by one. However, this also decreases the number of constraining equations by one. Hence, there is no overall change in the number of degrees of freedom.

As an illustration of the Gibbs phase rule, let us consider the equilibrium between the solid, liquid and gas phases of a pure substance, i.e. one component. In this case we have $C = 1$ and $P = 3$, which gives $f = 0$. Hence, for this equilibrium, there are no free intensive variables; there is only one pressure and temperature at which all three phases can coexist. This point is called the **triple point** (see Figure 7.1). At the triple point of H_2O , $T = 273.16$ K, 0.01°C and $p = 611 \text{ Pa} = 6.11 \times 10^{-3} \text{ bar}$. This unique condition for the coexistence of the three phases may be used in defining the kelvin temperature scale.

If the various components of the system also chemically react through R independent reactions, then, in addition to Equation (7.2.2), for the chemical equilibrium, the R affinities, A_k , of each of the chemical reactions must equal zero:

$$A_1 = 0, \quad A_2 = 0, \quad A_3 = 0, \dots, \quad A_R = 0 \quad (7.2.3)$$

Consequently, the number of degrees of freedom is further decreased by R and we have

$$f = C - R - P + 2 \quad (7.2.4)$$

In older statements of the phase rule, the term ‘number of independent components’ is used to represent $(C - R)$. In a reaction such as $\text{A} \rightleftharpoons \text{B} + 2\text{C}$, if the amount B and C is entirely a result of decomposition of A , then the amount of B and C is determined by the amount of A that has converted to B and C ; in this case the mole fractions of B and C are related, $x_C = 2x_B$. This additional constraint, which depends on the initial preparation of the system, decreases the degrees of freedom by one.

In addition to the phase rule identified by Gibbs, there is another general observation that Pierre Duhem made in his treatise *Traité Élémentaire de Mécanique Chimique*, which is referred to as **Duhem's theorem**. It states:

Whatever the number of phases, components and chemical reactions, if the initial molar amounts N_k of all the components are specified, the equilibrium state of a closed system is completely specified by two independent variables.

The proof of this theorem is as follows. The state of the entire system is specified by the pressure p , temperature T and the molar amounts N_k^i , in which the superscript indicates the P phases and the subscript the C component – a total of CP molar amounts in P phases. Thus, the total number of variables that specify a system is $CP + 2$. Considering the constraints on these variables, for the equilibrium of each component k between the phases we have

$$\mu_k^1(p, T) = \mu_k^2(p, T) = \mu_k^3(p, T) = \dots = \mu_k^P(p, T) \quad (7.2.5)$$

a total of $(P - 1)$ equations for each component, a total of $C(P - 1)$ equations. In addition, since the total molar amount, say $N_{k,\text{total}}$, of each component is specified, we have $\sum_{i=1}^P N_k^i = N_{k,\text{total}}$ for each component, a total of C equations. Thus, the total number of constraints is $C(P - 1) + C$. Hence, the total number of independent equations is $CP + 2 - C(P - 1) - C = 2$.

The addition of chemical reactions does not change this conclusion because each chemical reaction α adds a new independent variable ξ_α , its extent of reaction, to each phase and at the same time adds the constraint for the corresponding chemical equilibrium $A_\alpha = 0$. Hence, there is no net change in the number of independent variables.

Comparing the Gibbs phase rule and the Duhem theorem, we see the following. The Gibbs phase rule specifies the total number of independent intensive variables regardless of the extensive variables in the system. In contrast, Duhem's equation specifies the total number of independent variables, intensive or extensive, in a closed system.

7.3 Binary and Ternary Systems

Figure 7.1 shows the phase diagram for a single-component system. The phase diagrams for systems with two and three components are more complex. In this section we shall consider examples of two- and three-component systems.

7.3.1 Binary Liquid Mixtures in Equilibrium with the Vapor

Consider a liquid mixture of two components, A and B, in equilibrium with their vapors. This system contains two phases and two components. The Gibbs phase rule tells us that such a system has two degrees of freedom. We may take these degrees of freedom to be the pressure and the mole fraction x_A of component A. Thus, if we consider a system in which the vapor pressure is to be set at a given value, for each value of the mole fraction x_A , there is a corresponding temperature at which the pressure will reach the set value; at this point the two phases are in equilibrium. For example, if the vapor pressure is to be 0.5 bar, for the liquid to be in equilibrium with its vapor the temperature T must be set at an appropriate value (T equals the boiling point at 0.5 bar).

If the applied pressure is the atmospheric pressure, then the temperature corresponds to the boiling point. In Figure 7.5, the curve I is the boiling point as a function of the mole fraction x_A ; the boiling points of the two

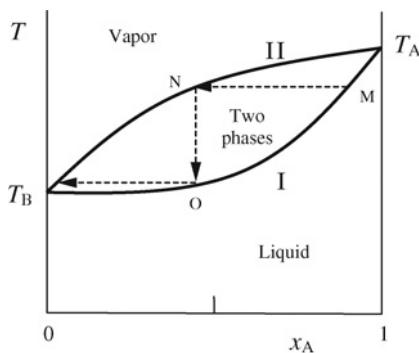


Figure 7.5 The boiling point versus composition of a mixture of two similar liquids, such as benzene and toluene.

components A and B are T_A and T_B respectively. Curve II shows the composition of the vapor at each boiling temperature. If a mixture with composition corresponding to the point M is boiled, then the vapor will have the composition corresponding to the point N; if this vapor is now collected and condensed, then its boiling point and composition will correspond to the point O. This process enriches the mixture in component B. For such systems, by continuing this process a mixture can be enriched in the more volatile component, which has the lower boiling point; the liquid at M is enriched in the component with the higher boiling point.

7.3.2 Azeotropes

The relation between the boiling point and the compositions of the liquid and the vapor phases shown in Figure 7.5 is not valid for all binary mixtures. For many liquid mixtures the boiling point curve is as shown in Figure 7.6. In this case, there is a value of x_A at which the composition of the liquid and the vapor are the same. Such systems are called **azeotropes**. The components of an azeotrope cannot be separated by distillation. For example, in the case of Figure 7.6a, starting at a point to the left of the maximum, if the mixture is boiled and the vapor collected, then the vapor will be enriched in component B while the remaining

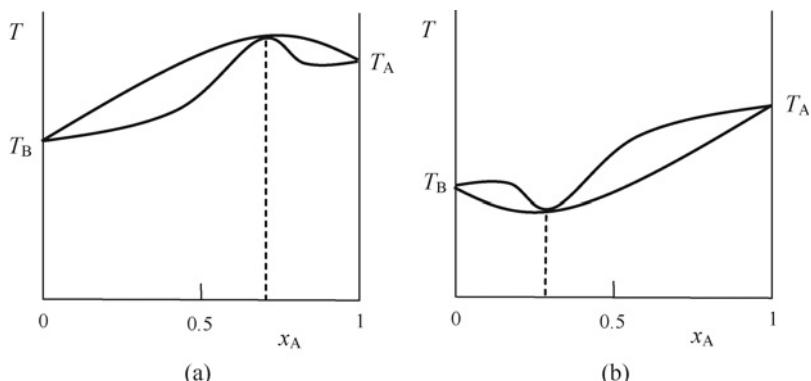


Figure 7.6 The boiling point versus composition of liquid and vapor phases of binary mixtures called azeotropes. Azeotropes have a point at which the vapor and the liquid phases have the same composition. At this point the boiling point is either (a) a maximum or (b) a minimum.

Table 7.2 Examples of azeotropes.

	Boiling point (°C)		
	Pure compound	Azeotrope	Azeotropic wt %
Azeotropes formed with water at $p = 1$ bar			
Boiling point of water = 100 °C			
Hydrogen chloride (HCl)	-85	108.58	20.22
Nitric acid (HNO ₃)	86	120.7	67.7
Ethanol (C ₂ H ₅ OH)	78.32	78.17	96
Azeotropes formed with acetone at $p = 1$ bar			
Boiling point of acetone ((CH ₃) ₂ CO) = 56.15 °C			
Cyclohexane (C ₆ H ₁₂)	80.75	53.0	32.5
Methyl acetate (CH ₃ COOCH ₃)	57.0	55.8	51.7
n-Hexane (C ₆ H ₁₄)	68.95	49.8	41
Azeotropes formed with methanol at $p = 1$ bar			
Boiling point of methanol (CH ₃ OH) = 64.7 °C			
Acetone ((CH ₃) ₂ CO)	56.15	55.5	88
Benzene (C ₆ H ₆)	80.1	57.5	60.9
Cyclohexane (C ₆ H ₁₂)	80.75	53.9	63.6

Source: D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 75th edition, 1994, CRC Press: Ann Arbor, MI.

liquid will be richer in component A and move towards the azeotropic composition. Thus, successive boiling and condensation results in pure B and a mixture with azeotropic composition, not pure A and pure B. The azeotropic composition and the corresponding boiling points for binary mixtures are tabulated. One may notice in Figure 7.6 that the boiling point corresponding to the azeotropic composition occurs at an extremum (maximum or minimum). That this must be so for thermodynamic reasons has been noted by Gibbs and later by Konovalov and Duhem. This observation is called the **Gibbs–Konovalov theorem** [4], which states that:

At constant pressure, in an equilibrium displacement of a binary system, the temperature of coexistence passes through an extremum if the composition of the two phases is the same.

We shall not discuss the proof of this theorem here. An extensive discussion of this and other related theorems may be found in the classic text by Prigogine and Defay [4]. Azeotropes are an important class of solutions whose thermodynamic properties we shall discuss in more detail in Chapter 8. Some examples of azeotropes are given in Table 7.2.

7.3.3 Solution in Equilibrium with Pure Solids: Eutectics

The next example we consider is a solid–liquid equilibrium of two components, A and B, which are miscible in the liquid state but not in the solid state. This system has three phases in all, the liquid with A + B, solid A and solid B.

We can understand the equilibrium of such a system by first considering the equilibrium of two-phase systems, the liquid and one of the two solids, A or B, and then extending it to three phases. In this case, the Gibbs phase rule tells us that, with two components and two phases, the number of degrees of freedom equals two. We can take these two degrees of freedom to be the pressure and composition. Thus, if the mole fraction x_A and the pressure are fixed, then the equilibrium temperature is also fixed. By fixing the pressure at a given

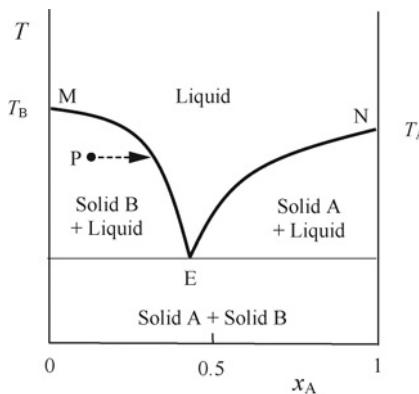


Figure 7.7 The phase diagram of a two-component system with three phases. The system has only one degree of freedom. For a fixed pressure, the three phases (the liquid, solid A and solid B) are at equilibrium at the **eutectic point** E. Along the curve ME, solid B is in equilibrium with the liquid and along the curve NE, solid A is in equilibrium with the liquid. The point of intersection E specifies the equilibrium composition and temperature when all three phases are in equilibrium. At a fixed T, if the system is initially at point P it will move towards the equilibrium curve ME. Below the eutectic point the solid is a mixture of solid A and solid B.

value (say the atmospheric pressure) one can obtain an equilibrium curve relating T and x_A . The two curves corresponding to solid A in equilibrium with the liquid and solid B in equilibrium with the liquid are shown in Figure 7.7. In this figure, along the curve EN, the solid A is in equilibrium with the liquid; along the curve EM, solid B is in equilibrium with the solution. The point of intersection of the two curves, E, is called the **eutectic point**, and the corresponding composition and temperature are called the **eutectic composition** and the **eutectic temperature**.

Now, if we consider a three-phase system, the liquid, solid A and solid B, all in equilibrium, then the Gibbs phase rule tells us that there is only one degree of freedom. If we take this degree of freedom to be the pressure and fix it at a particular value, then there is only one point (T, x_A) at which the three phases are in equilibrium. This is the eutectic point. This is the point at which the chemical potentials of solid A and solid B are equal to their corresponding chemical potentials in the liquid mixture. Since the chemical potentials of solids and liquids do not change much with changes in pressure, the eutectic composition and temperature are insensitive to variations in pressure.

7.3.4 Ternary Systems

As was noted by Gibbs, the composition of a solution containing three components may be represented by points within an equilateral triangle whose sides have a length equal to one. Let us consider a system with components A, B and C. As shown in Figure 7.8, a point P may be used to specify the mole fractions x_A , x_B and x_C as follows. From the point P, lines are drawn parallel to the sides of the equilateral triangle. The length of these lines can be used to represent the mole fractions x_A , x_B and x_C . It is left as an exercise to show that such a construction ensures that $x_A + x_B + x_C = 1$. In this representation of the composition, we see that:

1. The vertices A, B and C correspond to pure substances.
2. A line parallel to a side of the triangle corresponds to a series of ternary systems in which one of the mole fractions remains fixed.

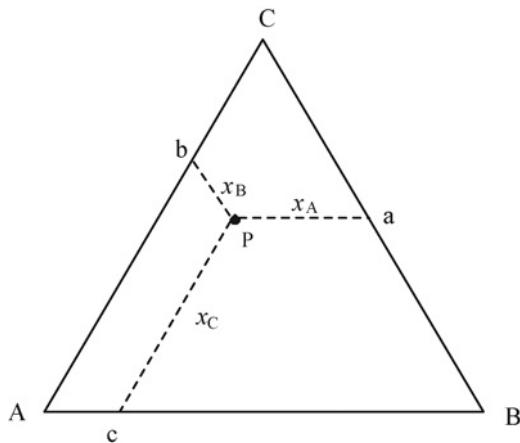


Figure 7.8 The composition of a ternary system consisting of components A, B and C can be represented on a triangular graph because $x_A + x_B + x_C = 1$. The composition is represented as a point P inside an equilateral triangle whose side has a length equal to one. The mole fractions are the lengths of the lines drawn parallel to the sides of the triangle. Showing that $x_A + x_B + x_C = 1$ for any point P is left as an exercise.

3. A line drawn through one of the apexes to the opposite side represents a set of systems in which the mole fractions of two components have a fixed ratio. As the apex is approached along this line, the system becomes increasingly richer in the component represented by the apex. The variation of some property of a three-component solution can be shown in a three-dimensional graph in which the base is the above composition triangle; the height will then represent the property.

As an example, let us consider three components, A, B and C, in two phases: a solution that contains A, B and C, and the other a solid phase of B in equilibrium with the solution. This system has three components and two phases and, hence, has three degrees of freedom, which may be taken as the pressure and the mole fractions x_A and x_B . At constant pressure, every value of x_A and x_B has a corresponding equilibrium temperature. In Figure 7.9a, the point P shows the composition of the solution at a temperature T . As the temperature decreases, the relative values of x_A and x_C remain the same while more of B turns into a solid. According to the observations in point (3) above, this means that the point moves along the line BP as shown by the arrow. As the temperature decreases, a point P' is reached at which the component C begins to crystallize. The system now has two solid phases and one solution phase and, hence, has two degrees of freedom. The composition of the system is now confined to the line $P'E$. With a further decrease in the temperature, component A also begins to crystallize at point E, which corresponds to the eutectic temperature. The system now has only one degree of freedom. At the eutectic temperature and composition, all three components will crystallize out in the eutectic proportions.

7.4 Maxwell's Construction and the Lever Rule

The reader might have noticed that the isotherms obtained from an equation of state, such as the van der Waals equation, do not coincide with the isotherms shown in Figure 7.2 at the part of the curve that is flat, i.e. where the liquid and vapor phases coexist. The flat part of the curve represents what is physically realized when

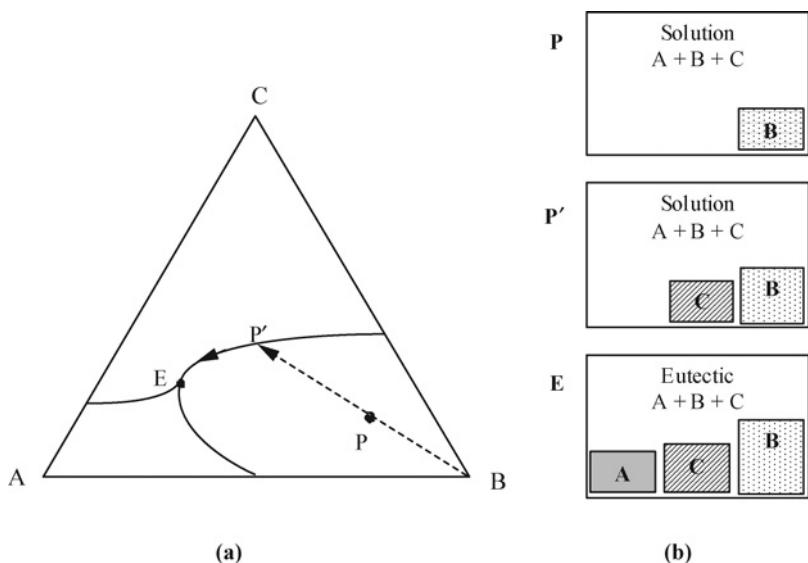


Figure 7.9 (a) The phase diagram of a ternary system showing the composition of the solution as it is cooled. At the point P the system consists of two phases: the solution ($A + B + C$) in equilibrium with solid B . As the temperature decreases, the composition moves along PP' . At P' the component C begins to crystallize and the composition moves along $P'E$ until it reaches the ternary eutectic point E , at which all components begin to crystallize. (b) The composition of the system at points P , P' and E .

a gas is compressed at a temperature below the critical temperature. Using the condition that the chemical potential of the liquid and the vapor phases must be equal at equilibrium, Maxwell was able to determine the location of the flat part of the curve.

Let us consider a van der Waals isotherm for $T < T_c$ (Figure 7.10). Imagine a steady decrease in volume starting at the point Q . Let the point P be such that, at this pressure, the chemical potentials of the liquid and the vapor phases are equal. At this point the vapor will begin to condense and the volume can be decreased with no change in the pressure. This decrease in volume can continue until all the vapor has condensed to a liquid at the point L . If the volume is maintained at some value between P and L , then liquid and vapor coexist. Along the line PL the chemical potentials of the liquid and the vapor are equal. Thus, the total change in the chemical potential along the curve $LMNOP$ must be equal to zero:

$$\int_{LMNOP} d\mu = 0 \quad (7.4.1)$$

Now, since the chemical potential is a function of T and p , and since the path is an isotherm, it follows from the Gibbs–Duhem relation that $d\mu = V_m dp$. Using this relation we may write the above integral as

$$\int_P^O V_m dp + \int_O^N V_m dp + \int_N^M V_m dp + \int_M^L V_m dp = 0 \quad (7.4.2)$$

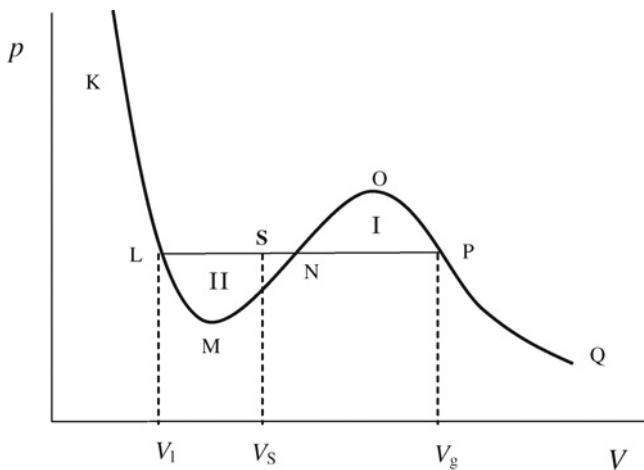


Figure 7.10 Maxwell's construction specifies the physically realized flat part LP with respect to the theoretical isotherm given by an equation of state such as the van der Waals equation. At equilibrium, the chemical potentials at the points L and P must be equal. As shown in the text, this implies that the physically realized states lie on a line LP that makes area I equal to area II .

The area I shown in Figure 7.10 is equal to

$$\int\limits_P^O V_m dp - \int\limits_N^O V_m dp = \int\limits_P^O V_m dp + \int\limits_O^N V_m dp$$

which is same as the first two integrals in Equation (7.4.2). Similarly, the sum of the second two terms equals the negative of area II .

Thus, Equation (7.4.2) may be interpreted as

$$\text{Area } I - \text{Area } II = 0 \quad (7.4.3)$$

This condition specifies how to locate or construct a flat line on which the chemical potentials of the liquid and the vapor are equal, the one that is physically realized. It is called the **Maxwell construction**.

At point P the substance is entirely in the vapor phase with volume V_g ; at the point L it is entirely in the liquid phase with volume V_1 . At any point S on the line LP , if a fraction x of substance is in the vapor phase, then the total volume V_S of the system is

$$V_S = xV_g + (1-x)V_1 \quad (7.4.4)$$

It follows that

$$x = \frac{V_S - V_1}{V_g - V_1} = \frac{SL}{LP} \quad (7.4.5)$$

From this relation it can be shown that (Exercise 7.10) the mole fraction x of the vapor phase and $(1-x)$ of the liquid phase satisfy

$$(SP)x = (SL)(1-x) \quad (7.4.6)$$

This relation is called the **lever rule**, in analogy with a lever supported at S , in equilibrium with weights V_1 and V_g attached to either end.

7.5 Phase Transitions

Phase transitions are associated with many interesting and general thermodynamic features. As described below, based on some of these features, phase transitions can be classified into different ‘orders’. Thermodynamic behavior in the vicinity of the critical points has been of much interest from the point of view of thermodynamic stability and extremum principles, discussed in Chapter 5. A classical theory of phase transitions was developed by Lev Landau; however, in the 1960s, experiments showed that the predictions of this theory were incorrect. This resulted in the development of the modern theory of phase transitions during the 1960s and the 1970s. The modern theory is based on the work of C. Domb, M. Fischer, L. Kadanoff, G.S. Rushbrooke, B. Widom, K. Wilson and others. In this section we will only outline some of the main results of the thermodynamics of phase transitions. A detailed description of the modern theory of phase transitions, which uses the mathematically advanced concepts of renormalization-group theory, is beyond the scope of this book. For a better understanding of this rich and interesting subject we refer the reader to books on this topic [1–3].

7.5.1 General Classification of Phase Transitions

When transition from a solid to a liquid or from a liquid to vapor takes place, there is a discontinuous change in the entropy. This can clearly be seen (see Figure 7.11) if we plot molar entropy $S_m = -(\partial G_m / \partial T)_p$ as function of T , for fixed p and N . The same is true for other derivatives of G_m , such as $V_m = (\partial G_m / \partial p)_T$. The chemical potential changes continuously, but its derivative is discontinuous. At the transition temperature, because of the existence of latent heat, the molar heat capacities ($\Delta Q / \Delta T$) have a ‘singularity’ in the sense they become infinite; i.e. heat absorbed ΔQ causes no change in temperature, i.e. $\Delta T = 0$. Transitions of this type are classified as **first-order** phase transitions.

The characteristic features of **second-order phase transitions** are shown in Figure 7.12. In this case, the changes in the thermodynamic quantities are not so drastic: changes in S_m and V_m are continuous, but their derivatives are discontinuous. Similarly, for the chemical potential it is the second derivative that is discontinuous; the molar heat capacity does not have a singularity, but it has a discontinuity. Thus, depending on the order of the derivatives that are discontinuous, phase transitions are classified as transitions of first or second order.

7.5.2 Behavior near the Critical Point

The classical theory of phase transitions was developed by Lev Landau to explain the coexistence of phases and the critical point at which the distinction between the phases disappears. Landau’s theory explains the

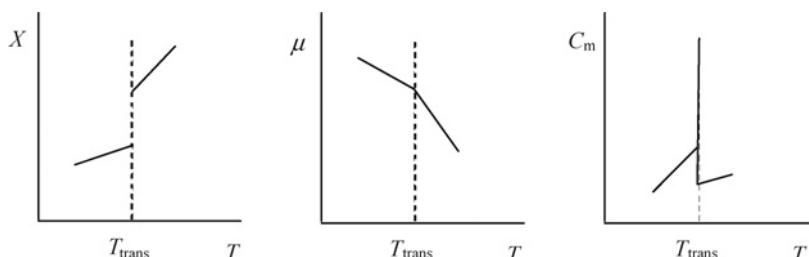


Figure 7.11 The change of thermodynamic quantities in a first-order phase transition that occurs at the temperature T_{trans} . X is a molar extensive quantity such as S_m or V_m that changes discontinuously.

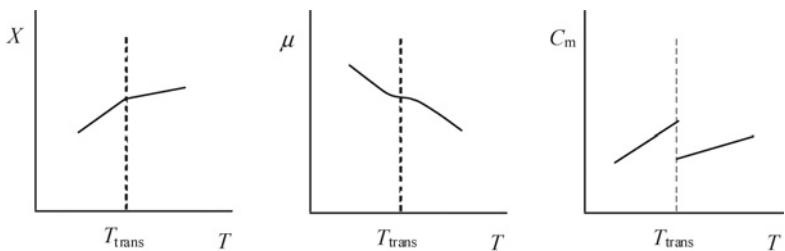


Figure 7.12 The change of thermodynamic quantities in a second-order phase transition that occurs at the temperature T_{trans} . X is a molar extensive quantity such as S_m or V_m whose derivative changes discontinuously.

critical behavior in terms of the minima of the Gibbs free energy. According to this theory, as shown in Figure 7.13, in the coexistence region, for a given p and T , G as a function of V has two minima. As the critical point is approached, the minima merge into one broad minimum. The classical theory of Landau makes several predictions regarding the behavior of systems near the critical point. The predictions of the theory are, in fact, quite general, valid for large classes of systems. Experiments done in the 1960s did not support these predictions. We shall list below some of the discrepancies between theory and experiments using the liquid–vapor transition as an example, but the experimental values are those obtained for many similar systems. Also, all the classical predictions can be verified using the van der Waals equation of state as an example.

- For the liquid–vapor transition, as the critical temperature was approached from below ($T < T_c$), the theory predicted that

$$V_{\text{mg}} - V_{\text{ml}} \propto (T_c - T)^\beta, \quad \beta = 1/2 \quad (7.5.1)$$

However, experiments showed that β was in the range 0.3–0.4, not equal to 0.5.

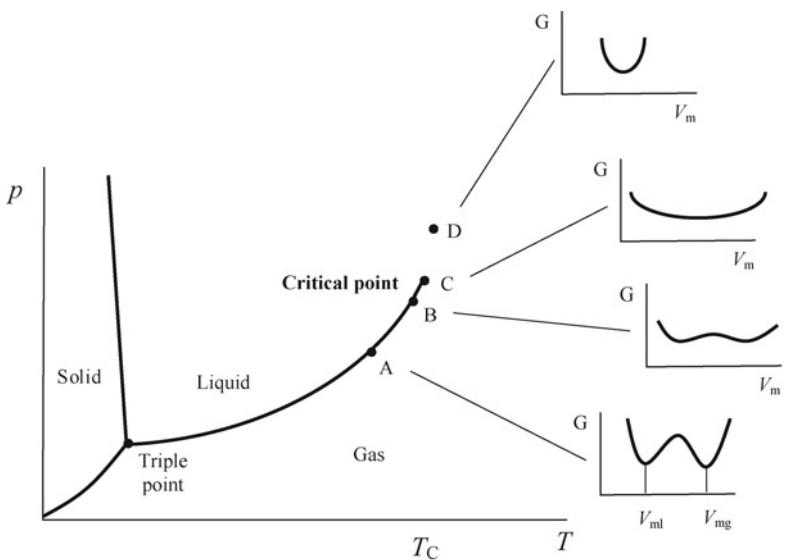


Figure 7.13 Classical theory of phase transitions is based on the shape of the Gibbs energy as a function of V . The Gibbs energies associated with the points A, B, C and D are shown in the insets. As the system moves from A to D, the Gibbs energy changes from a curve with two minima to a curve with one minimum, as shown in the small figures.

- Along the critical isotherm, as the critical pressure p_c is approached from above, the theory predicted

$$V_{\text{mg}} - V_{\text{ml}} \propto (p - p_c)^{1/\delta}, \quad \delta = 3 \quad (7.5.2)$$

Experiments place the value of δ in the range 4.0–5.0.

- When the gas can be liquefied, it is easy to see that the isothermal compressibility $\kappa_T = -(1/V)(\partial V/\partial p)_T$ diverges during the transition (the flat part of the p – V isotherm). Above the critical temperature, since there is no transition to liquid there is no divergence. According to classical theory, as the critical temperature is approached from above, the divergence of κ_T should be according to

$$\kappa_T \propto (T - T_c)^{-\gamma}, \quad \gamma = 1 \quad (7.5.3)$$

Experimental values of γ were found to be in the range 1.2–1.4.

- We have seen in Chapter 6 that the values of molar heat capacity $C_{\text{m}V}$ for real and ideal gases are the same if the pressure is a linear function of the temperature. This means that the value of $C_{\text{m}V}$ does not diverge (though the value of C_p diverges). Thus, according to classical theory, if

$$C_{\text{m}V} \propto (T - T_c)^{-\alpha} \quad \text{then} \quad \alpha = 0 \quad (7.5.4)$$

Experimentally, the value of α found was in the range –0.2 to +0.3.

The failure of the classical or Landau theory initiated a reexamination of the critical behavior. The main reason for the discrepancy was found to be the role of fluctuations. Near the critical point, due to the flat nature of the Gibbs energy, large long-range fluctuations arise in the system, and these were not properly included in Landau's theory. Kenneth Wilson incorporated these fluctuations into the theory through the development of new mathematical techniques and the theory of the **renormalization group**. The modern theory of critical behavior not only predicts the experimental values of the exponents α , β , γ and δ more successfully than the classical theory but it also relates these exponents. For example, the modern theory predicts that

$$\beta = \frac{2 - \alpha}{1 + \delta} \quad \text{and} \quad \gamma = \frac{(\alpha - 2)(1 - \delta)}{1 + \delta} \quad (7.5.5)$$

Since a detailed presentation of the theory of the renormalization group is beyond the scope of this book, we will leave the reader with only this brief outline of the limitations of the classical theory and accomplishments of the modern theory.

References

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2. Ma, S.-K., *Modern Theory of Critical Phenomena*. 1976, Addison-Wesley: New York.
3. Pfeuty, P., Toulouse, G., *Introduction to the Renormalization Group and Critical Phenomena*. 1977, John Wiley & Sons, Inc.: New York.
4. Prigogine, I., Defay, R., *Chemical Thermodynamics*, fourth edition. 1967, Longmans: London.

Examples

Example 7.1 A chemical reaction occurs in CCl_4 at room temperature, but it is very slow. To increase its speed to a desired value, the temperature needs to be increased to 80 °C. Since CCl_4 boils at 77 °C at $p = 1.00 \text{ atm}$, the pressure has to be increased so that CCl_4 will boil at a temperature higher than 80 °C. Using the data in Table 7.1, calculate the pressure at which CCl_4 will boil at 85 °C.

Solution From the Clausius–Clapeyron equation we have

$$\ln p - \ln(1.00 \text{ atm}) = \frac{30.0 \times 10^3}{8.314} \left(\frac{1}{350} - \frac{1}{358} \right) = 0.230$$

$$p = (1.00 \text{ atm})e^{0.23} = 12.6 \text{ atm}$$

Example 7.2 If a system contains two immiscible liquids (such as CCl_4 and CH_3OH), how many phases are there?

Solution The system will consist of three layers. A layer rich in CCl_4 , a layer rich in CH_3OH and a layer of vapor of CCl_4 and CH_3OH . Thus, there are three phases in this system.

Example 7.3 Determine the number of degrees of freedom of a two-component liquid mixture in equilibrium with its vapor.

Solution In this case $C = 2$, $P = 2$. Hence, the number of degrees of freedom $f = 2 - 2 + 2 = 2$. These two degrees of freedom can be, for example, T and the mole fraction x_1 of one of the components. The pressure of the system (vapor phase in equilibrium with the liquid) is completely specified by x_1 and T .

Example 7.4 How many degrees of freedom does an aqueous solution of the weak acid CH_3COOH have?

Solution The acid decomposition is



The number of components is $C = 4$ (water, CH_3COOH , CH_3COO^- and H^+). The number of phases is $P = 1$. There is one chemical reaction in equilibrium; hence $R = 1$. However, since the concentrations of CH_3COO^- and H^+ are equal, the degrees of freedom are reduced by one. Hence, the number of degrees of freedom $f = C - R - P + 2 - 1 = 4 - 1 - 1 + 2 - 1 = 3$.

Exercises

- 7.1 The heat of vaporization of hexane is 30.8 kJ mol^{-1} . The boiling point of hexane at a pressure of 1.00 atm is 68.9°C . What will the boiling point be at a pressure of 0.50 atm ?
- 7.2 The atmospheric pressure decreases with height. The pressure at a height h above sea level is given approximately by the barometric formula $p = p_0 e^{-Mgh/RT}$, in which, p_0 is the pressure at sea level, $M = 0.0289 \text{ kg mol}^{-1}$ and $g = 9.81 \text{ ms}^{-2}$. Assume that the enthalpy of vaporization of water is $\Delta H_{\text{vap}} = 40.6 \text{ kJ mol}^{-1}$ and predict at what temperature water will boil at a height of 3.5 km .
- 7.3 At atmospheric pressure, CO_2 turns from solid to gas, i.e. it sublimates. Given that the triple point of CO_2 is at $T = 216.58 \text{ K}$ and $p = 518.0 \text{ kPa}$, how would you obtain liquid CO_2 ?
- 7.4 In a two-component system, what is the maximum number of phases that can be in equilibrium?
- 7.5 Determine the number of degrees of freedom for the following systems:
 - (a) solid CO_2 in equilibrium with CO_2 gas;
 - (b) an aqueous solution of fructose;
 - (c) $\text{Fe(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{FeO(s)} + \text{H}_2\text{(g)}$.

- 7.6** Draw qualitative figures of T versus x_A curves (Figure 7.6) for the azeotropes in Table 7.2.
- 7.7** In Figure 7.8, show that $P_a + P_b + P_c = 1$ for any point P.
- 7.8** In the triangular representation of the mole fractions of a ternary solution, show that along the line joining an apex and a point on the opposite side, the ratio of two of the mole fractions remains constant while the mole fraction of the third component changes.
- 7.9** On triangular graph paper, mark points representing the following compositions:
- (a) $x_A = 0.2, x_B = 0.4, x_C = 0.4$
 - (b) $x_A = 0.5, x_B = 0, x_C = 0.5$
 - (c) $x_A = 0.3, x_B = 0.2, x_C = 0.5$
 - (d) $x_A = 0, x_B = 0, x_C = 1.0$.
- 7.10** Obtain the lever rule (7.4.6) from (7.4.5).
- 7.11** When the van der Waals equation is written in terms of the reduced variables p_r , V_r and T_r (see Equation (1.4.6)), the critical pressure, temperature and volume are equal to one. Consider small deviations from the critical point, $p_r = 1 + \delta p$ and $V_r = 1 + \delta V$ on the critical isotherm. Show that δV is proportional to $(\delta p)^{1/3}$. This corresponds to the classical prediction (7.5.2).

8

Thermodynamics of Solutions

8.1 Ideal and Nonideal Solutions

Many properties of solutions can be understood through thermodynamics. For example, we can understand how the boiling and freezing points of a solution change with composition, how the solubility of a compound changes with temperature and how the osmotic pressure depends on the concentration.

We begin by obtaining the chemical potential of a solution. As noted in Chapter 5 (Equation (5.3.5)), the general expression for the chemical potential of a substance may be written as $\mu(p, T) = \mu^0(p_0, T) + RT \ln a$, in which a is the activity and μ^0 is the chemical potential of the standard state in which $a = 1$. For an ideal gas mixture, in Equation (6.1.9) we saw that the chemical potential of a component can be written in terms of its mole fraction x_k in the form $\mu_k(p, T, x_k) = \mu_k^0(p_0, T) + RT \ln x_k$. We shall see in this section that properties of many dilute solutions can be described by a chemical potential of the same form. This has led to the following definition of an **ideal solution** as a solution for which

$$\boxed{\mu_k(p, T, x_k) = \mu_k^0(p, T) + RT \ln x_k} \quad (8.1.1)$$

where $\mu^0(p, T)$ is the chemical potential of a reference state that is independent of x_k . We stress that the similarity between ideal gas mixtures and ideal solutions is only in the dependence of the chemical potential on the mole fraction; the dependence on the pressure, however, is entirely different, as can be seen from the general expression for the chemical potential of a liquid (Equation (6.3.8)).

In Equation (8.1.1), if the mole fraction of the ‘solvent’ x_s is nearly equal to one, i.e. for dilute solutions, then for the chemical potential of the solvent the reference state $\mu_k^0(p, T)$ may be taken to be $\mu_k^*(p, T)$, the chemical potential of the pure solvent. For the other components, $x_k \ll 1$; as we shall see below, Equation (8.1.1) is still valid in a small range, but in general the reference state is not $\mu_k^*(p, T)$. Solutions for which (8.1.1) is valid for all values of x_k are called **perfect solutions**. When $x_k = 1$, since we must have $\mu_k = \mu_k^*(p, T)$, it follows that for perfect solutions

$$\boxed{\mu_k(p, T, x_k) = \mu_k^*(p, T) + RT \ln x_k, \quad \forall x_k} \quad (8.1.2)$$

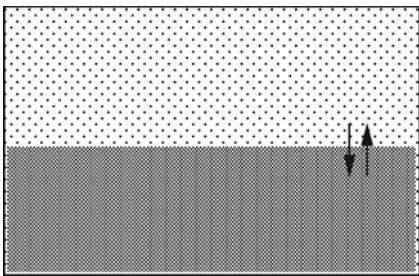


Figure 8.1 Equilibrium between a solution and its vapor.

The activity of **nonideal solutions** is expressed as $a_k = \gamma_k x_k$ in which γ_k is the **activity coefficient**, a quantity introduced by G.N. Lewis. Thus, the chemical potential of nonideal solutions is written as

$$\begin{aligned}\mu_k(p, T, x_k) &= \mu_k^0(p, T) + RT \ln a_k \\ &= \mu_k^*(p, T) + RT \ln(\gamma_k x_k)\end{aligned}\quad (8.1.3)$$

The activity coefficient $\gamma_k \rightarrow 1$ as $x_k \rightarrow 1$.

Let us now look at conditions under which ideal solutions are realized. We consider a solution with many components, whose mole fractions are x_i , in equilibrium with its vapor (see Figure 8.1). At equilibrium, the affinities for the conversion of the liquid to the gas phase are zero for each component i ; i.e. for each component the chemical potentials in the two phases are equal. If we use the ideal gas approximation for the component in the vapor phase we have

$$\mu_{i,1}^0(p_0, T) + RT \ln a_i = \mu_{i,g}^0(p_0, T) + RT \ln(p_i/p_0) \quad (8.1.4)$$

in which the subscripts 1 and g indicate the liquid and gas phases. The physical meaning of the activity a_i can be seen as follows. Consider a pure liquid in equilibrium with its vapor. Then $p_i = p_i^*$, the vapor pressure of a pure liquid in equilibrium with its vapor. Since a_i is nearly equal to one for a pure liquid, $\ln(a_i) \approx 0$. Hence, Equation (8.1.4) can be written as

$$\mu_{i,1}^0(p_0, T) = \mu_{i,g}^0(p_0, T) + RT \ln(p_i^*/p_0) \quad (8.1.5)$$

Subtracting Equation (8.1.5) from (8.1.4) we find that

$$RT \ln a_i = RT \ln(p_i/p_i^*) \quad \text{or} \quad a_i = \frac{p_i}{p_i^*}$$

(8.1.6)

i.e. the activity is the ratio of the partial vapor pressure p_i of the component in a solution and its vapor pressure p^* when it is a pure substance. By measuring the vapor pressure of a substance, its activity can be determined.

For an ideal solution, Equation (8.1.4) takes the form

$$\mu_{i,1}^0(p, T) + RT \ln(x_i) = \mu_{i,g}^0(p_0, T) + RT \ln(p_i/p_0) \quad (8.1.7)$$

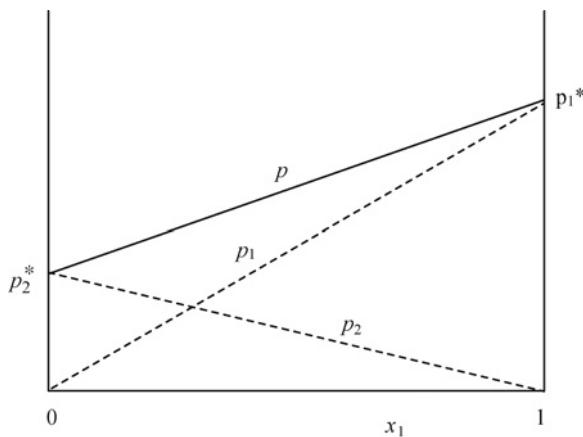


Figure 8.2 The vapor pressure diagram of a **perfect binary solution** for which Equation (8.1.1) is valid for all values of the mole fraction x_1 . Here p_1^* and p_2^* are the vapor pressures of the pure substances, p_1 and p_2 are the partial pressures of the two components in the mixture and p is the total vapor pressure.

From this equation it follows that the partial pressure in the vapor phase and the mole fraction of a component can be written as

$$p_i = K_i x_i \quad (8.1.8)$$

in which

$$K_i(p, T) = p_0 \exp\left(\frac{\mu_{i,1}^0(p, T) - \mu_{i,g}^0(p_0, T)}{RT}\right) \quad (8.1.9)$$

As indicated, the term $K_i(p, T)$ is, in general, a function of p and T , but since the chemical potential of the liquid $\mu_{i,1}^0(p, T)$ changes little with p , it is essentially a function of T . K_i has the dimensions of pressure. For any component, when $x_i = 1$, we must have $K(p^*, T) = p^*$, the vapor pressure of the pure substance (Figure 8.2). (This is consistent with Equation (8.1.9) because when we set $p = p_0 = p^*$, because the vapor and the liquid are in equilibrium, the exponent $\mu_1^0(T, p^*) - \mu_g^0(T, p^*) = 0$.) At a given temperature T , if $x_1 \approx 1$ for a particular component, which is called the ‘solvent’ or the major component, then, since the change of K_i is small for changes in pressure, we may write

$$p_1 = p_1^* x_1 \quad (8.1.10)$$

Experiments conducted by François-Marie Raoult (1830–1901) in the 1870s showed that if the mole fraction of the solvent is nearly equal to unity, i.e. for dilute solutions, then Equation (8.1.10) is valid. For this reason, (8.1.10) is called **Raoult’s law**. The chemical potential of the vapor phase of the solvent $\mu_{s,g}(p_s, T) = \mu_{s,g}(p_0, T) + RT \ln(p_s/p_0)$ can now be related to its mole fraction in the solution, x_s , by using Raoult’s law and by setting $p_0 = p^*$:

$$\begin{aligned} \mu_{s,g}(p_s, T) &= \mu_{s,g}(p^*, T) + RT \ln x_s \\ &= \mu_{s,l}^*(T) + RT \ln x_s \end{aligned} \quad (8.1.11)$$

Table 8.1 Henry's law constants at 25 °C for atmospheric gases.

Gas	$K (10^4 \text{ atm})$	Volume in the atmosphere (ppm)
N ₂ (g)	8.5	780 900
O ₂ (g)	4.3	209 500
Ar(g)	4.0	9 300
CO ₂ (g)	0.16	380
CO(g)	5.7	—
He(g)	13.1	5.2
H ₂ (g)	7.8	0.5
CH ₄ (g)	4.1	1.5
C ₂ H ₂ (g)	0.13	—

Source: D.R. Lide (ed.), CRC Handbook of Chemistry and Physics, 75th edition, 1994, CRC Press: Ann Arbor, MI.

For a minor component of a solution, when its mole fraction $x_k \ll 1$, Equation (8.1.10) is not valid but Equation (8.1.8) is still valid. This relation is called **Henry's law** after William Henry (1774–1836), who studied this aspect for the solubility of gases [1]:

$$p_i = K_i x_i, \quad x_i \ll 1 \quad (8.1.12)$$

The constant K_i is called Henry's constant. Some values of Henry's constants are given in Table 8.1. In the region where Henry's law is valid, K_i is not equal to the vapor pressure of the pure substance. The graphical representation of Henry's constant is shown in Figure 8.3. Also, where Henry's law is valid, in general, the chemical potential of the reference state μ_i^0 is not the same as the chemical potential of the pure substance.

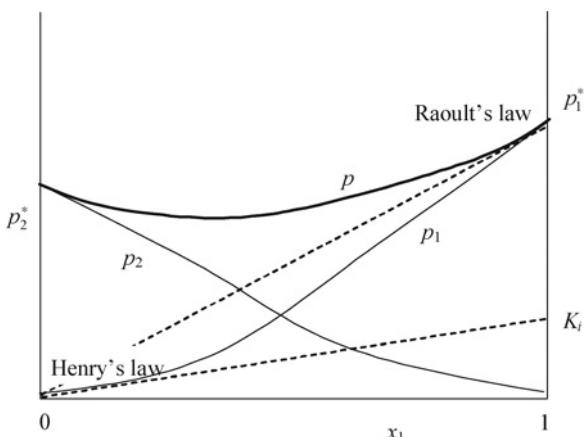


Figure 8.3 The vapor pressure diagram of a binary solution. When the mole fraction is very small or nearly equal to one, we have ideal behavior. The minor component obeys Henry's law, while the major component obeys Raoult's law. Here p_1^* and p_2^* are the vapor pressures of the pure substances, p_1 and p_2 are the partial pressures of the two components in the mixture and p is the total vapor pressure. The deviation from the partial pressure predicted by Henry's law or Raoult's law can be used to obtain the activity coefficients.

Only for a perfect solution do we have $K_i = p_i^*$ when $x_i \ll 1$, but such solutions are very rare. Many dilute solutions obey Raoult's and Henry's laws to a good approximation.

When the solution is not dilute, the **nonideal** behavior is described using the **activity coefficients**, γ_i , in the chemical potential:

$$\mu_i(p, T, x_i) = \mu_i^0(p, T) + RT \ln(\gamma_i x_i) \quad (8.1.13)$$

The factor γ_i quantifies the deviation from Raoult's or Henry's law. For nonideal solutions, as an alternative to the activity coefficient, an **osmotic coefficient** ϕ_i is defined through

$$\mu_i(p, T, x_i) = \mu_i^0(p, T) + \phi_i RT \ln(x_i) \quad (8.1.14)$$

As we will see in the following section, the significance of the osmotic coefficient lies in the fact that it is the ratio of the osmotic pressure to that expected for ideal solutions. From Equations (8.1.13) and (8.1.14) it is easy to see that

$$\phi_k - 1 = \frac{\ln \gamma_k}{\ln x_k} \quad (8.1.15)$$

8.2 Colligative Properties

By using the chemical potential of ideal solutions we can derive several properties of ideal solutions that depend on the *total number of the solute particles* and not on the chemical nature of the solute. (For example, a 0.2 M solution of NaCl will have colligative concentration of 0.40 M due to the dissociation into Na^+ and Cl^- .) Such properties are collectively called **colligative properties**.

8.2.1 Changes in Boiling and Freezing Points

Equation (8.1.11) could be used to obtain an expression for the increase in the boiling point and the decrease in the freezing point of solutions (Figure 8.4). As we noted in Chapter 7, a liquid boils when its vapor pressure $p = p_{\text{ext}}$, the atmospheric (or applied external) pressure. Let T^* be the boiling temperature of the pure solvent and T the boiling temperature of the solution. We assume that the mole fraction of the solvent is x_2 and that of the solute is x_1 . We also assume that the solute is nonvolatile so that the gas phase in equilibrium with the

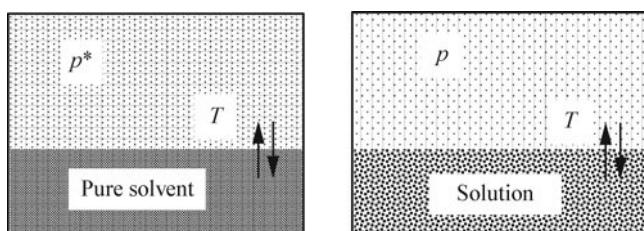


Figure 8.4 The vapor pressure of a solution with a nonvolatile solute is less than that of a pure solvent. Consequently, the boiling point of a solution increases with the solute concentration.

solution is purely the solvent. At equilibrium, the chemical potential of the solvent in the liquid phase and that of the pure solvent gas phase (which we denote by μ^*) must be equal:

$$\mu_{2,g}^*(p_{\text{ext}}, T) = \mu_{2,l}(p_{\text{ext}}, T, x_2) \quad (8.2.1)$$

Using Equation (8.1.11), and noting that $\mu_{2,l}^*$ is essentially independent of p , we can now write this equation as

$$\mu_{2,g}^*(p_{\text{ext}}, T) = \mu_{2,l}(p_{\text{ext}}, T, x_2) = \mu_{2,l}^*(T) + RT \ln(x_2) \quad (8.2.2)$$

Since the chemical potential of a pure substance $\mu = G_m$, the molar Gibbs energy, we have

$$\frac{\mu_{2,g}^*(p_{\text{ext}}, T) - \mu_{2,l}^*(T)}{RT} = \frac{\Delta G_m}{RT} = \frac{\Delta H_m - T\Delta S_m}{RT} = \ln x_2 \quad (8.2.3)$$

in which Δ denotes the difference between the liquid and the gas phase. Generally, ΔH_m does not vary much with temperature. Therefore, $\Delta H_m(T) = \Delta H_m(T^*) = \Delta H_{\text{vap}}$. Also, $\Delta S_m = \Delta H_{\text{vap}}(T)/T^*$ and $x_2 = (1 - x_1)$, in which $x_1 \ll 1$ is the mole fraction of the solute. With these observations we can write Equation (8.2.3) as

$$\ln(1 - x_1) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad (8.2.4)$$

If the difference $T - T^* = \Delta T$ is small, then it is easy to show that the terms containing T and T^* can be approximated to $-\Delta T/T^{*2}$. Furthermore, since $\ln(1 - x_1) \approx -x_1$ when $x_1 \ll 1$, we can approximate Equation (8.2.4) by the relation

$$\boxed{\Delta T = \frac{RT^{*2}}{\Delta H_{\text{vap}}} x_1} \quad (8.2.5)$$

which relates the increase in boiling point to the mole fraction of the solute. In a similar way, by considering a pure solid in equilibrium with the solution, one can derive the following relation for the decrease in freezing point ΔT in terms of the enthalpy of fusion ΔH_{fus} , the mole fraction x_k of the solute and the freezing point T^* of the pure solvent:

$$\boxed{\Delta T = \frac{RT^{*2}}{\Delta H_{\text{fus}}} x_1} \quad (8.2.6)$$

The change in the boiling point and the freezing point are often expressed in terms of **molality**, i.e. *moles of solute/kilogram of solvent*, instead of mole fraction. For dilute solutions, the conversion from mole fraction x to molality m is easily done. If M_s is the molar mass of the solvent in kilograms, then the mole fraction of the solute

$$x_1 = \frac{N_1}{N_1 + N_2} \approx \frac{N_1}{N_2} = M_s \left(\frac{N_1}{M_s N_2} \right) = M_s m_1$$

Equations (8.2.5) and (8.2.6) are often written as

$$\Delta T = K(m_1 + m_2 + \dots + m_s) \quad (8.2.7)$$

Table 8.2 Ebullioscopic and cryoscopic constants.

Compound	K_b ($^{\circ}\text{C}$ kg mol $^{-1}$)	T_b ($^{\circ}\text{C}$)	K_f ($^{\circ}\text{C}$ kg mol $^{-1}$)	T_f ($^{\circ}\text{C}$)
Acetic acid, CH_3COOH	3.07	118	3.90	16.7
Acetone, $(\text{CH}_3)_2\text{CO}$	1.71	56.3	2.40	-95
Benzene, C_6H_6	2.53	80.10	5.12	5.53
Carbon disulfide, CS_2	2.37	46.5	3.8	-111.9
Carbon tetrachloride, CCl_4	4.95	76.7	30	-23
Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$	5.26	211	6.90	5.8
Phenol, $\text{C}_6\text{H}_5\text{OH}$	3.04	181.8	7.27	40.92
Water, H_2O	0.51	100.0	1.86	0.0

Source: G.W.C. Laye and T.H. Laby (eds), *Tables of Physical and Chemical Constants*, 1986, Longmans: London.

in which the molalities of all the ‘s’ species of solute particles is shown explicitly. The constant K is called the **ebullioscopic constant** for changes in boiling point and the **cryoscopic constant** for changes in freezing point. The values of ebullioscopic and cryoscopic constants for some liquids are given in Table 8.2.

8.2.2 Osmotic Pressure

When a solution and pure solvent are separated by a semipermeable membrane (see Figure 8.5a), which is permeable to the solvent but not the solute molecules, the solvent flows into the chamber containing the solution until equilibrium is reached. This process is called **osmosis** and was noticed in the mid-eighteenth century. In 1877, a botanist named Pfeffer made a careful quantitative study of it. Jacobus Henricus van’t Hoff (1852–1911), who was awarded the first Nobel Prize in chemistry in 1901 for his contributions to thermodynamics and chemistry [1], found that a simple equation, similar to that of an ideal gas, could describe the observed data.

As shown in Figure 8.5, let us consider a solution and a pure solvent separated by a membrane that is permeable to the solvent but not the solute. Initially, the chemical potentials of the solvent on the two sides of the membrane may not be equal, the chemical potential on the solution side being smaller. Unequal chemical

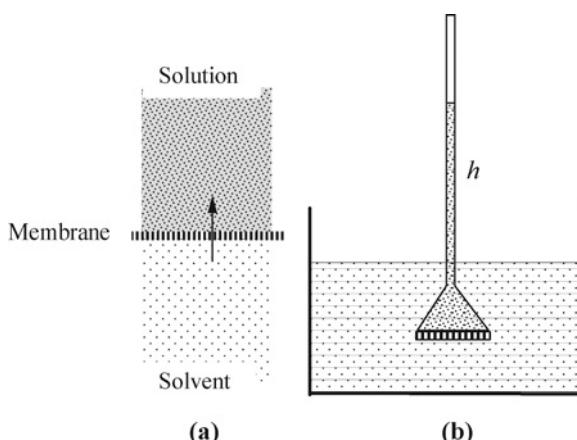


Figure 8.5 Osmosis: (a) the pure solvent flows towards the solution through a semipermeable membrane (b) the flow stops when chemical potentials of the solvent in the two chambers are equal.

potentials will cause a flow of the solvent from a higher to a lower chemical potential, i.e. a flow of pure solvent towards the solution. The affinity driving this solvent flow is



*Jacobus van 't Hoff (1852–1911).
(Reproduced by courtesy of the AIP Emilio Segré Visual Archive, Brittle Book Collection.)*

$$A = \mu^*(p, T) - \mu(p', T, x_2) \quad (8.2.8)$$

in which x_2 is the mole fraction of the solvent, p' is the pressure of the solution and p is the pressure of the pure solvent. Equilibrium is reached when the chemical potentials become equal and the corresponding affinity (8.2.8) equals zero. As noted above, for an ideal solution, the chemical potential of the major component (solvent) is given by $\mu(p', T) = \mu^*(p', T) + RT \ln x_2$, in which μ^* is the chemical potential of the pure solvent. Hence the affinity of this system can be written as

$$A = \mu^*(p, T) - \mu^*(p', T) - RT \ln x_2 \quad (8.2.9)$$

When $p = p'$, the affinity takes the following simple form:

$$A = -RT \ln x_2 \quad (8.2.10)$$

The flow of the solvent into the solution can generate a pressure difference between the solvent and the solution (Figure 8.5b). The flow continues until the difference between solvent pressure p and solution pressure p' makes $A = 0$. When $A = 0$, the pressure difference $(p' - p) = \pi$ is called the **osmotic pressure**. In the experimental setup shown in Figure 8.5b, the liquid level in the solution rises to a height h above the pure-solvent level when equilibrium is reached. The excess pressure in the solution $\pi = h\rho g$, in which ρ is the solution density and g is the acceleration due to gravity. At equilibrium, from Equation (8.2.9) it follows that

$$A = 0 = \mu^*(p, T) - \mu^*(p + \pi, T) - RT \ln x_2 \quad (8.2.11)$$

At constant temperature, the change in the chemical potential with pressure $d\mu = (\partial\mu/\partial p)_T dp = V_m dp$, where V_m is the partial molar volume. Since the partial molar volume of a liquid changes very little with pressure, we may assume it to be a constant equal to V_m^* , the solvent molar volume (because when $\mu = \mu^*$, $V_m = V_m^*$). Hence, we may write

$$\begin{aligned} \mu^*(p + \pi, T) &\approx \mu^*(p, T) + \int_p^{p+\pi} d\mu = \mu^*(p, T) + \int_p^{p+\pi} V_m^* dp \\ &= \mu^*(p, T) + V_m^* \pi \end{aligned} \quad (8.2.12)$$

Also, as we noted before, for dilute solutions, $\ln(x_2) = \ln(1 - x_1) \approx -x_1$. If N_1 is the molar amount of the solute and N_2 is the molar amount of the solvent, then, since $N_2 \gg N_1$, we see that $x_1 = N_1/(N_1 + N_2) \approx N_1/N_2$. Hence, we see that $\ln(x_2) \approx -N_1/N_2$. Using Equation (8.2.12) and the fact that $\ln(x_2) \approx -N_1/N_2$, Equation (8.2.11) can be written as

$$RT \frac{N_1}{N_2} = V_m^* \pi$$

i.e.

$$RT N_1 = N_2 V_m^* \pi = V \pi \quad (8.2.13)$$

in which $V = N_2 V_m^*$ is nearly the volume of the solution (the correction due to the solute being small). This shows that the osmotic pressure π obeys an ideal-gas-like equation:

$$\boxed{\pi = \frac{N_{\text{solute}} RT}{V_{\text{solution}}} = [S] RT} \quad (8.2.14)$$

in which $[S]$ is the molar concentration of the solution. This is the **van 't Hoff equation** for the osmotic pressure. The osmotic pressure is as if an ideal gas consisting of the solute particles is occupying a volume equal to the solution volume. By measuring the osmotic pressure, one can determine the molar amount N_{solute} of a solute. Thus, if the mass of the solute is known, then its molar mass can be calculated. The measurement of osmotic pressure is used to determine the molar mass or molecular weight of large biomolecules for which semipermeable membranes can be easily found (Exercise 8.10).

Table 8.3 shows a comparison between experimentally measured osmotic pressures and those calculated using the van 't Hoff equation (8.2.14) for an aqueous solution of sucrose. We see that for concentrations up to about 0.2 M the van 't Hoff equation agrees with experimental values. Deviation from the van 't Hoff equation is not necessarily due to deviation from ideality. In deriving the van 't Hoff equation, we also assumed a dilute

Table 8.3 Comparison between theoretical osmotic pressure calculated using van 't Hoff's equation and the experimentally observed osmotic pressure for an aqueous solution of sucrose at two temperatures.

Concentration (mol L ⁻¹)	T = 273 K		T = 333 K		π (atm)	
	π (atm)		Concentration (mol L ⁻¹)	π (atm)		
	Experiment	Theory		Experiment		
0.029 22	0.65	0.655	0.098	2.72	2.68	
0.058 43	1.27	1.330	0.1923	5.44	5.25	
0.131 5	2.91	2.95	0.370 1	10.87	10.11	
0.273 9	6.23	6.14	0.533	16.54	14.65	
0.532 8	14.21	11.95	0.685 5	22.33	18.8	
0.876 6	26.80	19.70	0.827 3	28.37	22.7	

Source: I. Prigogine and R. Defay, *Chemical Thermodynamics*, 4th edition, 1967, Longmans: London.

solution. Using Equations (8.1.11) and (8.2.12), it is easy to see that the osmotic pressure can also be written as

$$\pi_{\text{ideal}} = \frac{-RT \ln x_2}{V_m^*} \quad (8.2.15)$$

where x_2 is the mole fraction of the solvent. Here we have indicated explicitly that the osmotic pressure in this expression is valid for ideal solutions. This formula was obtained by J.J. van Larr in 1894.

For nonideal solutions, instead of an activity coefficient γ , an osmotic coefficient ϕ is defined through

$$\mu(p, T, x_2) = \mu^*(p, T) + \phi RT \ln x_2 \quad (8.2.16)$$

in which μ^* is the chemical potential of the pure solvent. At equilibrium, when the affinity vanishes and osmotic pressure is π we have the equation

$$\mu^*(p, T) = \mu^*(p + \pi, T) + \phi RT \ln x_2 \quad (8.2.17)$$

Following the same procedure as above, we arrive at the following expression for the osmotic pressure of a nonideal solution:

$$\pi = \frac{-\phi RT \ln x_2}{V_m^*} \quad (8.2.18)$$

Equation (8.2.18) was proposed by Donnan and Guggenheim in 1932. From Equations (8.2.15) and (8.2.18) it follows that $\phi = \pi/\pi_{\text{ideal}}$. Hence, the name 'osmotic coefficient' is used for ϕ . We can also relate the affinity to the osmotic pressure. When the solution and the pure solvent are at the same pressure the affinity is $A = \mu^*(p, T) - \mu^*(p, T) - \phi RT \ln x_2 = -\phi RT \ln x_2$. Using this in Equation (8.2.18) we see that

$$\pi = \frac{A}{V_m^*} \quad \text{when } p_{\text{solution}} = p_{\text{solvent}} \quad (8.2.19)$$

Another approach for the consideration of nonideal solutions is similar to that used to obtain the virial equation for real gases. In this case the osmotic pressure is written as

$$\pi = [S]RT(1 + B(T)[S] + \dots) \quad (8.2.20)$$

in which $B(T)$ is a constant that depends on the temperature. The experimental data on the osmotic pressure of polymer solutions (such as polyvinyl chloride in cyclohexanone) shows a fairly linear relation between $\pi/[S]$ and $[S]$. Also, the value of $B(T)$ changes sign from negative to positive as the temperature increases. The temperature at which B equals zero is called the **theta temperature**. If the concentration is expressed in grams per liter, which we shall denote by $[C]$, then Equation (8.2.20) can be written as

$$\boxed{\pi = \frac{[C]RT}{M_s} \left\{ 1 + B(T) \frac{[C]}{M_s} + \dots \right\}} \quad (8.2.21)$$

in which M_s is the molar mass of the solute. With this equation, a plot of $\pi/[C]$ versus $[C]$ is expected to be linear with an intercept equal to RT/M_s . From the intercept, the molar mass can be determined. From the slope, equal to BRT/M_s^2 , the ‘virial constant’ B can be obtained.

8.3 Solubility Equilibrium

The solubility of a solid in a solvent depends on the temperature. **Solubility** is the concentration when the solid solute is in equilibrium with the solution: it is the concentration at saturation. Thermodynamics gives us a quantitative relation between solubility and temperature. In considering the solubilities of solids one must distinguish between ionic solutions and nonionic solutions. When ionic solids, such as NaCl, dissolve in polar solvents, such as water, the solutions contain ions, Na^+ and Cl^- . Since ions interact strongly even in dilute solutions, the activities cannot be approximated well by mole fractions. For nonionic solutions, such as sugar in water or naphthalene in acetone, the activity of the dilute solution can be approximated by the mole fraction.

8.3.1 Nonionic Solutions

For dilute nonionic solutions, we may assume ideality and use the expression (8.1.1) for the chemical potential to analyze the conditions for thermodynamic equilibrium. Solutions of higher concentrations require a more detailed theory (as can be found, for instance, in the classic text by Prigogine and Defay [2]). Recall that, as it does for liquids, the chemical potential of a solid varies very little with pressure and so it is essentially a function only of the temperature. If $\mu_s^*(T)$ is the chemical potential of the pure solid in equilibrium with the solution, then we have (using Equation (8.1.1))

$$\mu_s^*(T) = \mu_1(T) = \mu_1^*(T) + RT \ln(x_1) \quad (8.3.1)$$

in which the μ_1 is the chemical potential of the solute in the solution phase (liquid phase), μ_1^* is the chemical potential of the pure solute in the liquid phase and x_1 is the mole fraction of the solute. Since $\Delta G_{\text{fus}}(T) = \mu_1^* - \mu_s^*$ is the molar Gibbs energy of fusion at temperature T , the above equation can be written in the form

$$\ln x_1 = -\frac{1}{R} \frac{\Delta G_{\text{fus}}}{T} \quad (8.3.2)$$

In this form the temperature dependence of the solubility is not explicit because ΔG_{fus} is itself a function of T . This expression can also be written in terms of the enthalpy of fusion ΔH_{fus} by differentiating this expression with respect to T and using the Gibbs–Helmholtz equation $d(\Delta G/T)/dT = -(\Delta H/T^2)$ (Equation (5.2.14)). Thus:

$$\boxed{\frac{d \ln(x_1)}{dT} = \frac{1}{R} \frac{\Delta H_{\text{fus}}}{T^2}} \quad (8.3.3)$$

Since ΔH_{fus} does not change much with T , this expression can be integrated to obtain a more explicit dependence of solubility with temperature.

8.3.2 Ionic Solutions

Ionic solutions, also called **electrolytes**, are dominated by electrical forces, which can be very strong. To get an idea of the strength of electrical forces, it is instructive to calculate the force of repulsion between two cubes of copper of side 1 cm in which one in a million Cu atoms is a Cu^+ ion, when the two cubes are 10 cm apart. The force is sufficient to lift a weight of 16×10^6 kg (Exercise 8.13).

Owing to the enormous strength of electrical forces, there is almost no separation between positive and negative ions in a solution; positive and negative charges aggregate to make the net charge in every macroscopic volume nearly zero, i.e. every macroscopic volume is electrically neutral. Solutions, and indeed most matter, maintain *electroneutrality* to a high degree. Thus if c_k (mol L⁻¹) are the concentrations of positive and negative ions with *ion numbers* (number of electronic charges) z_k , the total charge carried by an ion per unit volume is $Fz_k c_k$, in which $F = eN_A$ is the Faraday constant, equal to the product of the electronic charge $e = 1.609 \times 10^{-19}$ C and the Avogadro number N_A . Since electroneutrality implies that the net charge is zero, we have

$$\sum_k Fz_k c_k = 0 \quad (8.3.4)$$

Let us consider the solubility equilibrium of a sparingly soluble electrolyte AgCl in water:



At equilibrium:

$$\mu_{\text{AgCl}} = \mu_{\text{Ag}^+} + \mu_{\text{Cl}^-} \quad (8.3.6)$$

In ionic systems, since the positive and negative ions always come in pairs, physically it is not possible to measure the chemical potentials μ_{Ag^+} and μ_{Cl^-} separately; only their sum can be measured. A similar problem arises for the definition of enthalpy and Gibbs energy of formation. For this reason, for ions, these two quantities are defined with respect to a new reference state based on the H^+ ions, as described in Box 8.1. For the chemical potential, a **mean chemical potential** is defined by

$$\mu_{\pm} = \frac{1}{2}(\mu_{\text{Ag}^+} + \mu_{\text{Cl}^-}) \quad (8.3.7)$$

so that Equation (8.3.6) becomes

$$\mu_{\text{AgCl}} = 2\mu_{\pm} \quad (8.3.8)$$

In general, for the decomposition of a neutral compound W into positive and negative ions, A^{Z+} and B^{Z-} respectively (with ion numbers Z^+ and Z^-), we have



in which v_+ and v_- are the stoichiometric coefficients. The mean chemical potential in this case is defined as

$$\mu_{\pm} = \frac{v_+ \mu_+ + v_- \mu_-}{v_+ + v_-} = \frac{\mu_{\text{salt}}}{v_+ + v_-} \quad (8.3.10)$$

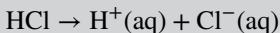
in which $\mu_{\text{salt}} \equiv v_+ \mu_+ + v_- \mu_-$. Here, we have written the chemical potential of the positive ion A^{Z+} as μ_+ and that of the negative ion B^{Z-} as μ_- .

Box 8.1 Enthalpy and the Gibbs free energy of formation of ions

When ionic solutions form, the ions occur in pairs; therefore, it is not possible to isolate the enthalpy of formation of a positive or negative ion. Hence, we cannot obtain the heats of formation of ions with the usual elements in their standard state as the reference state. For ions, the enthalpy of formation is tabulated by defining the ΔH_f^0 of formation of H^+ as zero at all temperatures. Thus

$$\Delta H_f^0[H^+(aq)] = 0 \text{ at all temperatures}$$

With this definition it is now possible to obtain the ΔH_f^0 of all other ions. For example, to obtain the heat of formation of Cl^- (aq), at a temperature T , the enthalpy of solution of HCl is measured. Thus, $\Delta H_f^0[Cl^-(aq)]$ is the heat of solution at temperature T of the reaction



The tabulated values of enthalpies are based on this convention. Similarly, for the Gibbs energy,

$$\Delta G_f^0[H^+(aq)] = 0 \text{ at all temperatures}$$

For ionic systems, it has become customary to use the **molality scale** (mol kg^{-1} solvent). This scale has the advantage that the addition of another solute does not change the molality of a given solute. The values of ΔG_f^0 and ΔH_f^0 for the formation of ions in water at $T = 298.15$ K are tabulated for the **standard state** of an ideal dilute solution at a concentration of 1 mol kg^{-1} . This standard state is given the subscript ‘ao’. Thus, the chemical potential or the activity of an ion is indicated by ‘ao’. The chemical potential of an ionized salt, $\mu_{\text{salt}} \equiv \nu_+ \mu_+ + \nu_- \mu_-$, and the corresponding activity are denoted with the subscript ‘ai’.

The activity coefficients γ of electrolytes are defined with respect to ideal solutions. For example, the mean chemical potential for $AgCl$ is written as

$$\begin{aligned}\mu_{\pm} &= \frac{1}{2} \left[\mu_{Ag^+}^0 + RT \ln(\gamma_{Ag^+} x_{Ag^+}) + \mu_{Cl^-}^0 + RT \ln(\gamma_{Cl^-} x_{Cl^-}) \right] \\ &= \mu_{\pm}^0 + RT \ln \sqrt{\gamma_{Ag^+} \gamma_{Cl^-} x_{Ag^+} x_{Cl^-}}\end{aligned}\quad (8.3.11)$$

where $\mu_{\pm}^0 = 1/2 (\mu_{Ag^+}^0 + \mu_{Cl^-}^0)$. Once again, since the activity coefficients of the positive and negative ions cannot be measured individually, a mean activity coefficient γ_{\pm} is defined by

$$\gamma_{\pm} = (\gamma_{Ag^+} \gamma_{Cl^-})^{1/2} \quad (8.3.12)$$

In the more general case of Equation (8.3.9), the **mean ionic activity coefficient** is defined as

$$\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)} \quad (8.3.13)$$

where we have used γ_+ and γ_- for the activity coefficients of the positive and negative ions.

The chemical potentials of dilute solutions may be expressed in terms of **molality** m_k (moles of solute per kilogram of solvent) or molarities c_k (moles of solute per liter of solution¹) instead of mole fractions x_k . In electrochemistry, it is more common to use molality m_k . For dilute solutions, since $x_k = N_k/N_{\text{solvent}}$, we have the following conversion formulas for the different units:

$$x_k = m_k M_s \quad \text{and} \quad x_k = V_{\text{ms}} c_k \quad (8.3.14)$$

¹The molarity of k is also expressed as $[k]$.

in which M_s is the molar mass of the solvent in kilograms and V_{ms} the molar volume of the solvent in liters. The corresponding chemical potentials then are written as

$$\mu_k^x = \mu_k^{x0} + RT \ln(\gamma_k x_k) \quad (8.3.15)$$

$$\begin{aligned} \mu_k^m &= \mu_k^{x0} + RT \ln M_s + RT \ln(\gamma_k m_k) \\ &= \mu_k^{m0} + RT \ln \left(\frac{\gamma_k m_k}{m^0} \right) \end{aligned} \quad (8.3.16)$$

$$\begin{aligned} \mu_k^c &= \mu_k^{x0} + RT \ln V_{ms} + RT \ln(\gamma_k c_k) \\ &= \mu_k^{c0} + RT \ln \left(\frac{\gamma_k c_k}{c^0} \right) = \mu_k^{c0} + RT \ln \left(\frac{\gamma_k [k]}{[k]^0} \right) \end{aligned} \quad (8.3.17)$$

in which the definitions of the reference chemical potentials μ_k^{m0} and μ_k^{c0} in each concentration scale are self-evident. The activity in the molality scale is written in the dimensionless form as $a_k = \gamma_k m_k / m^0$, in which m^0 is the standard value of molality equal to 1 mol of solute per kilogram of solvent. Similarly, the activity in the molarity scale is written as $a_k = \gamma_k c_k / c^0$, in which c^0 equals 1 mol per liter of solution. For electrolytes the mean chemical potential μ_{\pm} is usually expressed in the molality scale; the tabulation of ΔG_f^0 and ΔH_f^0 for the formation of ions in water at $T = 298.15$ K is usually for the standard state of an ideal dilute solution at a concentration of 1 mol kg⁻¹. This standard state is given the subscript ‘ao’.

In the commonly used molality scale, the solution equilibrium of AgCl expressed in Equation (8.3.8) can now be written as

$$\mu_{\text{AgCl}}^0 + RT \ln a_{\text{AgCl}} = 2\mu_{\pm}^{m0} + RT \ln \left[\frac{\gamma_{\pm}^2 m_{\text{Ag}^+} m_{\text{Cl}^-}}{(m^0)^2} \right] \quad (8.3.18)$$

Since the activity of a solid is nearly equal to one, $a_{\text{AgCl}} \approx 1$. Hence, we obtain the following expression for the **equilibrium constant**² for solubility in the molality scale:

$$K_m(T) \equiv \frac{\gamma_{\pm}^2 m_{\text{Ag}^+} m_{\text{Cl}^-}}{(m^0)^2} = a_{\text{Ag}^+} a_{\text{Cl}^-} = \exp \left(\frac{\mu_{\text{AgCl}}^0 - 2\mu_{\pm}^{m0}}{RT} \right) \quad (8.3.19)$$

The equilibrium constant for electrolytes is also called the **solubility product** K_{SP} . For sparingly soluble electrolytes such as AgCl, even at saturation the solution is very dilute and $\gamma_{\pm} \approx 1$. In this limiting case, the solubility product

$$K_{\text{SP}} \approx m_{\text{Ag}^+} m_{\text{Cl}^-} \quad (8.3.20)$$

in which we have not explicitly included m^0 , which has a value equal to one.

8.3.3 Activity, Ionic Strength and Solubility

A theory of ionic solutions developed by Peter Debye and Erich Hückel in 1923 (which is based on statistical mechanics) provides an expression for the activity. We shall only state the main result of this theory,

²A general definition of the equilibrium constant is discussed in Chapter 9.

which works well for dilute electrolytes. The activity depends on a quantity called the **ionic strength I** defined by

$$I = \frac{1}{2} \sum_k z_k^2 m_k \quad (8.3.21)$$

The activity coefficient of an ion k in the molality scale is given by

$$\log_{10}(\gamma_k) = -Az_k^2 \sqrt{I} \quad (8.3.22)$$

in which

$$A = \frac{1}{2.3026} (2\pi N_A \rho_s)^{1/2} \left(\frac{N_A e^2}{4\pi \epsilon_0 \epsilon_r RT} \right)^{3/2} \quad (8.3.23)$$

where ρ_s is the density of the solvent, e is the electronic charge, $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ is the permittivity of a vacuum and ϵ_r the relative permittivity of the solvent ($\epsilon_r = 78.54$ for water). For ions in water, at $T = 298.15 \text{ K}$, we find $A = 0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$. Thus, at 25°C the activity of ions in dilute solutions can be approximated well by the expression

$$\log_{10}(\gamma_k) = -0.509 z_k^2 \sqrt{I} \quad (8.3.24)$$

The Debye–Hückel theory enables us to understand how solubility is influenced by ionic strength. For example, let us look at the solubility of AgCl. If the $m_{\text{Ag}^+} = m_{\text{Cl}^-} = S$, the *solubility*, we may write the equilibrium constant K_m as

$$K_m(T) \equiv \gamma_{\pm}^2 m_{\text{Ag}^+} m_{\text{Cl}^-} = \gamma_{\pm}^2 S^2 \quad (8.3.25)$$

The ionic strength depends not only on the concentration of Ag^+ and Cl^- ions, but also on all the other ions. Thus, for example, the addition of nitric acid, HNO_3 , which adds H^+ and NO_3^- ions to the system, will change the activity coefficient γ_{\pm} . However, the equilibrium constant, which is a function of T only (as is evident from Equation (8.3.19)), remains unchanged if T is constant. As a result, the value of m (or solubility in molal) will change with the ionic strength I . If the concentration of HNO_3 (which dissociates completely) is m_{HNO_3} , then the ionic strength of the solution is

$$I = \frac{1}{2} (m_{\text{Ag}^+} + m_{\text{Cl}^-} + m_{\text{H}^+} + m_{\text{NO}_3^-}) = S + m_{\text{HNO}_3} \quad (8.3.26)$$

Using Equation (8.3.12) for γ_{\pm} for AgCl and substituting Equation (8.3.24) in (8.3.25) we can obtain the following relation between the solubility S of AgCl and the concentration of HNO_3 :

$$\log_{10}(S) = \frac{1}{2} \log_{10}(K_m(T)) + 0.509 \sqrt{S + m_{\text{HNO}_3}} \quad (8.3.27)$$

If $S \ll m_{\text{HNO}_3}$, then the above relation can be approximated by

$$\log_{10}(S) = \frac{1}{2} \log_{10}(K_m(T)) + 0.509 \sqrt{m_{\text{HNO}_3}} \quad (8.3.28)$$

Thus, a plot of $\log S$ versus $\sqrt{m_{\text{HNO}_3}}$ should yield a straight line, which is indeed found to be the case experimentally. In fact, such plots can be used to determine the equilibrium constant K_m and the activity coefficients.

8.4 Thermodynamic Mixing and Excess Functions

8.4.1 Perfect Solutions

A perfect solution is one for which the chemical potential of the form $\mu_k(p, T, x_k) = \mu_k^*(p, T) + RT \ln(x_k)$ is valid for all values of the mole fraction x_k . The molar Gibbs energy of such a solution is

$$G_m = \sum_k x_k \mu_k = \sum_k x_k \mu_k^* + RT \sum_k x_k \ln x_k \quad (8.4.1)$$

If each of the components were separated, then the total Gibbs energy for the components is the sum $G_m^* = \sum_k x_k G_{mk}^* = \sum_k x_k \mu_k^*$, in which we have used the fact that, for a pure substance, G_{mk}^* , the molar Gibbs energy of k , is equal to the chemical potential μ_k^* . Hence, the change (decrease) in the *molar* Gibbs energy due to the *mixing* of the components in the solution is

$$\Delta G_{\text{mix}} = RT \sum_k x_k \ln x_k \quad (8.4.2)$$

and

$$G_m = \sum_k x_k G_{mk}^* + \Delta G_{\text{mix}} \quad (8.4.3)$$

Since the molar entropy $S_m = -(\partial G_m / \partial T)_p$, it follows from Equations (8.4.2) and (8.4.3) that

$$S_m = \sum_k x_k S_{mk}^* + \Delta S_{\text{mix}} \quad (8.4.4)$$

$$\Delta S_{\text{mix}} = -R \sum_k x_k \ln x_k \quad (8.4.5)$$

where ΔS_{mix} is the molar entropy of mixing. This shows that, during the formation of a perfect solution from pure components at a fixed temperature, the decrease in G is $\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}$. Since $\Delta G = \Delta H - T\Delta S$, we can conclude that, for the formation of a perfect solution at a fixed temperature, $\Delta H = 0$. This can be verified explicitly by noting that the Helmholtz equation (5.2.11) can be used to evaluate the enthalpy. For G given by Equations (8.4.2) and (8.4.3) we find

$$H_m = -T^2 \left(\frac{\partial}{\partial T} \frac{G_m}{T} \right) = \sum_k x_k H_{mk}^* \quad (8.4.6)$$

Thus, the enthalpy of the solution is the same as the enthalpy of the pure components and there is no change in the enthalpy of a perfect solution due to mixing. Similarly, by noting that $V_m = (\partial G_m / \partial p)_T$, it is easy to see (Exercise 8.16) that there is no change in the molar volume due to mixing, i.e. $\Delta V_{\text{mix}} = 0$; the total volume is the sum of the volumes of the components in the mixture. Furthermore, since $\Delta U = \Delta H - p\Delta V$, we see also that $\Delta U_{\text{mix}} = 0$. Thus, for a *perfect solution*, the *molar quantities* for mixing are

$$\Delta G_{\text{mix}} = RT \sum_k x_k \ln x_k \quad (8.4.7)$$

$$\Delta S_{\text{mix}} = -R \sum_k x_k \ln x_k \quad (8.4.8)$$

$$\Delta H_{\text{mix}} = 0 \quad (8.4.9)$$

$$\Delta V_{\text{mix}} = 0 \quad (8.4.10)$$

$$\Delta U_{\text{mix}} = 0 \quad (8.4.11)$$

In a perfect solution, the irreversible process of mixing of the components at constant p and T is entirely due to the increase in entropy; no heat is evolved or absorbed.

8.4.2 Ideal Solutions

Dilute solutions may be ideal over a small range of mole fractions x_i . In this case the molar enthalpy H_m and the molar volume V_m may be a linear function of the partial molar enthalpies H_{mi} and partial molar volumes V_{mi} . Thus:

$$H_m = \sum_i x_i H_{mi} \quad \text{and} \quad V_m = \sum_i x_i V_{mi} \quad (8.4.12)$$

However, the partial molar enthalpies H_{mi} may not be equal to the molar enthalpies of pure substances if the corresponding mole fractions are small. The same is true for the partial molar volumes. On the other hand, if x_i is nearly equal to one, then H_{mi} will be nearly equal to the molar enthalpy of the pure substance. A dilute solution for which Equation (8.4.12) is valid will exhibit ideal behavior, but it may have a nonzero enthalpy of mixing. To see this more explicitly, consider a dilute ($x_1 \gg x_2$) binary solution for which H_{m1}^* and H_{m2}^* are the molar enthalpies of the two pure components. Then, before mixing, the molar enthalpy is

$$H_m^* = x_1 H_{m1}^* + x_2 H_{m2}^* \quad (8.4.13)$$

After mixing, since for the major component (for which $x_1 \approx 1$) we have $H_{m1}^* = H_{m1}$, the molar enthalpy will be

$$H_m = x_1 H_{m1}^* + x_2 H_{m2} \quad (8.4.14)$$

The molar enthalpy of mixing is then the difference between the above two enthalpies:

$$\Delta H_{\text{mix}} = H_m - H_m^* = x_2 (H_{m2} - H_{m2}^*) \quad (8.4.15)$$

In this way, an ideal solution may have a nonzero enthalpy of mixing. The same may be true for the volume of mixing.

8.4.3 Excess Functions

For nonideal solutions, the molar Gibbs energy of mixing is

$$\Delta G_{\text{mix}} = RT \sum_i x_i \ln(\gamma_i x_i) \quad (8.4.16)$$

The difference between the Gibbs energies of mixing of perfect and nonideal solutions is called the **excess Gibbs energy**, which we shall denote by ΔG_E . From Equations (8.4.7) and (8.4.16) it follows that

$$\Delta G_E = RT \sum_i x_i \ln \gamma_i \quad (8.4.17)$$

Other excess functions, such as excess entropy and enthalpy, can be obtained from ΔG_E . For example:

$$\Delta S_E = - \left(\frac{\partial \Delta G_E}{\partial T} \right)_p = -RT \sum_i x_i \frac{\partial \ln \gamma_i}{\partial T} - R \sum_i x_i \ln x_i \quad (8.4.18)$$

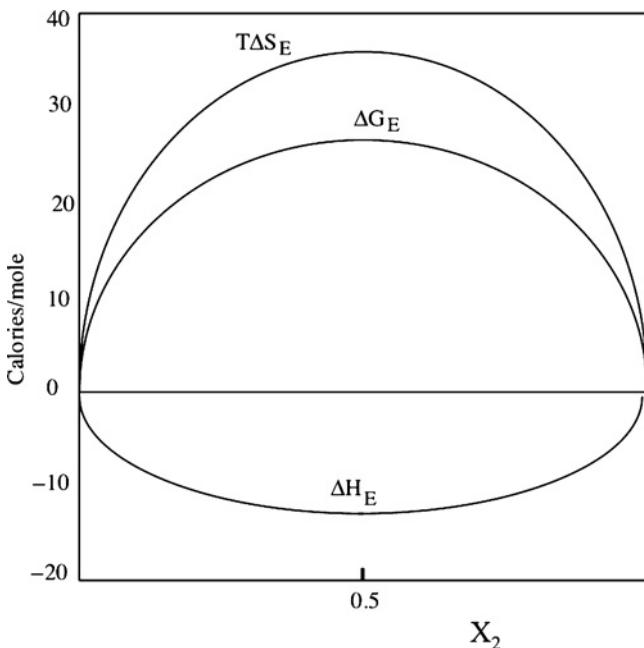


Figure 8.6 Thermodynamic excess function for a solution of *n*-heptane (component 1) and *n*-hexadecane (component 2) at 20 °C. The graph shows molar excess functions as a function of the mole fraction x_2 of *n*-hexadecane.

Similarly ΔH_E can be obtained using the relation

$$\Delta H_E = -T^2 \left(\frac{\partial}{\partial T} \frac{\Delta G_E}{T} \right) \quad (8.4.19)$$

These excess functions can be obtained experimentally through measurements of vapor pressures and heats of reaction (see Figure 8.6 for an example of an excess function).

8.4.4 Regular and Athermal Solutions

Nonideal solutions may be classified into two limiting cases. In one limiting case, called **regular solutions**, $\Delta G_E \approx \Delta H_E$; i.e. most of the deviation from ideality is due to the excess enthalpy of mixing. Since $\Delta G_E = \Delta H_E - T\Delta S_E$, it follows that for regular solutions $\Delta S_E \approx 0$. Furthermore, since $\Delta S_E = -(\partial \Delta G_E / \partial T)_p$, from Equation (8.4.17) it follows that the activity coefficients

$$\ln \gamma_i \propto \frac{1}{T} \quad (8.4.20)$$

For regular binary solutions, the activities may be approximated by the function $\gamma_k = \alpha x_k^2 / (RT)$.

The other limiting case of nonideal solutions is when $\Delta G_E \approx -T\Delta S_E$, in which case the deviation from ideality is mostly due to the excess entropy of mixing and $\Delta H_E \approx 0$. In this case, using Equation (8.4.17) in (8.4.19), we see that $\ln \gamma_i$ are independent of T . Such solutions are called **athermal solutions**. Solutions in which the component molecules are of nearly the same size but differ in intermolecular forces generally behave like regular solutions. Solutions whose component molecules have very different sizes but do not differ significantly in their intermolecular forces, as in the case of monomers and polymers, are examples of athermal solutions.

8.5 Azeotropy

In Chapter 7 we discussed azeotropes briefly. We shall apply the thermodynamics of solutions that was presented in the previous sections of this chapter to azeotropes. For an azeotrope in equilibrium with its vapor, the composition of the liquid and the vapor phases are the same. At a fixed pressure, a liquid mixture is an azeotrope at a particular composition called the **azeotropic composition**. In a closed system, an **azeotropic transformation** is one in which there is an exchange of matter between two phases without a change in the composition. In this regard, an azeotrope is similar to the vaporization of a pure substance. This enables us to obtain the activity coefficients of azeotropes just as can be done for a pure substance.

Let us consider a binary azeotrope. As we have seen in Section 8.1, the chemical potentials of the components can be written in the form $\mu_k(T, p, x_k) = \mu_k^0(T, p) + RT \ln(\gamma_k x_k)$, in which activity coefficient γ_k quantifies the deviation from ideality. If $\gamma_{k,l}$ and $\gamma_{k,g}$ are the activity coefficients of component k in the liquid and gas phases respectively, then by considering an azeotropic transformation it can be shown that (Exercise 8.17)

$$\ln\left(\frac{\gamma_{k,g}}{\gamma_{k,l}}\right) = \int_{T_k^*}^T \frac{\Delta H_{\text{vap},k}}{RT^2} dT - \frac{1}{RT} \int_{p^*}^p \Delta V_{mk}^* dp \quad (8.5.1)$$

in which $\Delta H_{\text{vap},k}$ is the heat of vaporization of component k and ΔV_{mk}^* is the change in the molar volume of the pure component between the liquid and the vapor phases. T^* is the boiling point of the pure solvent at pressure p^* . If we consider an azeotropic transformation at a fixed pressure, e.g. $p = p^* = 1$ atm, then since ΔH_{vap} generally does not change much with T , we obtain

$$\ln\left(\frac{\gamma_{k,g}}{\gamma_{k,l}}\right) = \frac{-\Delta H_{\text{vap},k}}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right) \quad (8.5.2)$$

For the activity coefficient of the vapor phase, if we use the ideal gas approximation, $\gamma_{k,g} = 1$. This gives us an explicit expression for the activity coefficient of the liquid phase:

$$\ln(\gamma_{k,l}) = \frac{\Delta H_{\text{vap},k}}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right) \quad (8.5.3)$$

With this expression, the activity coefficient of a component of an azeotrope can be calculated, and it gives a simple physical meaning to the activity coefficient. Molecular theories of solutions give us more insight into the relation between the intermolecular forces and the thermodynamics of azeotropes [3].

References

1. Laidler, K.J., *The World of Physical Chemistry*. 1993, Oxford University Press: Oxford.
2. Prigogine, I., Defay, R., *Chemical Thermodynamics*, fourth edition. 1967, Longmans: London.
3. Prigogine, I., *Molecular Theory of Solutions*. 1957, Interscience Publishers, New York.

Examples

Example 8.1 In the oceans, to a depth of about 100 m the concentration of O₂ is about 0.25×10^{-3} mol L⁻¹. Compare this value with the value obtained using Henry's law assuming equilibrium between the atmospheric oxygen and the dissolved oxygen.

Solution The partial pressure of O₂ in the atmosphere is $p_{\text{O}_2} \approx 0.2 \text{ atm}$. Using Henry's law constant in Table 8.1 we have, for the mole fraction of the dissolved oxygen x_{O_2} ,

$$p_{\text{O}_2} = K_{\text{O}_2} x_{\text{O}_2}$$

Hence:

$$x_{\text{O}_2} = \frac{p_{\text{O}_2}}{K_{\text{O}_2}} = \frac{0.2 \text{ atm}}{4.3 \times 10^4 \text{ atm}} = 4.6 \times 10^{-6}$$

i.e. there are 4.6×10^{-6} mol of O₂ per mole of H₂O. Noting that 1 L of H₂O is equal to 55.5 mol, the above mole fraction of O₂ can be converted into a concentration in moles per liter:

$$c_{\text{O}_2} = 4.6 \times 10^{-6} \times 55.5 \text{ mol L}^{-1} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$$

which is equal to the measured concentration of O₂ in the oceans.

Example 8.2 In an aqueous solution of NH₃ at 25.0 °C, the mole fraction of NH₃ is 0.05. For this solution, calculate the partial pressure of water vapor assuming ideality. If the vapor pressure is found to be 3.40 kPa, what is the activity a of water and what is its activity coefficient γ ?

Solution If p^* is the vapor pressure of pure water at 25.0 °C, then, according to Raoult's law (8.1.10), the vapor pressure of the above solution is given by $p = x_{\text{H}_2\text{O}} p^* = 0.95 p^*$. The value of p^* can be obtained as follows. Since water boils at 373.0 K at $p = 1.0 \text{ atm} = 101.3 \text{ kPa}$, we know that its vapor pressure is 101.3 kPa at 373.0 K. Using the Clausius–Clapeyron equation, we can calculate the vapor pressure at 25.0 °C = 298.0 K:

$$\ln p_1 - \ln p_2 = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

With $p_2 = 1 \text{ atm}$, $T_2 = 373.0$, $T_1 = 298.0$, $\Delta H_{\text{vap}} = 40.66 \text{ kJ mol}^{-1}$ (see Table 7.1), the vapor pressure, p_1 (atm), can be computed:

$$\ln(p_1/\text{atm}) = -3.299$$

i.e.

$$\begin{aligned} p_1 &= \exp(-3.299) \text{ atm} = 0.0369 \text{ atm} = 101.3 \times 0.0369 \text{ kPa} \\ &= 3.73 \text{ kPa} = p^* \end{aligned}$$

Hence, the vapor pressure p^* of pure water at 25 °C is 3.738 kPa. For the above solution in which the mole fraction of water is 0.95, the vapor pressure for an ideal solution according to Raoult's law should be

$$p = 0.95 \times 3.73 \text{ kPa} = 3.54 \text{ kPa}$$

For an ideal solution, the activity a is the same as the mole fraction x_1 . As shown in Equation (8.1.6), in the general case the activity $a = p/p^*$. Hence, if the measured vapor pressure is 3.40 kPa, then the activity

$$a_1 = 3.40/3.738 = 0.909$$

The activity coefficient is defined by $a_k = \gamma_k x_k$. Hence, $\gamma_1 = a_1/x_1 = 0.909/0.95 = 0.956$.

Example 8.3 Living cells contain water with many ions. The osmotic pressure corresponds to that of an NaCl solution of about 0.15 M. Calculate the osmotic pressure at $T = 27^\circ\text{C}$.

Solution Osmotic pressure depends on the ‘colligative concentration’, i.e. the number of particles per unit volume. Since NaCl dissociates into Na^+ and Cl^- ions, the colligative molality of the above solution is 0.30 M. Using the van ’t Hoff equation (8.2.14), we can calculate the osmotic pressure π :

$$\pi = RT[S] = (0.0821 \text{ L atm K}^{-1}\text{mol}^{-1})(300.0 \text{ K})(0.30 \text{ mol L}^{-1}) = 7.40 \text{ atm}$$

If an animal cell is immersed in water, then the water flowing into the cell due to osmosis will exert a pressure of about 7.4 atm and causes the cell to burst. Plant cell walls are strong enough to withstand this pressure.

Example 8.4 At $p = 1$ atm, the boiling point of an azeotropic mixture of $\text{C}_2\text{H}_5\text{OH}$ and CCl_4 is 338.1 K. The heat of vaporization of $\text{C}_2\text{H}_5\text{OH}$ is $38.58 \text{ kJ mol}^{-1}$ and its boiling point is 351.4 K. Calculate the activity coefficient of ethanol in the azeotrope.

Solution This can be done by direct application of Equation (8.5.3), where $\Delta H_{\text{l,vap}} = 38.58 \text{ kJ mol}^{-1}$, $T = 338.1 \text{ K}$ and $T^* = 351.4 \text{ K}$:

$$\ln(\gamma_{\text{l,k}}) = \frac{38.5 \times 10^3}{8.314} \left(\frac{1}{338.1} - \frac{1}{351.4} \right) = 0.519$$

i.e.

$$\gamma_{\text{l,k}} = 1.68$$

Exercises

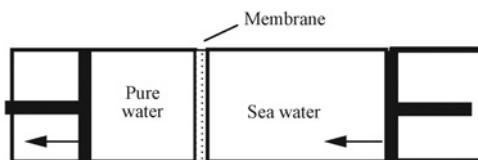
- 8.1 Obtain Equation (8.1.8) from Equation (8.1.7).
- 8.2 14.0 g of NaOH is dissolved in 84.0 g of H_2O . The solution has a density of $1.114 \times 10^3 \text{ kg m}^{-3}$. For the two components, NaOH and H_2O , in this solution, obtain (a) the mole fractions, (b) the molality and (c) molarity.
- 8.3 The composition of the atmosphere is shown in Table 8.1. Using Henry’s law constants, calculate the concentrations of N_2 , O_2 and CO_2 in a lake.
- 8.4 Obtain Equation (8.2.5) from Equation (8.2.4) for small changes in the boiling point of a solution.
- 8.5 (a) The solubility of $\text{N}_2(\text{g})$ in water is about the same as in blood serum. Calculate the concentration (in mol L^{-1}) of N_2 in the blood.
(b) The density of seawater is 1.01 g mL^{-1} . What is the pressure at a depth of 100 m? What will the blood serum concentration (in mol L^{-1}) of N_2 be at this depth? If divers rise too fast, then any excess N_2 can form bubbles in the blood, causing pain, paralysis and distress in breathing.
- 8.6 Assuming Raoult’s law holds, predict the boiling point of a 0.5 M aqueous solution of sugar. Do the same for NaCl, but note that the number of particles (ions) per molecule is twice that of a nonionic solution. Raoult’s law is a colligative property that depends on the number of solute particles.
- 8.7 Ethylene glycol ($\text{OH}-\text{CH}_2-\text{CH}_2-\text{OH}$) is used as an antifreeze. (Its boiling point is 197 °C and freezing point is -17.4°C).
(a) Look up the density of ethylene glycol in the *CRC Handbook* or other tables and write a general formula for the freezing point of a mixture of $X \text{ mL}$ of ethylene glycol in 1.00 L of water for X in the range 0–100 mL.

- (b)** If the lowest expected temperature is about $-10\text{ }^{\circ}\text{C}$, what is the minimum amount of ethylene glycol (milliliters ethylene glycol per liter of H_2O) you need in your coolant?
- (c)** What is the boiling point of the coolant that contains 300 mL of ethylene glycol per liter of water?
- 8.8** What will be the boiling point of a solution of 20.0 g of urea ($(\text{NH}_2)_2\text{CO}$) in 1.25 kg of nitrobenzene (use Table 8.2).
- 8.9** A 1.89 g pellet of an unknown compound was dissolved to 50 mL of acetone. The change in the boiling point was found to be $0.64\text{ }^{\circ}\text{C}$. Calculate the molar mass of the unknown compound. The density of acetone is 0.7851 g mL^{-1} and the value of the ebullioscopic constant K_b may be found in Table 8.2.
- 8.10** A solution of 4.00 g of hemoglobin in 100 mL was prepared and its osmotic pressure was measured. The osmotic pressure was found to be 0.0130 atm at 280 K. (a) Estimate the molar mass of hemoglobin. (b) If 4.00 g of NaCl is dissolved in 100 mL of water, what would the osmotic pressure be? (Molecular weights of some proteins: ferricytochrome C, 12 744; myoglobin, 16 951; lysozyme, 14 314; immunoglobulin G, 156 000; myosin, 570 000.)
- 8.11** The concentration of the ionic constituents of seawater are:

Ion	Cl^-	Na^+	SO_4^{2-}	Mg^{2+}	Ca^{2+}	K^+	HCO_3^-
Concentration (M)	0.55	0.46	0.028	0.054	0.010	0.010	0.0023

Many other ions are present in much lower concentrations. Estimate the osmotic pressure of seawater due to its ionic constituents.

- 8.12** The concentration of NaCl in seawater is approximately 0.5 M. In the process of reverse osmosis, seawater is forced through a membrane impermeable to the ions to obtain pure water. The applied pressure has to be larger than the osmotic pressure.



- (a)** At $25\text{ }^{\circ}\text{C}$, what is the minimum pressure needed to achieve reverse osmosis? What is the work done in obtaining 1.0 L of pure water from seawater?
- (b)** If the cost of 1 kW h of electrical power is about \$0.15, what would be the energy cost of producing 100 L of water from seawater through reverse osmosis if the process is 50% efficient in using the electrical power to obtain pure water?
- (c)** Suggest another process to obtain pure water from seawater.
- 8.13** Consider two cubes of copper of side 1 cm. In each cube, assume that one out of a million Cu atoms is Cu^+ . Using Coulomb's law, calculate the force between the two cubes if they are placed at a distance of 10 cm.
- 8.14** Calculate the ionic strength and the activity coefficients of a 0.02 M solution of CaCl_2 .
- 8.15** The solubility product of AgCl is 1.77×10^{-10} . Calculate the concentration of Ag^+ ions in equilibrium with solid AgCl .

- 8.16** Show that for a perfect solution the molar volume of mixing $\Delta V_{\text{mix}} = 0$.
- 8.17** Consider a binary azeotrope. The chemical potentials of a component, say 2, in the gas and the liquid phases can be written as

$$\mu_{2,g}(T, p, x) = \mu_{2,g}^*(T, p) + RT \ln(\gamma_{2,g} x_2)$$

and

$$\mu_{2,l}(T, p, x) = \mu_{2,l}^*(T, p) + RT \ln(\gamma_{2,l} x_2)$$

in which μ^* is the chemical potential of the pure substance. Note that the mole fraction is the same in the two phases. Use Equation (5.3.7) to derive the relation (8.5.1).

- 8.18** A regular solution is one for which the excess entropy $\Delta S_E = 0$. Show that this implies that $\ln \gamma_i \propto 1/T$ in which γ_i is the activity coefficient.

9

Thermodynamics of Chemical Transformations

9.1 Transformations of Matter

Transformations of matter take place in many ways, through chemical, nuclear and elementary particle reactions. We shall speak of ‘chemical transformations’ in this broader sense. Though thermodynamics was founded in our daily experience, its reach is vast, ranging from the most simple changes like the melting of ice, to the state of matter during the first few minutes after the ‘big bang’, to the radiation that fills the entire universe today.

Let us begin by looking at the transformation that matter undergoes at various temperatures. Box 9.1 gives an overview of the reactions that take place at various temperatures, ranging from those during the first few minutes after the ‘big bang’ [1] to terrestrial and interstellar temperatures. All these transformations or reactions can be associated with enthalpies of reaction and an equilibrium characterized by the vanishing of the corresponding affinities.

Our present knowledge of the universe is based on the radiation emitted by galaxies that we can detect and on the motion of galaxies due to gravitational forces exerted by matter that is visible and invisible. Astrophysical data on observable gravitational effects indicate that only about 4% of the energy density in the universe is in the form of the protons, neutrons and electrons that make up ordinary matter in all the visible galaxies. Of the rest, 74% is in an unknown form spread diffusely throughout the universe; this is called **dark energy**. The remaining 22% is matter in galaxies that is not visible and is called **dark matter**; its presence is inferred through the gravitational effects it has on visible matter. The universe is also filled with thermal radiation¹ at a temperature of about 2.73 K (usually called **cosmic microwave background**) and particles called neutrinos, which interact only very weakly with protons, neutrons and electrons.

The small amount of matter that is in the form of stars and galaxies is not in thermodynamic equilibrium. The affinities for the reactions that are currently occurring in the stars are not zero. The nuclear reactions in the stars produce all the known elements from hydrogen [2–4]. Hence, the observed properties, such as the abundance of elements in stars and planets, cannot be described using the theory of chemical equilibrium.

¹The precise thermodynamic nature of thermal radiation is discussed in Chapter 11.

Box 9.1 Transformation of matter at various temperatures

Temperature $> 10^{10}$ K. This was the temperature during the first few minutes of the universe after the ‘big bang’. At this temperature, the thermal motion of the protons and neutrons is so violent that even the strong nuclear forces cannot bind them as nuclei of elements. Electron–positron pairs appear and disappear spontaneously and are in thermal equilibrium with radiation. (The threshold for electron–positron pair production is about 6×10^9 K.)

Temperature range 10^9 – 10^7 K. At about 10^9 K, nuclei begin to form and nuclear reactions occur in this range. Temperatures as high as 10^9 are reached in stars and supernova, where heavier elements are synthesized from H and He. The *binding energy per nucleon* (proton or neutron) is in the range $(1.0\text{--}1.5) \times 10^{-12}$ J $\approx (6.0\text{--}9.0) \times 10^6$ eV, which corresponds to $(6.0\text{--}9.0) \times 10^8$ kJ mol $^{-1}$.

Temperature range 10^6 – 10^4 K. In this range, electrons bind to nuclei to form atoms, but the bonding forces between atoms are not strong enough to form stable molecules. At a temperature of about 1.5×10^5 K, hydrogen atoms begin to ionize. The ionization energy of 13.6 eV corresponds to 1310 kJ mol $^{-1}$. Heavier atoms require larger energies for complete ionization. Complete ionization of carbon, for example, requires 490 eV of energy, which corresponds to 47187 kJ mol $^{-1}$.* Carbon atoms will be completely dissociated at $T \approx 5 \times 10^6$ K into electrons and nuclei. In this temperature range, matter exists as free electrons and nuclei, a state of matter called *plasma*.

Temperature range 10 – 10^4 K. Chemical reactions take place in this range. The chemical bond energies are of the order of 10^2 kJ mol $^{-1}$. The C–H bond energy is about 414 kJ mol $^{-1}$. At a temperature of about 5×10^4 K, chemical bonds will begin to break. The intermolecular forces, such as hydrogen bonds, are of the order 10 kJ mol $^{-1}$. The enthalpy of vaporization of water, which is essentially the breaking of hydrogen bonds, is about 40 kJ mol $^{-1}$.

* $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} = 96.3 \text{ kJ mol}^{-1}$; $T = (\text{Energy in J mol}^{-1})/R = (\text{Energy in J})/k_B$.

A knowledge of the rates of reactions and the history of the star or planet is necessary to understand the abundance of elements.

When a system reaches thermodynamic equilibrium, however, its history is of no importance. Regardless of the path leading to equilibrium, the state of equilibrium can be described by general laws. In this chapter we shall first look at the nature of chemical reactions and equilibrium; then we study the relation between entropy production and the rates of chemical reactions that drive the system to equilibrium.

9.2 Chemical Reaction Rates

In studying chemical reactions and their evolution to equilibrium, it is also our purpose to look explicitly at the entropy production while the reactions are in progress. In other words, we would like to obtain explicit expressions for the entropy production $d_i S/dt$ in terms of the rates of reactions. The introduction of reaction rates takes us beyond the classical thermodynamics of equilibrium states that was formulated by Gibbs and others.

In general, the laws of thermodynamics cannot specify reaction rates. Though affinity is the driving force of chemical reactions, the rates are not determined solely by affinities, but depend on many factors, such as the presence of catalysts which does not change the affinity. However, as we shall see in later chapters, close to the thermodynamic equilibrium – called the ‘linear regime’ – thermodynamic formalism can be used to

show that rates are linearly related to the affinities. The general topic of specifying the rates of chemical reactions has become a subject in itself and goes by the name of ‘chemical kinetics’. Kinetic equations express reaction rates as functions of state variables. Some basic aspects of chemical kinetics will be discussed in this section.

We have already seen that the entropy production due to a chemical reaction may be written in the form (see Equation (4.1.16))

$$\frac{d_i S}{dt} = \frac{A}{T} \frac{d\xi}{dt} \quad (9.2.1)$$

in which ξ is the extent of reaction introduced in Section 2.5 and A is the affinity, expressed in terms of the chemical potentials. The time derivative of ξ is related to the rate of reaction. The precise definition of the rate of reaction is given in Box 9.2. For the following simple reaction²:



Box 9.2 Reaction rate and reaction velocity

The reaction rate is defined as the number of reactive events per second per unit volume. It is usually expressed as mol L⁻¹ s⁻¹. Chemical reactions depend on collisions. In most reactions, only a very small fraction of the collisions result in a chemical reaction. For each reacting species, since the number of collisions per unit volume is proportional to its concentration, the rates are proportional to the product of the concentrations. A **reaction rate** refers to conversion of the reactants to the products or vice versa. Thus, for the reaction



the **forward rate** $R_f = k_f[\text{Cl}][\text{H}_2]$ and the **reverse rate** $R_r = k_r[\text{HCl}][\text{H}]$, in which k_f and k_r are the rate constants. In a reaction, both forward and reverse reactions take place simultaneously. For thermodynamic considerations, we define the **velocity** of a reaction as the **rate of net conversion** of the reactants to products. Thus:

$$\text{Reaction velocity } v = \text{Forward rate} - \text{Reverse rate}$$

$$\begin{aligned} &= k_f[\text{Cl}][\text{H}_2] - k_r[\text{HCl}][\text{H}] \\ &= R_f - R_r \end{aligned}$$

In a homogeneous system, the reaction velocity v is given in terms of the extent of reaction:

$$v = \frac{d\xi}{V dt} = R_f - R_r$$

in which V is the volume of the system. In practice, monitoring the progress of a reaction by noting the change in some property (such as spectral absorption or refractive index) of the system generally amounts to monitoring the change in the extent of reaction ξ .

²For a detailed study of this reaction, see *Science*, **273** (1996), 1519.

the affinity A and the extent of reaction ξ are defined by

$$A = \mu_{\text{Cl}} + \mu_{\text{H}_2} - \mu_{\text{HCl}} - \mu_{\text{H}} \quad (9.2.3)$$

$$\frac{d\xi}{-1} = \frac{dN_{\text{Cl}}}{-1} = \frac{dN_{\text{H}_2}}{-1} = \frac{dN_{\text{HCl}}}{1} = \frac{dN_{\text{H}}}{1} \quad (9.2.4)$$

As explained in Box 9.2, the forward reaction rate is $k_f[\text{Cl}][\text{H}_2]$, in which the square brackets indicate concentrations and k_f is the forward rate constant, which depends on temperature. Similarly, the reverse reaction rate is $k_r[\text{HCl}][\text{H}]$. The time derivative of ξ is the *net rate of conversion* of reactants Cl and H₂ to the products HCl and H due to the forward and reverse reactions. Since the reaction rates are generally expressed as functions of concentrations, it is more convenient to define this net rate per unit volume. Accordingly, we define a **reaction velocity** v as

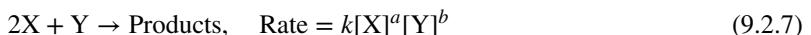
$$v = \frac{d\xi}{V dt} = k_f[\text{Cl}][\text{H}_2] - k_r[\text{HCl}][\text{H}] \quad (9.2.5)$$

Note that this equation follows from Equation (9.2.4) and the definition of the forward and reverse rates. For example, in a homogeneous system, the rate of change of the concentration of Cl is $d(N_{\text{Cl}}/V)/dt = -k_f[\text{Cl}][\text{H}_2] + k_r[\text{HCl}][\text{H}]$. More generally, if R_f and R_r are the forward and reverse reaction rates, we have

$$v = \frac{d\xi}{V dt} = R_f - R_r \quad (9.2.6)$$

The reaction velocity units are mol L⁻¹ s⁻¹.

In the above example, the rate of reaction bears a direct relation to the stoichiometry of the reactants, but this is not always true. In general, for a reaction such as



in which k is a temperature-dependent **rate constant** and the exponents a and b are not necessarily integers. The rate is said to be of *order a* in [X] and of *order b* in [Y]. The sum of all the orders of the reactants, $a + b$, is the **order of the reaction**. Reaction rates can take complex forms because they may be the result of many intermediate steps with widely differing rates that depend on the presence of catalysts. If all the intermediate steps are known, then each step is called an **elementary step**. Rates of elementary steps do bear a simple relation to the stoichiometry: the exponents equal the stoichiometric coefficients. If reaction (9.2.7) were an elementary step, for example, then its rate would be $k[\text{X}]^2[\text{Y}]$.

In many cases, the temperature dependence of the rate constant is given by the **Arrhenius equation**:

$$k = k_0 e^{-E_a/RT} \quad (9.2.8)$$

Svante Arrhenius (1859–1927) proposed it in 1889 and showed its validity for a large number of reactions [5,6]. The term k_0 is called the **pre-exponential factor** and E_a the **activation energy**. For the forward reaction of Equation (9.2.2), $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$, we have, for example, $k_0 = 7.9 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ and $E_a = 23 \text{ kJ mol}^{-1}$. When T varies over a wide range, the Arrhenius equation was found to be inaccurate in predicting the variation of the rate constant, though it is quite useful for many reactions.



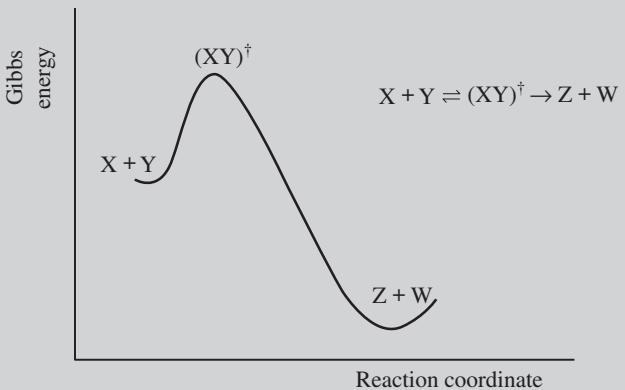
Svante August Arrhenius (1859–1927).

A more recent theory that is based on statistical mechanics and quantum theory was developed in the 1930s by Wigner, Pelzer, Eyring, Polanyi and Evans. According to this theory, the reaction occurs through a **transition state** (see Box 9.3). We shall discuss transition state theory in some detail later in this chapter. The concept of a transition state leads to the following expression for the rate constant:

$$k = \kappa \left(\frac{k_B T}{h} \right) e^{-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT} = \kappa \left(\frac{k_B T}{h} \right) e^{-\Delta G^\ddagger/RT} \quad (9.2.9)$$

in which $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant and h is Planck's constant. The terms ΔH^\ddagger and ΔS^\ddagger are the transition-state enthalpy and entropy respectively, as explained briefly in Box 9.3. The term κ is small, of the order of unity, which is characteristic of the reaction. A catalyst increases the rate of reaction by altering the transition state such that $(\Delta H^\ddagger - T\Delta S^\ddagger) = \Delta G^\ddagger$ decreases.

Box 9.3 Arrhenius equation and transition state theory



According to the Arrhenius equation, the rate constant of a chemical reaction is of the form

$$k = k_0 e^{-E_a/RT}$$

The rate constant k has this form because, for the reactants to convert to products, the collisions must have sufficient energy to overcome an energy barrier. As shown in the above figure, the transformation from the reactants to the products is schematically represented with a ‘reaction coordinate’ and the energy of the molecules undergoing the reaction.

According to the transition state theory, the reactants X and Y reversibly form a **transition state** $(XY)^{\ddagger}$. The transition state then irreversibly transforms to the products. The difference in the enthalpy and entropy between the free molecules X and Y and the transition state are denoted by ΔH^{\ddagger} and ΔS^{\ddagger} respectively. The main result of the transition state theory (which is obtained using principles of statistical mechanics and quantum mechanics) is that the rate constant is of the form

$$k = \kappa (k_B T / h) \exp[-(\Delta H^{\ddagger} - T \Delta S^{\ddagger}) / RT] = \kappa (k_B T / h) \exp[-\Delta G^{\ddagger} / RT]$$

in which $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant and $h = 6.626 \times 10^{-34} \text{ J s}$ is Planck’s constant; κ is a term of the order of unity that is characteristic of the reaction.

A catalyst increases the rate of reaction by altering the transition state such that $(\Delta H^{\ddagger} - T \Delta S^{\ddagger}) = \Delta G^{\ddagger}$ decreases.

9.2.1 Rate Equations Using the Extent of Reactions

Reaction rates are generally determined empirically. The mechanisms of reactions, which detail all the elementary steps, are usually a result of long and detailed study. Once the reaction rate laws are known, the time variation of the concentration can be obtained by integrating the rate equations, which are coupled differential equations. (Box 9.4 lists elementary first- and second-order reactions.) For example, if we have an elementary reaction of the form



then the concentrations are governed by the following differential equations:

$$-\frac{1}{V} \frac{d\xi}{dt} = \frac{d[X]}{dt} = -k_f[X] + k_r[Y]^2 \quad (9.2.11)$$

$$2 \frac{1}{V} \frac{d\xi}{dt} = \frac{d[Y]}{dt} = 2k_f[X] - 2k_r[Y]^2 \quad (9.2.12)$$

Box 9.4 Elementary reactions

To obtain an explicit analytic expression for the concentrations of the reactants and products as a function of time, we must solve differential equations such as (9.2.11) and (9.2.12). Generally, this is possible only in the case of simple reactions. For more complex reactions, one can obtain numerical solutions using a computer. Two elementary reactions for which we can obtain explicit expressions for the concentrations as functions of time are given below.

First-order reaction. For a decomposition reaction $X \rightarrow \text{Products}$, in which the reverse reaction rate is so small that it can be neglected, we have the differential equation

$$\frac{d[X]}{dt} = -k_f[X]$$

It is easy to see that solution of this equation is

$$[X](t) = [X]_0 e^{-k_f t}$$

in which $[X]_0$ is the concentration at time $t = 0$. This is the well-known exponential decay; in a given amount of time, $[X]$ decreases by the same fraction. In particular, the time it takes for any initial value of $[X]$ to decrease by a factor of 1/2 is the **half-life**. It is usually denoted by $t_{1/2}$. The half-life can be computed by noting that $\exp(-k_f t_{1/2}) = 1/2$, i.e.

$$t_{1/2} = \frac{\ln(2)}{k_f} = \frac{0.6931}{k_f}$$

Second-order reaction. For the elementary reaction $2X \rightarrow \text{Products}$, if the reverse reaction can be neglected, the rate equation is

$$\frac{d[X]}{dt} = -2k_f[X]^2$$

The solution is obtained by evaluating

$$\int_{[X]_0}^{[X]} \frac{d[X]}{[X]^2} = - \int_0^t 2k_f dt$$

which gives us

$$\frac{1}{[X]} - \frac{1}{[X]_0} = 2k_f t$$

Given $[X]_0$ at $t = 0$ and k_f , this expression gives us the value $[X]$ at any time t .

Without loss of generality, we may assume $V = 1$ and simplify the notation. These two equations are not independent. *In fact, there is only one independent variable ξ for every independent reaction.* If $[X]_0$ and $[Y]_0$ are the values of the concentrations at $t = 0$, then by assigning $\xi(0) = 0$ and using $d\xi = -d[X]$ and $2d\xi = d[Y]$ it is easy to see that $[X] = [X]_0 - \xi$ and $[Y] = [Y]_0 + 2\xi$. Substituting these values into Equation (9.2.1) we obtain

$$\frac{d\xi}{dt} = k_f([X]_0 - \xi) - k_r([Y]_0 + 2\xi)^2 \quad (9.2.13)$$

In this equation, the initial concentrations $[X]_0$ and $[Y]_0$ appear explicitly and $\xi(0) = 0$ for all initial concentrations. The solution $\xi(t)$ of such an equation can be used to obtain the rate of entropy production, as will be shown explicitly in Section 9.5. Differential equations such as these, and more complicated system of equations, can be solved numerically on a computer, e.g. using software such as *Mathematica* or *Maple* (sample programs are provided in Appendix 9.1). Furthermore, in describing reactions involving solid phases, concentration cannot be used to describe the change in the amount of a solid phase; the extent of reaction ξ , which represents the change in the total amounts of a reactant or product, is a convenient variable for this purpose.

When many reactions are to be considered simultaneously, we will have one ξ for each independent reaction, denoted by ξ_k , and the entire system will be described by a set of coupled differential equations in ξ_k . Only in a few cases can we find analytical solutions to such equations, but they can be readily solved numerically using *Mathematica*, *Maple* or other software that is designed specifically for solving rate equations.

9.2.2 Reaction Rates and Activities

Though reaction rates are generally expressed in terms of concentrations, one could equally well express them in terms of activities. In fact, we shall see in the following sections that the connection between affinities and reaction rates can be made more easily if the reaction rates are expressed in terms of activities. For example, for the elementary reaction



the forward rate R_f and the reverse rate R_r may be written as

$$R_f = k_f a_X a_Y \quad \text{and} \quad R_r = k_r a_W^2 \quad (9.2.15)$$

The rate constants k_f and k_r in Equation (9.2.15) will have units of $\text{mol L}^{-1} \text{ s}^{-1}$; their numerical values and units differ from those of the rate constants when R_f and R_r are expressed in terms of concentrations (Exercise 9.11).

Experimentally, we know that reaction rates do depend on the activities; they are not specified by concentrations alone. For example, at fixed values of temperature and concentrations of the reactants, it is well known that the rates of ionic reactions can be altered by changing the ionic strength of the solution (usually known as the ‘salt effect’). This change in the rate is due to a change in the activities. It has become general practice, however, to express the reaction rates in terms of the concentrations and to include the effects of changing activities in the rate constants. Thus, the rate constants are considered functions of the ionic strength when rates are expressed in terms of concentrations. Alternatively, if the rates are expressed in terms of activities, then the rate constant is independent of the ionic strength; a change in rate due to a change in ionic strength would be because activity depends on ionic strength.

9.3 Chemical Equilibrium and the Law of Mass Action

In this section we shall study chemical equilibrium in detail. At equilibrium, the pressure and temperature of all components and phases are equal; the affinities and the corresponding reaction velocities vanish. For example, for a reaction such as



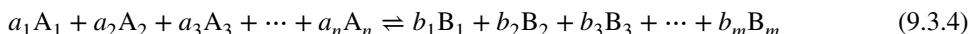
at equilibrium we have

$$A = \mu_{\text{X}} + \mu_{\text{Y}} - 2\mu_{\text{Z}} = 0 \quad \text{and} \quad \frac{d\xi}{dt} = 0 \quad (9.3.2)$$

or

$$\mu_{\text{X}} + \mu_{\text{Y}} = 2\mu_{\text{Z}} \quad (9.3.3)$$

The condition that the ‘thermodynamic force’, affinity A , equals zero implies that the corresponding ‘thermodynamic flow’, i.e. the reaction velocity $d\xi/dt$, also equals zero. The condition $A = 0$ means that at equilibrium the ‘stoichiometric sum’ of the chemical potentials of the reactants and products are equal, as in Equation (9.3.3). This result can be generalized to an arbitrary chemical reaction of the form



in which the a_k are the stoichiometric coefficients of the reactants A_k and the b_k are the stoichiometric coefficients of the products B_k . The corresponding condition for chemical equilibrium will then be

$$a_1\mu_{\text{A}_1} + a_2\mu_{\text{A}_2} + a_3\mu_{\text{A}_3} + \cdots + a_n\mu_{\text{A}_n} = b_1\mu_{\text{B}_1} + b_2\mu_{\text{B}_2} + b_3\mu_{\text{B}_3} + \cdots + b_m\mu_{\text{B}_m} \quad (9.3.5)$$

Such equalities of chemical potentials are valid for all reactions: changes of phase, and chemical, nuclear and elementary particle reactions. Just as a difference in temperature drives the flow of heat until the temperatures difference vanishes, a nonzero affinity drives a chemical reaction until the affinity vanishes.

To understand the physical meaning of the mathematical conditions such as Equation (9.3.3) or (9.3.5), we express the chemical potential in terms of experimentally measurable quantities. We have seen in Section 5.3 (Equation (5.3.5)) that the chemical potential in general can be expressed as

$$\mu_k(p, T) = \mu_k^0(T) + RT \ln a_k \quad (9.3.6)$$

in which a_k is the activity and $\mu_k^0(T_0) = \Delta G_f^0[k, T]$ is the standard molar Gibbs energy of formation (Box 5.1), the value of which may be found in data tables. This being a general expression, for gases, liquids and solids we have the following explicit expressions:

- *Ideal gas*: $a_k = p_k/p_0$, where p_k is the partial pressure.
- *Real gases*: expressions for activity can be derived using Equation (6.2.30), as was shown in Section 6.2.
- *Pure solids and liquids*: $a_k \approx 1$.
- *Solutions*: $a_k \approx \gamma_k x_k$, where γ_k is the activity coefficient and x_k is the mole fraction.

For ideal solutions, $\gamma_k = 1$. For nonideal solutions, γ_k is obtained by various means, depending on the type of solution. The chemical potential can also be written in terms of the concentrations by appropriately redefining μ_k^0 .

We can now use Equation (9.3.6) to express the condition for equilibrium (9.3.3) in terms of the activities, which are experimentally measurable quantities:

$$\mu_X^0(T) + RT \ln(a_{X,\text{eq}}) + \mu_Y^0(T) + RT \ln(a_{Y,\text{eq}}) = 2[\mu_Z^0(T) + RT \ln(a_{Z,\text{eq}})] \quad (9.3.7)$$

where the equilibrium values of the activities are indicated by the subscript ‘eq’.

This equation can be rewritten as

$$\boxed{\frac{a_{Z,\text{eq}}^2}{a_{X,\text{eq}} a_{Y,\text{eq}}} = \exp \left[\frac{\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)}{RT} \right] \equiv K(T)} \quad (9.3.8)$$

$K(T)$, as defined above, is called the **equilibrium constant**. It is a function only of temperature. That the equilibrium constant as defined above is a function of T only is an important thermodynamic result. It is called the **law of mass action**. $\mu_k^0(T) = \Delta G_f^0[k, T]$ is the standard molar Gibbs energies of formation of compound k at a temperature T . The ‘Standard Thermodynamic Properties’ table at the end of the book lists this quantity at $T = 298.15$ K. It is convenient and conventional to define the **Gibbs energy of reaction** ΔG_r as

$$\begin{aligned} \Delta G_r^0(T) &= -[\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)] \\ &= 2\Delta G_f^0[Z, T] - \Delta G_f^0[X, T] - \Delta G_f^0[Y, T] \end{aligned} \quad (9.3.9)$$

The equilibrium constant is then written as

$$\begin{aligned} K(T) &= \exp(-\Delta G_r^0/RT) \\ &= \exp[-(\Delta H_r^0 - T\Delta S_r^0)/RT] \end{aligned} \quad (9.3.10)$$

in which ΔG_r^0 , ΔH_r^0 and ΔS_r^0 are respectively the standard Gibbs energy, enthalpy and entropy of the reaction at temperature T , though their temperature dependence is usually not explicitly indicated. The activities in Equation (9.3.8) can be written in terms of partial pressures p_k or mole fractions x_k . If reaction (9.3.1) were an ideal-gas reaction, then $a_k = p_k/p_0$. With $p_0 = 1$ bar and p_k measured in bars, the equilibrium constant takes the form

$$\frac{p_{Z,\text{eq}}^2}{p_{X,\text{eq}} p_{Y,\text{eq}}} = K_p(T) = \exp(-\Delta G_r^0/RT) \quad (9.3.11)$$

At a given temperature, regardless of the initial partial pressures, the chemical reaction (9.3.1) will irreversibly evolve towards the state of equilibrium in which the partial pressures will satisfy Equation (9.3.11). This is one form of the *law of mass action*. K_p is the *equilibrium constant* expressed in terms of the partial pressures. Since in an ideal gas mixture $p_k = (N_k/V)RT = [k]RT$ (in which R is in units of bar L mol⁻¹ K⁻¹), the law of mass action can also be expressed in terms of the concentrations of the reactants and products:

$$\frac{[Z]_{\text{eq}}^2}{[X]_{\text{eq}} [Y]_{\text{eq}}} = K_c(T) \quad (9.3.12)$$

in which K_c is the equilibrium constant expressed in terms of the concentrations. In general, for a reaction of the form, $aX + bY \rightleftharpoons cZ$ it is easy to obtain the relation $K_c = (RT)^\alpha K_p$, where $\alpha = a + b - c$ (Exercise 9.14). In the particular case of reaction (9.3.1) α happens to be zero.

If one of the reactants were a pure liquid or a solid, then the equilibrium constant will not contain corresponding ‘concentration’ terms. For example, let us consider the reaction



Since $a_{C(s)} \approx 1$ for the solid phase, the equilibrium constant in this case is written as

$$\frac{a_{CO,eq}^2}{a_{O_2,eq} a_{C,eq}^2} = \frac{p_{CO,eq}^2}{p_{O_2,eq}} = K_p(T) \quad (9.3.14)$$

Equations (9.3.9) and (9.3.10) provide us with the means of calculating the equilibrium constant $K(T)$ using the tabulated values of $\Delta G_f^0[k]$. If the activities are expressed in terms of partial pressures, then we have K_p . Some examples are shown in Box 9.5.

Box 9.5 The equilibrium constant

A basic result of equilibrium chemical thermodynamics is that the equilibrium constant $K(T)$ is a function of only temperature. It can be expressed in terms of the standard Gibbs energy of reaction ΔG_r^0 (Equations (9.3.9) and (9.3.10)):

$$K(T) = \exp[-\Delta G_r^0/RT]$$

For a reaction such as $O_2(g) + 2C(s) \rightleftharpoons 2CO(g)$ the equilibrium constant at 298.15 K can be calculated using the tabulated values of standard Gibbs energy of formation ΔG_f^0 at $T = 298.15$ K:

$$\begin{aligned} \Delta G_r^0 &= 2\Delta G_f^0[CO] - 2\Delta G_f^0[C] - \Delta G_f^0[O_2] \\ &= -2(137.2) \text{ kJ mol}^{-1} - 2(0) - (0) = -274.4 \text{ kJ mol}^{-1} \end{aligned}$$

Using this value in the expression $K(T) = \exp[-\Delta G_r^0/RT]$ we can calculate $K(T)$ at $T = 298.15$:

$$K(T) = \exp[-\Delta G_r^0/RT] = \exp[274.4 \times 10^3 / (8.314 \times 298.15)] = 1.18 \times 10^{48}$$

Similarly, for the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, at $T = 298.15$ K,

$$\begin{aligned} \Delta G_r^0 &= \Delta G_f^0[CH_3OH] - \Delta G_f^0[CO] - 2\Delta G_f^0[H_2] \\ &= -161.96 \text{ kJ mol}^{-1} - (-137.2 \text{ kJ mol}^{-1}) - 2(0) = -24.76 \text{ kJ mol}^{-1} \end{aligned}$$

The equilibrium constant is

$$K(T) = \exp[-\Delta G_r^0/RT] = \exp[24.76 \times 10^3 / (8.314 \times 298.15)] = 2.18 \times 10^4.$$

9.3.1 Relation between the Equilibrium Constants and the Rate Constants

Chemical equilibrium can also be described as a state in which the forward rate of every reaction equals its reverse rate. If the reaction $X + Y \rightleftharpoons 2Z$ is an elementary step, and if we express the reaction rates in terms of the activities, then when the velocity of the reaction is zero we have

$$k_f a_X a_Y = k_r a_Z^2 \quad (9.3.15)$$

From a theoretical viewpoint, writing the reaction rates in terms of activities rather than concentrations is better because the state of equilibrium is directly related to activities, not concentrations.

Comparing Equation (9.3.15) and the equilibrium constant (9.3.8), we see that

$$K(T) = \frac{a_Z^2}{a_X a_Y} = \frac{k_f}{k_r} \quad (9.3.16)$$

Thus, the equilibrium constant can also be related to the rate constants k_r and k_f when the rates are expressed in terms of the activities. It must be emphasized that Equation (9.3.8) is valid even if the forward and reverse rates do not have the form shown in Equation (9.3.15); in other words, Equation (9.3.8) is valid whether the reaction $X + Y \rightleftharpoons 2Z$ is an elementary reaction step or not. *The relation between the activities and the equilibrium constant is entirely a consequence of the laws of thermodynamics; it is independent of the kinetic rates of the forward and reverse reactions.*

9.3.2 The van't Hoff Equation

Using Equation (9.3.10), the temperature variation of the equilibrium constant $K(T)$ can be related to the enthalpy of reaction ΔH_r . From Equation (9.3.10) it follows that

$$\frac{d \ln K(T)}{dT} = -\frac{d}{dT} \frac{\Delta G_r}{RT} \quad (9.3.17)$$

However, according to the Gibbs–Helmholtz equation (5.2.14), the variation of ΔG with temperature is related to ΔH by $[\partial(\Delta G/T)/\partial T] = -\Delta H/T^2$. Using this in the above equation we have

$$\frac{d \ln K(T)}{dT} = \frac{\Delta H_r}{RT^2}$$

(9.3.18)

This relation enables us to deduce how the equilibrium constant $K(T)$ depends on the temperature. It is called the **van't Hoff equation**. In many situations of interest, the heat of reaction ΔH_r changes very little with temperature and may be assumed to be a constant equal to the standard enthalpy of reaction at 298.15 K, which we denote by ΔH_r^0 . Thus, we may integrate Equation (9.3.18) and obtain

$$\ln K(T) = \frac{-\Delta H_r^0}{RT} + C \quad (9.3.19)$$

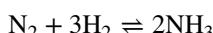
Experimentally, $K(T)$ can be obtained at various temperatures. According to Equation (9.3.19), a plot of $\ln K(T)$ versus $1/T$ should result in a straight line with a slope equal to $-\Delta H_r^0/R$. This method can be used to obtain the values of ΔH_r^0 .

9.3.3 Response to Perturbation from Equilibrium: The Le Chatelier–Braun Principle

When a system is perturbed from its state of equilibrium, it will relax to a new state of equilibrium. Le Chatelier and Braun noted in 1888 that a simple principle may be used to predict the direction of the response to a perturbation from equilibrium. Le Chatelier stated this principle thus:

Any system in chemical equilibrium undergoes, as a result of a variation in one of the factors governing the equilibrium, a compensating change in a direction such that, had this change occurred alone it would have produced a variation of the factors considered in the *opposite* direction.

To illustrate this principle, let us consider the reaction



in equilibrium. In this reaction, the total molar amount of all components decreases when the reactants convert to products. If the pressure of this system is suddenly increased, then the system's response will be the production of more NH_3 , which decreases the total molar amount and thus the pressure. The compensating change in the system is in a direction *opposite* to that of the perturbation. The new state of equilibrium will

contain more NH₃. Similarly, if a reaction is exothermic, if heat is supplied to the system, then the product will be converted to reactants, which has the effect of opposing the increase in temperature. Though this principle has its usefulness, it does not always give unambiguous results. For this reason, a more general approach under the name ‘theorems of moderation’ has been developed [7]. This approach provides a very precise and accurate description of the response of a system in equilibrium to a perturbation from this state, which is always the evolution to another state of equilibrium.

Le Chatelier’s principle only describes the response of a system in thermodynamic equilibrium; it says nothing about the response of a system that is maintained in a nonequilibrium state. Indeed, the response of a nonequilibrium system to small changes in temperature could be extraordinarily complex. This is obviously evident in living organisms, which are nonequilibrium systems. In the case of alligators, for example, the sex of an offspring depends on the incubation temperature of the eggs [8]: temperatures below 30 °C produce all females, while temperatures above 34 °C produce all males.

9.4 The Principle of Detailed Balance

There is an important aspect of the state of chemical equilibrium, and the state of thermodynamic equilibrium in general, that must be noted, namely the **principle of detailed balance**.

We observed earlier that, for a given reaction, the state of equilibrium depends only on the stoichiometry of the reaction, not its actual mechanism. For example, in the reaction X + Y ⇌ 2Z considered above, if the forward and reverse reaction rates were given by

$$R_f = k_f a_X a_Y \quad \text{and} \quad R_r = k_r a_Z^2 \quad (9.4.1)$$

respectively, then the result that $a_Z^2/a_X a_Y = K(T)$ is at equilibrium can be interpreted as the balance between forward and reverse reactions:

$$R_f = k_f a_X a_Y = R_r = k_r a_Z^2$$

so that

$$\frac{a_Z^2}{a_X a_Y} = K(T) = \frac{k_f}{k_r} \quad (9.4.2)$$

However, the equilibrium relation $a_Z^2/a_X a_Y = K(T)$ was not obtained using any assumption regarding the kinetic mechanism of the reaction. It remains valid even if there was a complex set of intermediate reactions that result in the overall reaction X + Y ⇌ 2Z. This feature could be understood through the **principle of detailed balance**, according to which:

In the state of equilibrium, every transformation is balanced by its exact opposite or reverse.

That the principle of detailed balance implies that $a_Z^2/a_X a_Y = K(T)$ regardless of the mechanism can be seen through the following example. Assume that the reaction really consists of two steps:



which results in the net reaction $X + Y \rightleftharpoons 2Z$. According to the principle of detailed balance, at equilibrium we must have

$$\frac{a_W}{a_X^2} = \frac{k_{fa}}{k_{ra}} \equiv K_a, \quad \frac{a_Z^2 a_X}{a_W a_Y} = \frac{k_{fb}}{k_{rb}} \equiv K_b \quad (9.4.5)$$

in which the subscripts a and b stand for reactions (9.4.3) and (9.4.4) respectively. The thermodynamic equation for equilibrium $a_Z^2/a_X a_Y = K(T)$ can now be obtained as the product of K_a and K_b :

$$K_a K_b = \frac{a_W a_Z^2 a_X}{a_X^2 a_W a_Y} = \frac{a_Z^2}{a_X a_Y} = K \quad (9.4.6)$$

From this derivation it is clear that this result will be valid for an arbitrary set of intermediate reactions.

The principle of detailed balance is a very general principle, valid for all transformations. It is in fact valid for the exchange of matter and energy between any two volume elements of a system in equilibrium. The amount of matter and energy transferred from volume element X to volume element Y exactly balances the energy and matter transferred from volume element Y to volume element X (see Figure 9.1). The same can be said of the interaction between the volume elements Y and Z and X and Z. One important consequence of this type of balance is that the removal or isolation of one of the volume elements from the system, say Z, does not alter the states of X or Y or the interaction between them. This is another way of saying that there is no long-range correlation between the various volume elements. As we shall see in later chapters, the principle of detailed balance is not valid in nonequilibrium systems that make a transition to organized dissipative structures. Consequently, the removal or isolation of a volume element at one part will alter the

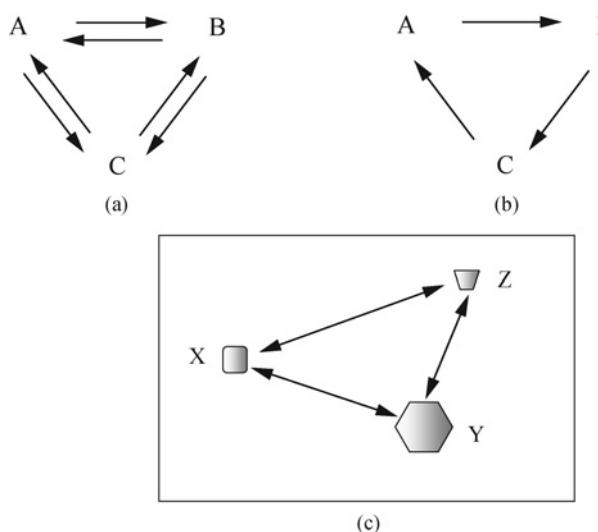


Figure 9.1 The principle of detailed balance. (a) The equilibrium between three interconverting compounds A, B and C is a result of ‘detailed balance’ between each pair of compounds. (b) Though a cyclic conversion from one compound to another as shown can also result in concentrations that remain constant in time, such a state is not the equilibrium state. (c) The principle of detailed balance has a more general validity. The exchange of matter (or energy) between any two regions of a system is balanced in detail; the amount of matter going from X to Y is balanced by exactly the reverse process.

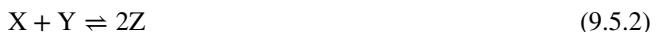
state of a volume element located elsewhere. It is then said to have long-range correlations. We can see this clearly if we compare a droplet of water that contains carbon compounds in thermal equilibrium and a living cell that is in an organized state far from thermodynamic equilibrium. Removal of a small part of the water droplet does not change the state of other parts of the droplet, whereas removing a small part of a living cell is likely to have a drastic influence on other parts of the cell.

9.5 Entropy Production due to Chemical Reactions

The formalism of the previous sections can now be used to relate entropy production to reaction rates more explicitly. In Chapter 4 we saw that the entropy production rate due to a chemical reaction is given by

$$\frac{d_i S}{dt} = \frac{A}{T} \frac{d\xi}{dt} \geq 0 \quad (9.5.1)$$

Our objective is to relate the affinity A and $d\xi/dt$ to the reaction rates, so that the entropy production is written in terms of the reaction rates. In order to do this, let us consider the reaction that we have considered before:



Assuming that this is an elementary step, we have for the forward and reverse rates

$$R_f = k_f a_X a_Y \quad \text{and} \quad R_r = k_r a_Z^2 \quad (9.5.3)$$

Since the forward and reverse rates must be equal at equilibrium, we have seen from Equation (9.4.2) that

$$K(T) = \frac{k_f}{k_r} \quad (9.5.4)$$

The velocity of reaction v , which is simply the difference between the forward and reverse reaction rates, is related to $d\xi/dt$ as shown in Equation (9.2.6). The reaction rates R_f and R_r can themselves be expressed as functions of the extent of reaction ξ , as was shown in Section 9.2:

$$\frac{1}{V} \frac{d\xi}{dt} = [R_f(\xi) - R_r(\xi)] \quad (9.5.5)$$

To obtain the velocity of reaction as a function of time, this differential equation has to be solved. An example is presented below.

Turning now to the affinity A , we can relate it to the reaction rates in the following manner. By definition, the affinity of the reaction (9.5.2) is

$$\begin{aligned} A &= \mu_X + \mu_Y - 2\mu_Z \\ &= \mu_X^0(T) + RT \ln(a_X) + \mu_Y^0(T) + RT \ln(a_Y) - 2[\mu_Z^0(T) + RT \ln(a_Z)] \\ &= [\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)] + RT \ln(a_X) + RT \ln(a_Y) - 2RT \ln(a_Z) \end{aligned} \quad (9.5.6)$$

Since $[\mu_X^0(T) + \mu_Y^0(T) - 2\mu_Z^0(T)] = -\Delta G_r^0 = RT \ln K(T)$, the above equation can be written as

$$A = RT \ln K(T) + RT \ln \left(\frac{a_X a_Y}{a_Z^2} \right) \quad (9.5.7)$$

This is an alternative way of writing the affinity. At equilibrium, $A = 0$. To relate A to the reaction rates, we use Equation (9.5.4) and combine the two logarithm terms:

$$A = RT \ln \left(\frac{k_f}{k_r} \right) + RT \ln \left(\frac{a_X a_Y}{a_Z^2} \right) = RT \ln \left(\frac{k_f a_X a_Y}{k_r a_Z^2} \right) \quad (9.5.8)$$

This leads us to the relations we are seeking if we use the expressions in (9.5.3) to write this expression in terms of the reaction rates:

$$A = RT \ln \left(\frac{R_f}{R_r} \right) \quad (9.5.9)$$

Clearly, this equation is valid for any elementary step because the rates of elementary steps are directly related to the stoichiometry. Now we can substitute Equations (9.5.5) and (9.5.9) in the expression for the entropy production rate (Equation (9.5.1)) and obtain

$$\frac{1}{V} \frac{d_i S}{dt} = \frac{1}{V} \frac{A}{T} \frac{d\xi}{dt} = R(R_f - R_r) \ln(R_f/R_r) \geq 0 \quad (9.5.10)$$

which is an expression that relates *entropy production rate per unit volume* to the reaction rates. (Note that R is the gas constant.) Also, as required by the Second Law, the right-hand side of this equation is positive, whether $R_f > R_r$ or $R_f < R_r$. Another point to note is that in Equation (9.5.10) the forward and reverse rates R_f and R_r can be expressed in terms of concentrations, partial pressures of the reactants or other convenient variables; the reaction rates need not be expressed only in terms of activities, as in Equation (9.5.3).

The above equation can be generalized to several simultaneous reactions, each indexed by the subscript k . The rate of total entropy production per unit volume is the sum of the rates at which entropy is produced in each reaction:

$$\frac{1}{V} \frac{d_i S}{dt} = \frac{1}{V} \sum_k \frac{A_k}{T} \frac{d\xi_k}{dt} = R \sum_k (R_{kf} - R_{kr}) \ln(R_{kf}/R_{kr}) \quad (9.5.11)$$

in which R_{kf} and R_{kr} are the forward and reverse reaction rates of the k th reaction. This expression is useful for computing the entropy production rate in terms of the reaction rates, but *it is valid only for elementary steps whose reaction rates are specified by the stoichiometry*. This is not a serious limitation, however, because every reaction is ultimately the result of many elementary steps. If the detailed mechanism of a reaction is known, then an expression for the entropy production rate can be written for any chemical reaction.

9.5.1 An Example

As an example of entropy production due to an irreversible chemical reaction, consider the simple reaction:



which is the interconversion or ‘racemization’ of molecules with mirror-image structures. Molecules that are not identical to their mirror image are said to be *chiral* and the two mirror-image forms are called *enantiomers*.

Let $[L]$ and $[D]$ be the concentrations of the enantiomers of a chiral molecule. If at time $t = 0$ the concentrations are $[L] = L_0$ and $[D] = D_0$, and $\xi(0) = 0$, then we have the following relations:

$$\frac{d[L]}{-1} = \frac{d[D]}{+1} = \frac{d\xi}{V} \quad (9.5.13)$$

$$[L] = L_0 - (\xi/V), \quad [D] = D_0 + (\xi/V) \quad (9.5.14)$$

Relations (9.5.14) are obtained by integrating (9.5.13) and using the initial conditions. For notational convenience we shall assume $V = 1$. At the end of the calculation we can reintroduce the V factor. Racemization can be an elementary first-order reaction for which the forward and reverse reactions are

$$R_f = k[L] = k(L_0 - \xi), \quad R_r = k[D] = k(D_0 + \xi) \quad (9.5.15)$$

Note that the rate constants for the forward and reverse reactions are the same due to symmetry: L must convert to D with the same rate constant as D to L . Also, from Equations (9.5.15) and (9.5.9) one can see that the affinity is a function of the state variable ξ for a given set of initial concentrations.

To obtain the entropy production as an explicit function of time, we must obtain R_f and R_r as functions of time. This can be done by solving the differential equation defining the velocity of this reaction:

$$\frac{d\xi}{dt} = R_f - R_r = k(L_0 - \xi) - k(D_0 + \xi)$$

i.e.

$$\frac{d\xi}{dt} = 2k \left(\frac{L_0 - D_0}{2} - \xi \right) \quad (9.5.16)$$

This first-order differential equation can be easily solved by defining $x = [(L_0 - D_0)/2] - \xi$ so that the equation reduces to $dx/dt = -2kx$. The solution is

$$\xi(t) = \frac{L_0 - D_0}{2} (1 - e^{-2kt}) \quad (9.5.17)$$

With this expression for $\xi(t)$, the rates in Equation (9.5.15) can be written as explicit functions of time:

$$R_f = \frac{k(L_0 + D_0)}{2} + \frac{k(L_0 - D_0)}{2} e^{-2kt} \quad (9.5.18)$$

$$R_r = \frac{k(L_0 + D_0)}{2} - \frac{k(L_0 - D_0)}{2} e^{-2kt} \quad (9.5.19)$$

With Equations (9.5.18) and (9.5.19), we can now also write the rate of entropy production (9.5.10) as an explicit function of time:

$$\begin{aligned} \frac{1}{V} \frac{d_i S}{dt} &= R(R_f - R_r) \ln(R_f/R_r) \\ \frac{1}{V} \frac{d_i S}{dt} &= R[k(L_0 - D_0)e^{-2kt}] \ln \left[\frac{(L_0 + D_0) + (L_0 - D_0)e^{-2kt}}{(L_0 + D_0) - (L_0 - D_0)e^{-2kt}} \right] \end{aligned} \quad (9.5.20)$$

As $t \rightarrow \infty$, the system reaches equilibrium, at which

$$\xi_{eq} = \frac{L_0 - D_0}{2} \quad \text{and} \quad [L]_{eq} = [D]_{eq} = \frac{L_0 + D_0}{2} \quad (9.5.21)$$

The volume term can be reintroduced by replacing ξ_{eq} by ξ_{eq}/V .

In Chapter 5 (see Equation (5.1.12)) we noted the relation between affinity A and the Gibbs energy G : $A = -(\partial G / \partial \xi)_{p,T}$. Both A and G are functions of state, which can be expressed as functions of ξ and the initial

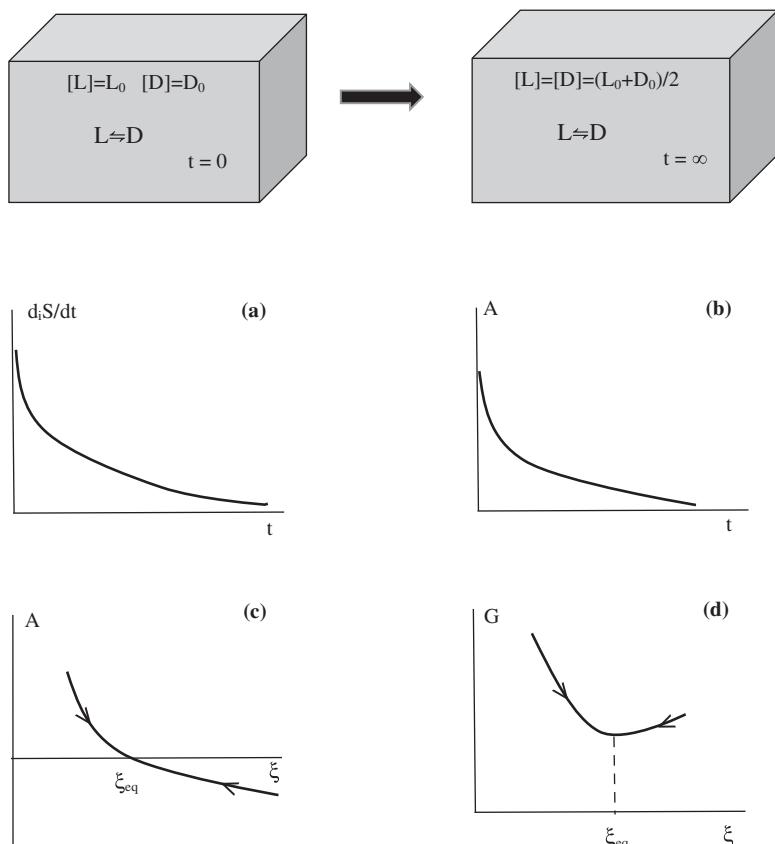


Figure 9.2 Racemization of enantiomers as an example of a chemical reaction. The associated entropy production, the time variations of A , are shown in (a) and (b). State functions A and G as functions of ξ are shown in (c) and (d).

molar amounts of reactants and products. As ξ approaches its equilibrium value ξ_{eq} , the Gibbs energy reaches its minimum value and the affinity A goes to zero, as shown in Figure 9.2.

The entropy production for more complex reactions can be obtained numerically using computers. *Mathematica* codes for the above example are given in Appendix 9.1. The student is encouraged to expand these codes for more complex reactions.

9.6 Elementary Theory of Chemical Reaction Rates

The rates of chemical reactions depend on several factors. In previous sections we discussed the dependence of rates on concentrations and introduced the Arrhenius and transition-state rate constants. According to the Arrhenius theory, the rate constant has the form $k_0 \exp(-E_a/RT)$, whereas transition-state theory gives a rate constant of the form $k_0 \exp(-\Delta G^\ddagger/RT)$. In this section we will introduce the reader to the theoretical basis that leads to these expressions.

9.6.1 The Arrhenius Theory of Rates

When the molecular nature of compounds became established, theories of rates of chemical reactions began to emerge. That molecules were in incessant and rapid chaotic motion was established by the kinetic theory of gases. A natural consequence was a view that chemical reactions were a consequence of molecular collisions. When molecules collide, somehow an atomic rearrangement occurs and the products are formed. However, not every collision between reacting molecules results in the formation of products. In fact, quantitative estimates indicated that only a very small fraction of the collisions were ‘reactive collisions’. This naturally raised the question as to why only certain collisions between reactant molecules resulted in the formation of products.

One of the first successful theories of reaction rates is due to the Swedish chemist Svante Arrhenius (1859–1927), but it is noted that others, especially van’t Hoff, also made important contributions to this theory [5, 6]. The success of the Arrhenius theory is mainly in explaining the temperature dependence of reaction rates. To explain why only a small fraction of molecular collisions resulted in reactions, the concept of ‘activation energy’ was introduced. This is the idea that the colliding molecules must have sufficient energy to activate the reaction, i.e. the breaking of bonds and formation of new bonds. That only a small fraction of molecules have the required activation energy was proposed by the German chemist L. Pfundler. To compute the probability that the collision has the required activation energy, the Boltzmann principle is taken as a guide. We recall that, according to the Maxwell–Boltzmann probability distribution, the probability that a molecule has energy E is proportional to $\exp(-E/RT)$. Using this principle, it could be argued that if a certain activation energy E_a is required in a collision between reacting molecules to generate the product, this will happen with a probability proportional to $\exp(-E_a/RT)$. Thus, the reaction rate must be proportional to a factor $\exp(-E_a/RT)$; that is, of all the collisions that occur in a unit volume in unit time, a fraction $k_0 \exp(-E_a/RT)$ will be reactive collisions. Thus, the Arrhenius rate constant

$$k = k_0 e^{-E_a/RT}$$

where k_0 is called the **pre-exponential factor**.

The next step is to compute the number of collisions that occur in unit time in a unit volume. For gases, this can be done using the Maxwell–Boltzmann distribution (Section 1.6). Let us consider the reaction $A + B \rightarrow \text{Products}$. Let r_A and r_B be the radii of the A and B molecules respectively. For small molecules, radii can be estimated from tabulated bond lengths. Figure 9.3 shows the path of a molecule of A as it undergoes collisions with molecules in its path. An observer located on the molecule A will observe a stream of molecules; collisions with molecules of B occur when the distance between the center of A and the center of a streaming B is equal to or less than the sum $r_A + r_B$. Consider a cylinder of radius $r_A + r_B$ with the path of the molecule A as its axis. Molecule A will collide with all B molecules in such a cylinder. From the viewpoint of an observer on A, molecules will be streaming at an average speed v_r , which is equal to the average relative velocity between A and B molecules. Thus, in unit time, on the average, a molecule of A will collide with all B molecules in the volume $\pi(r_A + r_B)^2 v_r$. The term $\pi(r_A + r_B)^2$ is called the **collision cross-section**. If n_B is the moles of B molecules per unit volume, then a single A molecule will collide with $\pi(r_A + r_B)^2 v_r n_B N_A$ molecules of B per unit time. Thus, the average total number of collisions between A and B molecules per unit volume per unit time, called the **collision frequency** z_{AB} , equals

$$z_{AB} = \pi(r_A + r_B)^2 v_r n_B N_A N_A^2 \quad (9.6.1)$$

in which n_A is the moles of A molecules per unit volume. Using the Maxwell–Boltzmann distribution it can be shown that the average relative velocity between A and B molecules is given by

$$v_r = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \quad \text{in which} \quad \mu = \frac{m_A m_B}{m_A + m_B} \quad (9.6.2)$$

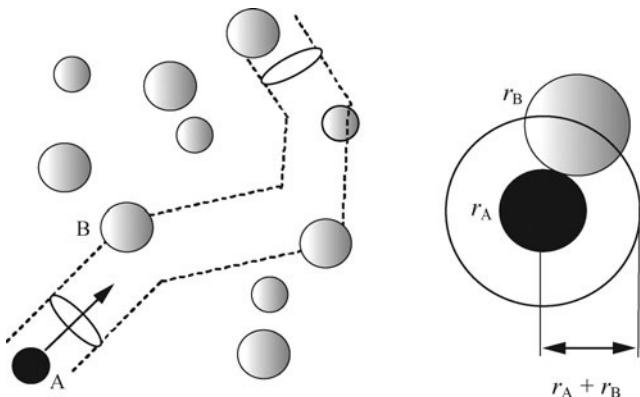


Figure 9.3 The elementary bimolecular reaction $A + B \rightarrow \text{Products}$ is a result of collisions between the molecules of A and B. Approximating the molecule's shape to be spherical, we assume the radii of molecules of A and B are r_A and r_B respectively. As shown, on average, in unit time, a molecule of A (filled sphere) will collide with all molecules in the cylinder of cross-section $\pi(r_A + r_B)^2$ and length v_r .

where m_A and m_B are the masses of molecules A and B respectively. The factor μ is called the **reduced mass**. Of all the collisions, only a fraction $\exp(-E_a/RT)$ are reactive collisions that result in the formation of products. Hence, the reaction rate (number of reactive collisions per unit time per unit volume) equals

$$\begin{aligned} \text{Rate} &= z_{AB} \exp(-E_a/RT) \\ &= N_A^2 \pi (r_A + r_B)^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} n_B n_A \exp(-E_a/RT) \end{aligned} \quad (9.6.3)$$

To specify the rate in moles per unit volume per unit time, we divide the above expression by N_A :

$$\text{Rate} (\text{mol m}^{-3} \text{s}^{-1}) = N_A (r_A + r_B)^2 \left(\frac{8\pi k_B T}{\mu} \right)^{1/2} \exp(-E_a/RT) n_A n_B \quad (9.6.4)$$

in which all quantities are in SI units. If the unit of length is taken to be decimeters, then the concentrations will be molarities [A] and [B] and the rate will be in the units of moles per liter. We can now identify the pre-exponential factor k_0 in the Arrhenius rate:

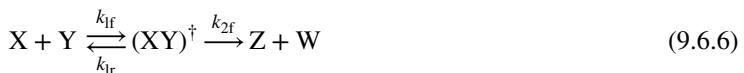
$$k_0 = N_A (r_A + r_B)^2 \left(\frac{8\pi k_B T}{\mu} \right)^{1/2} \quad (9.6.5)$$

At $T = 300$ K, the value of k_0 is of the order of $10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$. The changes in k_0 due to changes in T are small compared with the corresponding changes in the exponential factor in the rate constant.

A number of other expressions were also suggested to explain the temperature dependence of reaction rates, as Laidler notes [6], but they found less and less support as experimental data were gathered. In addition, the expression suggested by Arrhenius had a strong theoretical basis that the other expressions lacked.

9.6.2 The Transition State Theory

Transition state theory postulates the existence of a transition state which is in equilibrium with the reactants. The transition state has an unstable mode that results in conversion to products. For a reaction $X + Y \rightarrow Z + W$, the transition-state mechanism is



The rate of product formation is $k_{2f}[XY^{\ddagger}]$. The assumption that the transition state is in equilibrium with the reactants implies that

$$[(XY)^{\ddagger}]/[X][Y] = k_{lf}/k_{lr} = K_1(T) = \exp(-\Delta G^{\ddagger}/RT) \quad (9.6.7)$$

in which $K_1(T)$ is the equilibrium constant and ΔG^{\ddagger} is the Gibbs energy of reaction. The reaction rate can now be written as

$$\text{Rate} = k_{2f}[(XY)^{\ddagger}] = k_{2f}K_1(T)[X][Y] \quad (9.6.8)$$

The use of statistical thermodynamics and quantum mechanics to calculate the rate constant gives $k_{2f} = \kappa(k_B T/h)$, in which κ is a term of the order of unity and h is the Planck's constant (see Box 9.3). Therefore, the rate constant has the form

$$k = \kappa \left(\frac{k_B T}{h} \right) \exp(-\Delta G^{\ddagger}/RT) \quad (9.6.9)$$

In contrast to the Arrhenius theory, the transition state theory has a *thermodynamic basis* and predicts the existence of a transition state. The pre-exponential factor it predicts is proportional to T ; this is in contrast to the Arrhenius theory, which predicts a $T^{1/2}$ dependence. The transition state theory predicts a change in the rate of reaction due to factors that might change ΔG^{\ddagger} . One such factor is the effect of solvents. In solutions, if the reactants are ionic, then it is observed that the reaction rate depends on the dielectric constant of the solvent. This effect, called the 'solvent effect', can be explained by noting that a change in the dielectric constant changes the value of ΔG^{\ddagger} . In general, the transition state theory gives more insight into the nature of a chemical reaction than the Arrhenius theory and is widely used.

9.7 Coupled Reactions and Flow Reactors

In the previous sections we discussed some basic aspects of chemical kinetics. In this section, we shall look at more complex reactions. Box 9.4 summarizes the main aspects of first- and second-order reactions. In these cases, the reverse reactions were not considered, but in many cases the reverse reaction cannot be ignored. We shall now consider some examples below.

9.7.1 Zero-Order Reactions

In certain conditions, the rate of a reaction can be essentially independent of the concentration of the initial reactants. For example, a reaction such as



could have a rate of product formation that is given by

$$\frac{d[Y]}{dt} = k \quad (9.7.2)$$

in which k is a constant. Such a reaction may be said to be of ‘zero order’ in the reactant X. Such a rate law clearly indicates that the reaction mechanism that controls the conversion of X to Y depends on the concentration of another compound and that increasing the amount of X does not increase the rate of conversion to Y. For example, let us assume that the formation of Y depends on X binding to a catalyst C to form a complex CX and that the complex CX converts to C and Y:



The rate of product formation depends on the amount of the complex CX. If all the catalyst is bound to the reactant X, then increasing the amount of X does not increase the rate of product formation. If $[C]_T$ is the total amount of C, then the rate of reaction when the complex is saturated is

$$\frac{d[Y]}{dt} = k_{2f}[C]_T \quad (9.7.4)$$

Such rates can be observed in reactions catalyzed by solid catalysts and in enzymes. The solution to Equation (9.7.2) is $[Y] = [Y]_0 + kt$.

9.7.2 Reversible First-Order Reaction

In general, the forward and the reverse rate constants are not equal and the rate equations are of the form



$$\frac{d[A]}{dt} = -R_f + R_r = -k_f[A] + k_r[B] \quad (9.7.6)$$

in which R_f and R_r are the forward and reverse reactions rates. Let $[A]_0$ and $[B]_0$ be the initial concentrations. In the above reaction, the total concentration, which we shall denote as $T = [A] + [B] = [A]_0 + [B]_0$, remains constant. Hence, the above rate equation can be rewritten as

$$\frac{d[A]}{dt} = -k_f[A] + k_r(T - [A]) = -(k_f + k_r)[A] + k_rT \quad (9.7.7)$$

The solution to this equation is

$$[A] = \frac{k_r}{k_f + k_r} T + \left([A]_0 - \frac{k_r}{k_f + k_r} T \right) e^{-(k_f + k_r)t} \quad (9.7.8)$$

The reaction could also be described in terms of the extent of reaction ξ , as was done in Section 9.5 for the racemization reaction $L \rightleftharpoons D$. This is left as an exercise for the student.

9.7.3 Consecutive First-Order Reactions

Sequential conversion of compounds is quite common in natural and industrial processes. Sequential transformations in Nature more often than not are cyclical. Let us consider a very simple example: conversion of A to B to C, in which the reverse reactions have negligible rates:



We assume that all the rates are first order and that, at $t = 0$, $[A] = [A]_0$, $[B] = 0$ and $[C] = 0$. The kinetic equations for the concentrations of A, B and C are

$$R_{1f} = k_{1f}[A], \quad R_{2f} = k_{2f}[B] \quad (9.7.10)$$

$$\frac{d[A]}{dt} = -R_{1f} = -k_{1f}[A] \quad (9.7.11)$$

$$\frac{d[B]}{dt} = R_{1f} - R_{2f} = k_{1f}[A] - k_{2f}[B] \quad (9.7.12)$$

$$\frac{d[C]}{dt} = R_{2f} = k_{2f}[B] \quad (9.7.13)$$

This set of coupled equations can be solved analytically. The solution to Equation (9.7.11) is

$$[A] = [A]_0 \exp(-k_{1f}t) \quad (9.7.14)$$

This solution can be substituted into the equation for [B], (9.7.12); we get

$$\frac{d[B]}{dt} + k_{2f}[B] = k_{1f}[A]_0 \exp(-k_{1f}t) \quad (9.7.15)$$

This is a first-order differential equation of the form $(dX/dt) + cX = f(t)$ in which c is a constant and $f(t)$ is a function of time. The general solution to such an equation is

$$X(t) = X(0)e^{-ct} + e^{-ct} \int_0^t e^{ct'} f(t') dt' \quad (9.7.16)$$

Using this general solution, we can write the solution to Equation (9.7.15) and show that

$$[B] = \frac{k_{1f}[A]_0}{k_{2f} - k_{1f}} (e^{-k_{1f}t} - e^{-k_{2f}t}) \quad (9.7.17)$$

in which we have used $[B]_0 = 0$. If the initial concentration $[C]_0 = 0$, then the total amount $[A] + [B] + [C] = [A]_0$. Using this relation, one can obtain the time variation of [C]:

$$\begin{aligned} [C] &= [A]_0 - [A] - [B] \\ &= [A]_0 \left[1 - e^{-k_{1f}t} - \frac{k_{1f}}{k_{2f} - k_{1f}} (e^{-k_{1f}t} - e^{-k_{2f}t}) \right] \end{aligned} \quad (9.7.18)$$

Alternatively, the rate equations can be written and solved in terms of the extents of reaction ξ_1 and ξ_2 of the two reactions (9.7.9). For simplicity, and without loss of generality, we shall assume the system volume $V = 1$ so that concentrations and ξ values can be related without explicitly including V . The extent of reaction for the two reactions and the corresponding changes in concentrations are related by

$$\frac{d[A_1]}{-1} = \frac{d[B_1]}{+1} = d\xi_1, \quad \frac{d[B_2]}{-1} = \frac{d[C_2]}{+1} = d\xi_2 \quad (9.7.19)$$

in which the subscripts indicate changes due to the first and second reactions in the consecutive reactions (9.7.9). The total change in the concentration of A is only due to the reaction A \rightarrow B and that of C is only due to B \rightarrow C, i.e.

$$d[A] = d[A_1] = -d\xi_1 \quad \text{or} \quad [A] = [A]_0 - \xi_1 \quad (9.7.20)$$

and

$$d[C] = d[C_2] = +d\xi_2 \quad \text{or} \quad [C] = [C]_0 + \xi_2 \quad (9.7.21)$$

where we have assumed $\xi = 0$ at $t = 0$ (the subscript 0 indicates values at $t = 0$). Since the change in the intermediate $[B]$ is due to both reactions, we write:

$$d[B] = d[B_1] + d[B_2] = d\xi_1 - d\xi_2 \quad \text{or} \quad [B] = [B]_0 + \xi_1 - \xi_2 \quad (9.7.22)$$

The velocities of the two reactions are

$$\frac{d\xi_1}{dt} = R_{1f} - R_{1r} = k_{1f}[A] = k_{1f}([A]_0 - \xi_1) \quad (9.7.23)$$

$$\frac{d\xi_2}{dt} = R_{2f} - R_{2r} = k_{2f}[B] = k_{2f}([B]_0 + \xi_1 - \xi_2) \quad (9.7.24)$$

These two first-order linear differential equations could be solved using the methods outlined above. By substituting the solutions $\xi_1(t)$ and $\xi_2(t)$ into Equations (9.7.20) to (9.7.22), the time variation of concentrations $[A]$, $[B]$ and $[C]$ can be obtained (Exercise 9.20). Describing the kinetics of reactions using extents of reaction has some notable aspects:

- Each extent of reaction is an independent variable and the number of independent variables in a set of reactions is equal to the number of extents of reaction. The time variations of all reacting species are expressed in terms of these independent variables.
- The initial values of all reactants appear explicitly in the equations and the initial values of all extents of reaction may be assumed to be zero.
- The rate of entropy production can be conveniently expressed in terms of the velocities $d\xi_k/dt$ and the chemical potentials of the reacting species.

9.7.4 The Steady-State Assumption

In many chemical reactions, the concentration of an intermediate compound or complex may be approximated to be constant. Take, for example, the following **Michaelis–Menten mechanism**, which describes enzyme reactions:



Enzyme E complexes with the substrate S to form the complex ES, which in turn transforms to product P and the enzyme. The complexation of E and S to form ES occurs very rapidly and reversibly. In contrast, the conversion of ES to P and E happens relatively slowly. The rapidity of the reaction $E + S \rightleftharpoons ES$ keeps the concentration of ES essentially a constant close to its equilibrium value; any decrease in $[ES]$ due to product formation is quickly compensated by the production of ES. Hence, we can assume that $[ES]$ is in a *steady state*, i.e. its time derivative is zero. Taking the two steps of the reaction (9.7.25), the steady-state assumption can be expressed as

$$\frac{d[ES]}{dt} = k_{1f}[E][S] - k_{1r}[ES] - k_{2f}[ES] = 0 \quad (9.7.26)$$

In the above reaction, the total concentration of enzyme $[E_0]$, in the free and complex form, is a constant:

$$[E] + [ES] = [E_0] \quad (9.7.27)$$

Combining Equations (9.7.26) and (9.7.27) we can write $k_{1f}([E_0] - [ES])[S] - k_{1r}[ES] - k_{2f}[ES] = 0$. From this, it follows that

$$[ES] = \frac{k_{1f}[E_0][S]}{k_{1f}[S] + (k_{1r} + k_{2f})} \quad (9.7.28)$$

The rate of formation of the product P is $k_{2f}[ES]$ and is usually written in the following form:

$$R = \frac{d[P]}{dt} = k_{2f}[ES] = \frac{k_{2f}[E_0][S]}{[S] + (k_{1r} + k_{2r})/k_{1f}} = \frac{R_{\max}[S]}{[S] + K_m} \quad (9.7.29)$$

in which $R_{\max} = k_{2f}[E_0]$ is the maximum rate of product formation and $K_m = (k_{1r} + k_{2r})/k_{1f}$. It can be seen from Equation (9.7.29) that the rate at which P is generated has the following properties:

- When $[S] \ll K_m$, the rate is proportional to $[S]$.
- When $[S] \gg K_m$, the rate reaches its maximum value and is independent of $[S]$.
- When $[S] = K_m$, that rate reaches half the maximum value.

9.7.5 Flow Reactors

Many industrial chemical reactions take place in a flow reactor into which reactants flow and from which products are removed. The kinetic equations for such systems must consider the inflow and outflow. To see how the kinetic equations are written for a flow reactor, let us consider the following reaction, which we assume requires a catalyst:



We assume that the reaction takes place in a solution. The solution containing A flows into the reactor (Figure 9.4) of volume V. In the reactor, activated by a catalyst, the conversion from A to B and C takes place. The fluid in the reactor is rapidly stirred so that we may assume that it is homogeneous. The outflow is a solution containing B, C and unconverted A. If the objective is to produce B and C, then the reaction should be rapid enough so that very little A is in the outflow. We consider a flow rate of f liters per second of a solution of concentration $[A]_{\text{in}}$ mol L⁻¹. Moles of A flowing into the reactor per second equals $[A]_{\text{in}}f$. Hence, the rate at which the concentration of A increases due to the inflow into the reactor of volume V is $[A]_{\text{in}}f/V$. Similarly, the rate of decrease in concentrations of A, B and C due to the outflow are $[A]/fV$, $[B]/fV$ and $[C]/fV$ respectively. The term f/V has units of s⁻¹. Its inverse, $V/f \equiv \tau$, is called the **residence time** (because

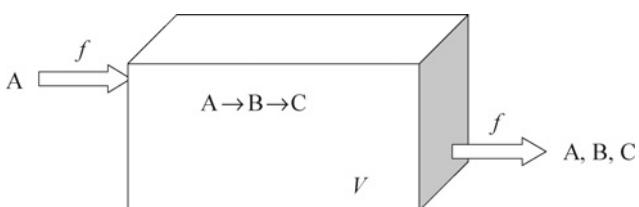


Figure 9.4 A flow reactor into which fluid containing A flows. Owing to a catalyst in the reactor, conversion of $A \rightarrow B \rightarrow C$ takes place in the reactor. The outflow consists of unconverted A and the products B and C. The amount of fluid flowing into the reactor per unit time is f . The inflow rate equals the outflow rate at steady state.

it roughly corresponds to the time the flowing fluid resides in the reactor before it flows out). Taking the flow into consideration, the kinetic equations for the reactor can be written as

$$\frac{d[A]}{dt} = [A]_{in}(f/V) - k_{1f}[A] - [A](f/V) \quad (9.7.31)$$

$$\frac{d[B]}{dt} = k_{1f}[A] - k_{2f}[B] - [B](f/V) \quad (9.7.32)$$

$$\frac{d[C]}{dt} = k_{2f}[B] - [C](f/V) \quad (9.7.33)$$

This set of linear coupled equations can be solved for steady states by setting $d[A]/dt = d[B]/dt = d[C]/dt = 0$. If, initially, the reactor contains no A, B or C, then the flow will result in an initial increase in the concentration of the three reactants and then the reactor will approach a steady state in which the concentrations are constant. The steady states, which we identify with a subscript ‘s’, are easily calculated:

$$[A]_s = \frac{[A]_{in}(f/V)}{k_{1f} + (f/V)} \quad (9.7.34)$$

$$[B]_s = \frac{k_{1f}[A]_s}{k_{2f} + (f/V)} \quad (9.7.35)$$

$$[C]_s = \frac{k_{2f}[B]_s}{f/V} \quad (9.7.36)$$

If the rate constants k_{1f} and k_{2f} are large compared with f/V , then the steady-state concentrations $[A]_s$ and $[B]_s$ will be small and $[C]_s$ will be large. This corresponds to almost complete conversion of A into product C, which will flow out of the reactor. On the other hand, if the flow rate is high, then the conversion in the reactor will only be partial. Because they are coupled linear equations, (9.7.31) to (9.7.33) can also be solved analytically; generally, however, chemical kinetics leads to coupled nonlinear equations, which cannot be solved analytically. They can, of course, be solved numerically.

The above simple example illustrates how kinetic equations for a reactor can be written. Generalizing it to reactions more complex than Equation (9.7.30) is straightforward. The purpose of some reactors is to combust fuel and generate heat. At the steady state, heat is generated at a constant rate. If the enthalpies of the reactions are known, then at a steady state, the rate at which heat is generated in the reactor can be calculated.

Appendix 9.1 *Mathematica* Codes

In *Mathematica*, numerical solutions to the rate equation can be obtained using the **NDSolve** command. Examples of the use of this command in solving simple rate equations are given below. The results can be plotted using the **Plot** command. Numerical output can be exported to graphing software using the **Export** command.

CODE A: LINEAR KINETICS X → PRODUCTS

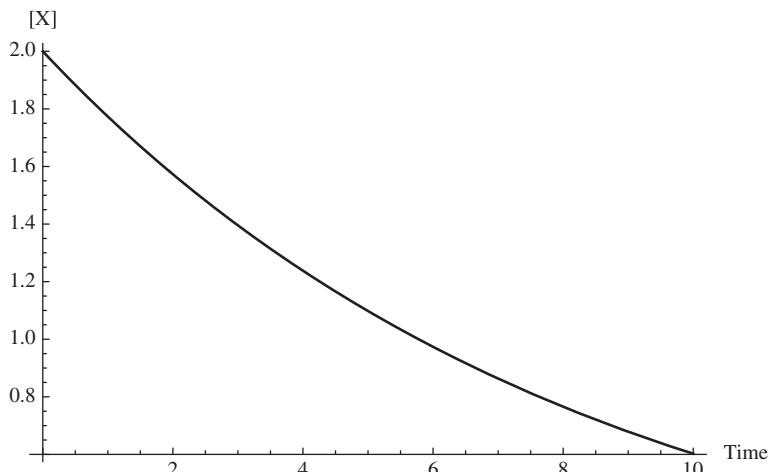
```
(* Linear Kinetics *)
```

```
k=0.12;
```

```
Soln1=NDSolve[{x'[t]== -k*x[t], x[0]==2.0},x,{t,0,10}]
{ {x->InterpolatingFunction[{{0.,10.}},<>]}}
```

The above output indicates that the solution as an interpolating function has been generated. The solution can be plotted using the following command. Here ‘/.Soln1’ specifies that the values of $X[t]$ are to be calculated using the interpolation function generated by Soln1.

```
Plot[Evaluate[x[t]/.Soln1],{t,0,10},
PlotStyle->{{Black,Thick}},
AxesLabel->{Time,"[X]"}]
```



To write output files for spreadsheets use the ‘Export’ command and the file format List. For more detail see the *Mathematica* help file for the Export command. In the command below, the output filename is: data1.txt. This file can be read by most spreadsheets and graphing software. The command ‘X[t]/.Soln1’ specifies that $X[t]$ is to be evaluated using Soln1 defined above. TableForm outputs data in a convenient form.

```
Export["data1.txt", Table[{t,x[t]/.Soln1},{t,1,10}]//TableForm,"List"]
```

data1.txt

To obtain a table of t and $X(t)$ the following command can be used.

```
Table[{t,x[t]/.Soln1},{t,1,5}]//TableForm
```

1	1.77384
2	1.57326
3	1.39535
4	1.23757
5	1.09762

CODE B: Mathematica CODE FOR THE REACTION $X + 2Y \rightleftharpoons 2Z$

In writing codes for kinetic equations, we shall define the forward and reverse rates, R_f and R_r respectively, and use these in the rate equations. Thus we avoid typing the same expression many times.

```
(* Reaction X+2Y ⇌ 2Z *)

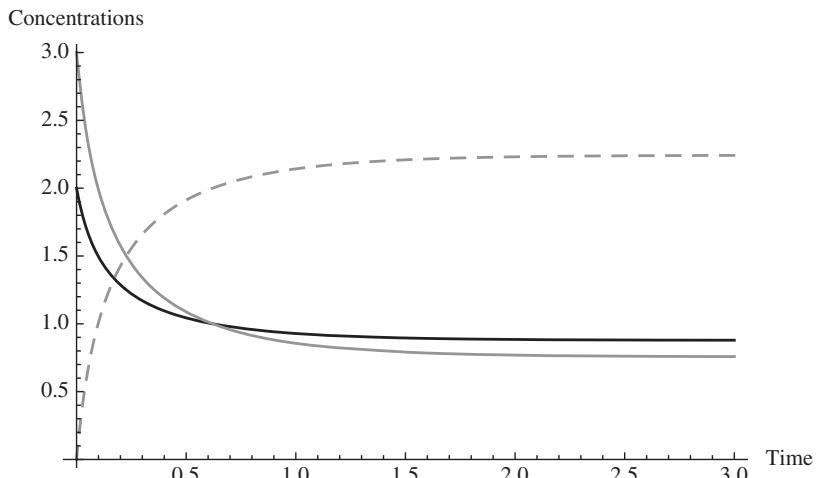
kf=0.5;kr=0.05;
Rf:=kf*X[t]*(Y[t]^2); Rr:=kr*Z[t]^2;

Soln2=NDSolve[{
  X'[t]== -Rf+Rr,
  Y'[t]== 2*(-Rf+Rr),
  Z'[t]== 2*(Rf-Rr),
  X[0]==2.0,Y[0]==3.0,Z[0]==0.0},
  {X,Y,Z},{t,0,3}]

{{X->InterpolatingFunction[{{0.,3.}},<>],
  Y->InterpolatingFunction[{{0.,3.}},<>],
  Z->InterpolatingFunction[{{0.,3.}},<>]}}}
```

The above output indicates that the solution as an interpolating function has been generated. The solution can be plotted using the following command:

```
Plot[Evaluate[{X[t],Y[t],Z[t]}/.Soln2],{t,0,3},
  AxesLabel->{Time,Concentrations},
  PlotStyle->{{Black,Thick},{GrayLevel[.5],Thick},
  {Dashed,Gray,Thick}}]
```



As shown in Code A, the data could be written to an output file that graphing software can read using the Export command.

CODE C: *Mathematica* CODE FOR RACEMIZATION REACTION $L \rightleftharpoons D$ AND CONSEQUENT ENTROPY PRODUCTION

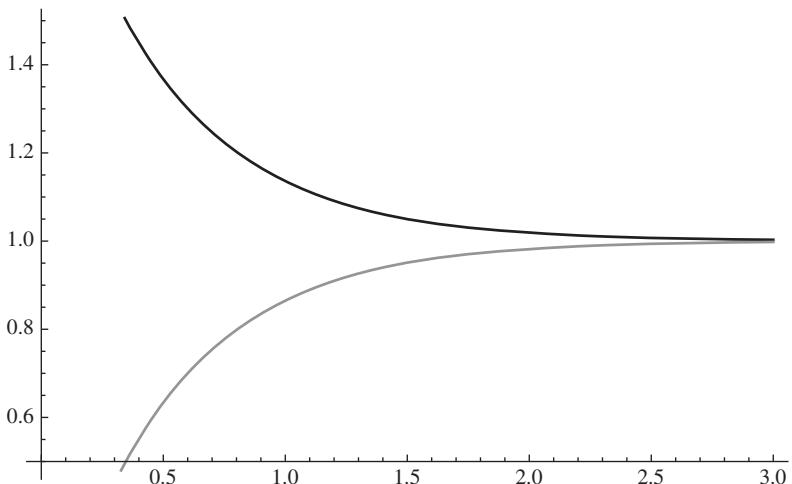
```
(* Racemization Kinetics: L ⇌ D *)
kf=1.0;kr=1.0;
Rf:=kf*XL[t]; Rr:=kr*XD[t];

Soln3=NDSolve[{\{ XL'[t]== -Rf+Rr,
    XD'[t]== Rf-Rr,
    XL[0]==2.0,XD[0]==0.001\},
    \{XL,XD\},\{t,0,3\}]

{\{XL->InterpolatingFunction[\{\{0.,3.\}\},\>],\>
  XD->InterpolatingFunction[\{\{0.,3.\}\},\>]\}}}
```

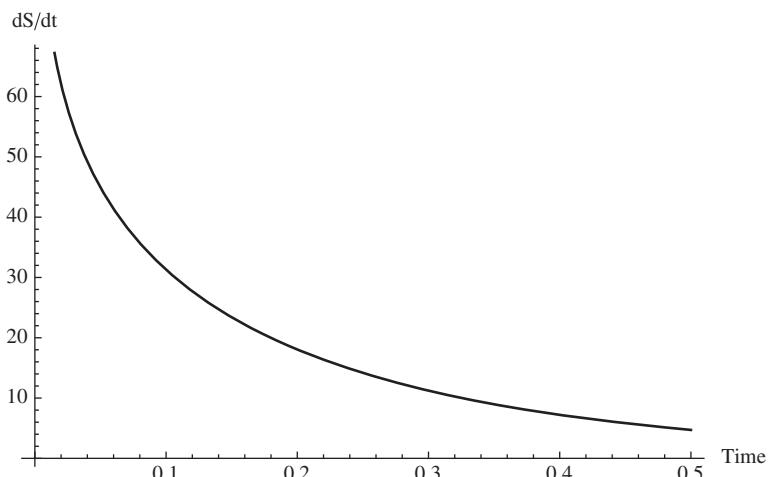
The output indicates an interpolating function has been generated. As before, the solution can be plotted.

```
Plot[Evaluate[\{XL[t],XD[t]\}/.Soln3],\{t,0,3\},
  PlotStyle-\>\{\{Black,Thick\},\{Gray,Thick\}\}]
```



The rate of entropy production can be obtained from the interpolating functions and the first equation in (9.5.20). Note: in *Mathematica*, log is ln.

```
(*Calculation of entropy production "sigma"*)
R=8.314; sigma=R*(Rf-Rr)*Log[Rf/Rr];
Plot[Evaluate[\{sigma\}/.Soln3],\{t,0,0.5\},
  PlotStyle-\>\{Thick\},AxesLabel-\>\{"Time","ds/dt"\}]
```



References

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Examples

Example 9.1 At a temperature T , the average energy $h\nu$ of a thermal photon is roughly equal to kT . As discussed in Chapter 2, at high temperatures electron–positron pairs will be spontaneously produced when the energy of photons is larger than rest energy $2mc^2$ of an electron positron pair (where m is the mass of the electron). Calculate the temperature at which electron–positron pair production occurs.

Solution For pair production:

$$h\nu = k_B T = 2mc^2 = (2 \times 9.10 \times 10^{-31} \text{ kg})(3.0 \times 10^8 \text{ m s}^{-1})^2 = 1.64 \times 10^{-13} \text{ J}$$

Hence, the corresponding $T = (1.64 \times 10^{-13} \text{ J}) / (1.38 \times 10^{-23} \text{ J K}^{-1}) = 1.19 \times 10^{10} \text{ K}$.

Example 9.2 Consider a second-order reaction $2\text{X} \rightarrow \text{Products}$ whose rate equation is $d[\text{X}] / dt = -2k_f[\text{X}]^2 = -k[\text{X}]^2$ in which we set $k = 2k_f$. (a) Show that the half-life $t_{1/2}$ for this reaction depends on the initial value of $[\text{X}]$ and is equal to $1/([X]_0 k)$. (b) Assume that $k = 2.3 \times 10^{-1} \text{ M}^{-1} \text{ S}^{-1}$ and obtain the value of $[\text{X}]$ at a time $t = 60.0 \text{ s}$ if the initial concentration $[\text{X}]_0 = 0.50 \text{ M}$.

Solution

- a. As shown in Box 9.4, the solution to the rate equation is

$$\frac{1}{[X]} - \frac{1}{[X]_0} = kt$$

Multiplying both sides by $[X]_0$ we obtain

$$\frac{[X]_0}{[X]} = 1 + [X]_0 kt$$

Since at $t = t_{1/2}$ the ratio $[X]_0/[X] = 2$, we must have $[X]_0 kt_{1/2} = 1$ or $t_{1/2} = 1/([X]_0 k)$.

- b. If the initial concentration $[X]_0 = 0.50\text{ M}$, $k = 0.23\text{ M}^{-1}\text{ S}^{-1}$ and $t = 60.0\text{ s}$ we have

$$\frac{1}{[X]} - \frac{1}{0.50} = 0.23 \times 60 \text{ mol L}^{-1}$$

Solving for $[X]$ we get $[X] = 0.063\text{ mol L}^{-1}$.

Example 9.3 For the water dissociation reaction $\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$ the enthalpy of reaction $\Delta H_r = 55.84\text{ kJ mol}^{-1}$. At 25°C , the value of the equilibrium constant $K = 1.00 \times 10^{-14}$ and pH is 7.0. At 50°C , what will the pH be?

Solution Given $K(T)$ at one temperature T_1 , its value at another temperature T_2 can be obtained using the van't Hoff equation (9.3.19):

$$\ln K(T_1) - \ln K(T_2) = \frac{-\Delta H_r}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

For this example, we have, for K at 50°C ,

$$\ln K = \ln(1.0 \times 10^{-14}) - \frac{55.84 \times 10^3}{8.314} \left(\frac{1}{323} - \frac{1}{298} \right) = -30.49$$

Hence, K at 50°C is equal to $\exp(-30.49) = 5.73 \times 10^{-14}$. Since the equilibrium constant $K = [\text{OH}^-][\text{H}^+]$ and because $[\text{OH}^-] = [\text{H}^+]$, we have

$$\text{pH} = -\log[\text{H}^+] = -\log[\sqrt{K}] = -\frac{1}{2} \log[5.73 \times 10^{-14}] = 6.62$$

Exercises

- 9.1** When the average kinetic energy of molecules is nearly equal to the chemical bond energy, molecular collisions will begin to break the bonds. (a) The C–H bond energy is about 414 kJ mol^{-1} . At what temperature will the C–H bonds in methane begin to break? (b) The average binding energy per nucleon (neutron or proton) is in the range $(6.0\text{--}9.0) \times 10^6\text{ eV}$ or $(6.0\text{--}9.0) \times 10^8\text{ kJ mol}^{-1}$. At what temperature do you expect nuclear reactions to take place?
- 9.2** For the reaction $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$, the activation energy $E_a = 23.0\text{ kJ mol}^{-1}$ and $k_0 = 7.9 \times 10^{10}\text{ mol}^{-1}\text{ L s}^{-1}$. What is the value of the rate constant at $T = 300.0\text{ K}$? If $[\text{Cl}] = 1.5 \times 10^{-4}\text{ mol L}^{-1}$ and $[\text{H}_2] = 1.0 \times 10^{-5}\text{ mol L}^{-1}$, what is the forward reaction rate at $T = 350.0\text{ K}$?

- 9.3** For the decomposition of urea in an acidic medium, the following data were obtained for rate constants at various temperatures:

Temperature (°C)	50	55	60	65	70
Rate constant k (10^{-8} s $^{-1}$)	2.29	4.63	9.52	18.7	37.2

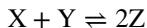
- (a)** Using an Arrhenius plot, obtain the activation energy E_a and the pre-exponential factor k_0 .
(b) Apply the transition state theory to the same data, plot $\ln(k/T)$ versus $1/T$ and obtain ΔH^\ddagger and ΔS^\ddagger of the transition state.
- 9.4** Consider the dimerization of the triphenylmethyl radical $\text{Ph}_3\text{C}^\bullet$, which can be written as the reaction



The forward and reverse rate constants for this reaction at 300 K are found to be $k_f = 0.406$ s $^{-1}$ and $k_r = 3.83 \times 10^2$ mol $^{-1}$ L s $^{-1}$. Assume that this reaction is an elementary step. At $t = 0$ the initial concentration of A and B are $[\text{A}]_0 = 0.041$ M and $[\text{B}]_0 = 0.015$ M.

- (a)** What is the velocity of the reaction at $t = 0$?
(b) If ξ_{eq} is the extent of reaction at equilibrium ($\xi = 0$ at $t = 0$), write the equilibrium concentrations of A and B in terms of $[\text{A}]_0$, $[\text{B}]_0$ and ξ_{eq} .
(c) Use (b) to obtain the value of ξ_{eq} by solving the appropriate quadratic equation and obtain the equilibrium concentrations of [A] and [B].

- 9.5** **(a)** Write the rate equations for the concentrations of X, Y and Z in the following reaction:



- (b)** Write the rate equation for the extent of reaction ξ .
(c) When the system reaches thermal equilibrium, $\xi = \xi_{\text{eq}}$. If $[\text{X}]_0$, $[\text{Y}]_0$ and $[\text{Z}]_0$ are the initial concentrations, write the equilibrium concentrations in terms of the initial concentrations and ξ_{eq} .
- 9.6** Radioactive decay is a first-order reaction. If N is the number of radioactive nuclei at any time, then $dN/dt = -kN$. ^{14}C is radioactive with a half-life of 5730 years. What is the value of k ? For this process, do you expect k to change with temperature?

- 9.7** If $d[\text{A}]/dt = -k[\text{A}]^\alpha$, show that the half-life is

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{(\alpha - 1)k[\text{A}]_0^{\alpha-1}}$$

- 9.8** Find an analytical solution to the reversible reaction $[\text{L}] \xrightleftharpoons[k_r]{k_f} [\text{D}]$, in which L and D are enantiomers. Enantiomeric excess (EE) is defined as

$$\text{EE} \equiv \frac{|[\text{L}] - [\text{D}]|}{[\text{L}] + [\text{D}]}$$

If the initial EE = 1.0, how long does it take for it to reach 0.5? (Amino acid racemization is used in dating of biological samples.)

- 9.9 (a)** For the bimolecular reaction $A + B \xrightarrow{k_f} P$ the rate equation is

$$\frac{d[A]}{dt} = -k_f[A][B]$$

When $[A]_0$ and $[B]_0$ are the initial concentrations, show that

$$\frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[A][B]_0}{[B][A]_0} \right) = -k_f t$$

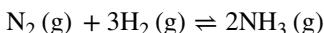
- (b)** Write the above rate equation in terms of the extent of reaction ξ and solve it.

- 9.10** The chirping rate of crickets depends on temperature. When the chirping rate is plotted against $1/T$ it is observed to follow the Arrhenius law (see K.J. Laidler, *J. Chem. Ed.*, **49** (1972), 343). How would you explain this observation?
- 9.11** Consider the reaction $X + Y \rightleftharpoons 2Z$ in the gas phase. Write the reaction rates in terms of the concentrations $[X]$, $[Y]$ and $[Z]$ as well as in terms of the activities. Find the relation between the rate constants in the two ways of writing the reaction rates.
- 9.12** When atmospheric CO_2 dissolves in water it produces carbonic acid H_2CO_3 (which causes natural rain to be slightly acidic). At 25.0°C the equilibrium constant K_a for the reaction $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ is specified by $pK_a = 6.63$. The enthalpy of this reaction $\Delta H_r = 7.66 \text{ kJ mol}^{-1}$. Calculate the pH at 25°C and at 35°C . (Use Henry's law to obtain $[\text{H}_2\text{CO}_3]$.)
- 9.13** Equilibrium constants can vary over an extraordinary range, as the following examples demonstrate. Obtain the equilibrium constants for the following reactions at $T = 298.15 \text{ K}$, using the tables for $\mu(p_0, T_0) = \Delta G_f^0$:
- (a) $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
 - (b) $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$
 - (c) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- 9.14 (a)** For a reaction of the form $aX + bY \rightleftharpoons cZ$, show that the equilibrium constants K_c and K_p are related by $K_c = (RT)^\alpha K_p$ where $\alpha = a + b - c$.
- (b)** Using the definition of enthalpy $H = U + pV$, show that the van't Hoff equation for a gas-phase reaction can also be written as

$$\frac{d \ln K_c}{dT} = \frac{\Delta U_r}{RT^2}$$

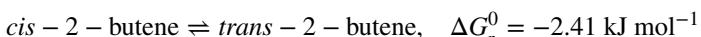
in which K_c is the equilibrium constant expressed in terms of concentrations.

- 9.15** Ammonia may be produced through the reaction of $\text{N}_2(\text{g})$ with $\text{H}_2(\text{g})$:



- (a)** Calculate the equilibrium constant of this reaction at 25°C using the thermodynamic tables.
- (b)** Assuming that there is no significant change in the enthalpy of reaction ΔH_r , use the van't Hoff equation to obtain the approximate ΔG_r and the equilibrium constant at 400°C .

- 9.16** 2-Butene is a gas that has two isomeric forms, cis and trans. For the reaction:



calculate the equilibrium constant at $T = 298.15 \text{ K}$. If the total amount of butene is 2.5 mol, then, assuming ideal gas behavior, determine the molar amounts of each isomer.

- 9.17** Determine if the introduction of a catalyst will alter the affinity of a reaction or not.
- 9.18** For the reaction $A \xrightleftharpoons[k_r]{k_f} B$, write the equation for the velocity of reaction $d\xi/dt$ in terms of the initial values $[A_0]$ and $[B_0]$ and obtain the solution $\xi(t)$.
- 9.19** For the reaction $X + 2Y \rightleftharpoons 2Z$, write explicitly the expression for the entropy production in terms of the rates and as a function of ξ .
- 9.20** As shown in Section 9.7, for the reaction $A \xrightarrow{k_{1f}} B \xrightarrow{k_{2f}} C$ the extents of reaction obey the equations

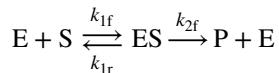
$$\frac{d\xi_1}{dt} = R_{1f} - R_{1r} = k_{1f}[A] = k_{1f}([A]_0 - \xi_1)$$

$$\frac{d\xi_2}{dt} = R_{2f} - R_{2r} = k_{2f}[B] = k_{2f}([B]_0 + \xi_1 - \xi_2)$$

Solve these equations with initial conditions $\xi_1 = \xi_2 = 0$ at $t = 0$. Assume $[A] = [A]_0$, $[B] = 0$ and $[C] = 0$ and show that

$$[C] = [A]_0 \left[1 - e^{-k_{1f}t} - \frac{k_{1f}}{k_{2f} - k_{1f}} (e^{-k_{1f}t} - e^{-k_{2f}t}) \right]$$

- 9.21** Write the complete set of rate equations for all the species in the Michaelis–Menten reaction mechanism:



Write *Mathematica/Maple* code to solve them numerically with the following numerical values for the rate constants and initial values (assuming all quantities are in appropriate units): $k_{1f} = 1.0 \times 10^2$, $k_{1r} = 5.0 \times 10^3$, $k_{2f} = 2.0 \times 10^3$ and, at $t = 0$, $[E] = 3.0 \times 10^{-4}$, $[S] = 2 \times 10^{-2}$, $[ES] = 0$, $[P] = 0$. Using the numerical solutions, check the validity of the steady-state assumption.

- 9.22** Calculate k_0 for the reaction between H₂ and O₂ at $T = 298$ K using the bond lengths 74 pm for H–H and 121 pm for O=O.

10

Fields and Internal Degrees of Freedom

The Many Faces of Chemical Potential

The concept of chemical potential is very general, applicable to almost any transformation of matter as long as there is a well-defined temperature. We have already seen how the condition for thermodynamic equilibrium for chemical reactions leads to the law of mass action. We shall now see how particles in a gravitational or electric field, electrochemical reactions and transport of matter through diffusion can all be viewed as ‘chemical transformations’ with associated chemical potential and affinity.

10.1 Chemical Potential in a Field

The formalism for the chemical potential presented in Chapter 9 can be extended to electrochemical reactions and to systems in a field, such as a gravitational field. When a field is present, the energy due to a field must be included in the expression for the system’s energy. As a result, the energy of a constituent depends on its location.

We start with a simple system: the transport of chemical species that carry electrical charge from a position where the electrical potential is ϕ_1 to a position where the potential is ϕ_2 . For simplicity, we shall assume that our system consists of two parts, each with a well-defined potential, while the system as a whole is closed (see Figure 10.1). The situation is as if the system consists of two phases and transport of particles dN_k is a ‘chemical reaction’. For the corresponding extent of reaction $d\xi_k$ we have

$$-dN_{1k} = dN_{2k} = d\xi_k \quad (10.1.1)$$

in which dN_{1k} and dN_{2k} are the changes in the molar amount in each part. The change in energy due to the transport of the ions is given by

$$dU = T dS - p dV + F\phi_1 \sum_k z_k dN_{1k} + F\phi_2 \sum_k z_k dN_{2k} + \sum_k \mu_{1k} dN_{1k} + \sum_k \mu_{2k} dN_{2k} \quad (10.1.2)$$

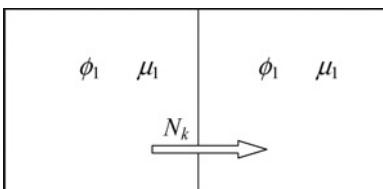


Figure 10.1 A simple situation illustrating the thermodynamics of a system in the presence of an electric field. We consider two compartments, one with associated potential ϕ_1 and the other ϕ_2 . It is as if there are two phases; ions will be transported from one to the other until the electrochemical potentials are equal.

in which z_k is the charge of ion k and F is the Faraday constant (the product of the electronic charge e and the Avogadro number N_A : $F = eN_A = 9.6485 \times 10^4 \text{ C mol}^{-1}$). Using Equation (10.1.1), the change in the entropy dS can now be written as

$$T dS = dU + p dV - \sum_k [(F\phi_1 z_k + \mu_{1k}) - (F\phi_2 z_k + \mu_{2k})] d\xi_k \quad (10.1.3)$$

In this expression, we see that the introduction of a potential ϕ associated with a field is equivalent to adding a term to the chemical potential. This makes it possible to extend the definition of the chemical potential to include the field. Thus, the **electrochemical potential** $\tilde{\mu}$, which was introduced by Guggenheim [1] in 1929, is defined as

$$\boxed{\tilde{\mu}_k = \mu_k + Fz_k\phi} \quad (10.1.4)$$

Clearly, such a formalism can be extended to any conservative field to which a potential may be associated. If ψ is the potential associated with the field, then the energy of interaction *per mole* of the component k may be written in the form $\tau_k \psi$. The ‘coupling constant’ for the electric field $\tau_k = Fz_k$ and for the gravitational field $\tau_k = M_k$, where M_k is the molar mass. The corresponding chemical potential, which includes the potential ψ associated with the field, is

$$\boxed{\tilde{\mu}_k = \mu_k + \tau_k \psi} \quad (10.1.5)$$

The affinity \tilde{A}_k for electrochemical reactions can be written just as it was done for other chemical reactions:

$$\tilde{A}_k = \tilde{\mu}_{1k} - \tilde{\mu}_{2k} = [(F\phi_1 z_k + \mu_{1k}) - (F\phi_2 z_k + \mu_{2k})] \quad (10.1.6)$$

The increase in entropy due to the transfer of charged particles from one potential to another can now be written as

$$d_i S = \sum_k \frac{\tilde{A}_k}{T} d\xi_k \quad (10.1.7)$$

At equilibrium:

$$\tilde{A}_k = 0 \quad \text{or} \quad \mu_{1k} - \mu_{2k} = -z_k(\phi_1 - \phi_2) \quad (10.1.8)$$

The basic equations of equilibrium electrochemistry follow from Equation (10.1.8).

As noted in Section 8.3 (and Exercise 8.13), electrical forces are very strong. In ionic solutions, the electrical field produced by even small changes in charge density results in very strong forces between the ions. Consequently, in most cases the concentrations of positive and negative ions are such that the net charge density is virtually zero; i.e. **electroneutrality** is maintained to a high degree. In a typical electrochemical

cell, most of the potential difference applied to the electrodes appears in the vicinity of the electrodes and only a small fraction of the total potential difference occurs across the bulk of the solution. The solution is electrically neutral to an excellent approximation. As a result, an applied electric field does not separate positive and negative charges and so does not create an appreciable concentration gradient.

When we consider the much weaker gravitational field, however, an external field can produce a concentration gradient. As noted above, for a gravitational field, the coupling constant τ_k is the molar mass M_k . For a gas in a uniform gravitational field, for example, $\psi = gh$, where g is the strength of the field and h is the height. Using Equation (10.1.8) we see that

$$\mu_k(h) = \mu_k(0) - M_kgh \quad (10.1.9)$$

For an ideal-gas mixture, using $\mu_k(h) = \mu_k^0(T) + RT \ln[p_k(h)/p_0]$ in the above equation, we obtain the well-known **barometric formula**:

$$p_k(h) = p_k(0)e^{-M_kgh/RT} \quad (10.1.10)$$

Note how this formula is derived assuming that the temperature T is uniform, i.e. the system is assumed to be in thermal equilibrium. The temperature of the Earth's atmosphere is not uniform; in fact, as shown in Figure 10.2, it varies between -60°C and $+20^\circ\text{C}$ in the troposphere and stratosphere, the two layers in which almost all of the atmospheric gases reside.

10.1.1 Entropy Production in a Continuous System

In considering thermodynamic systems in a field, we often have to consider continuous variation of the thermodynamic fields. In this case, $\tilde{\mu}$ is a function of position and entropy has to be expressed in terms of entropy density $s(\mathbf{r})$, i.e. entropy per unit volume, which depends on position \mathbf{r} . For simplicity, let us consider a one-dimensional system, i.e. a system in which the entropy and all other variables, such as μ , change only along one direction, say x (Figure 10.3). Let $s(x)$ be the entropy density per unit length. We shall assume that the temperature is constant throughout the system. Then the entropy in a small volume element between x and $x + \delta$ is equal to $s(x)\delta$. An expression for affinity in this small volume element can be written as

$$\tilde{A}_k = \tilde{\mu}_k(x) - \tilde{\mu}_k(x + \delta) = \tilde{\mu}_k(x) - \left(\tilde{\mu}_k(x) + \frac{\partial \tilde{\mu}_k}{\partial x} \delta \right) = -\frac{\partial \tilde{\mu}_k}{\partial x} \delta \quad (10.1.11)$$

The velocity of the reaction $d\xi_k/dt$ for this elemental volume is the flow of particles of component k , i.e. the particle current of k . We shall denote this particle current of k by J_{Nk} . Then by writing expression (10.1.7) for the rate of entropy production in this elemental volume we obtain

$$\frac{d_i(s(x)\delta)}{dt} = \sum_k \frac{\tilde{A}_k}{T} \frac{d\xi_k}{dt} = - \sum_k \frac{1}{T} \left(\frac{\partial \tilde{\mu}_k}{\partial x} \right) \delta \frac{d\xi_k}{dt} \quad (10.1.12)$$

Simplifying this expression and using the definition $J_{Nk} = d\xi_k/dt$, the following expression for *entropy production per unit length* due to particle flow is obtained:

$$\frac{d_i(s(x))}{dt} = - \sum_k \frac{1}{T} \left(\frac{\partial \tilde{\mu}_k}{\partial x} \right) J_{Nk} \quad (10.1.13)$$

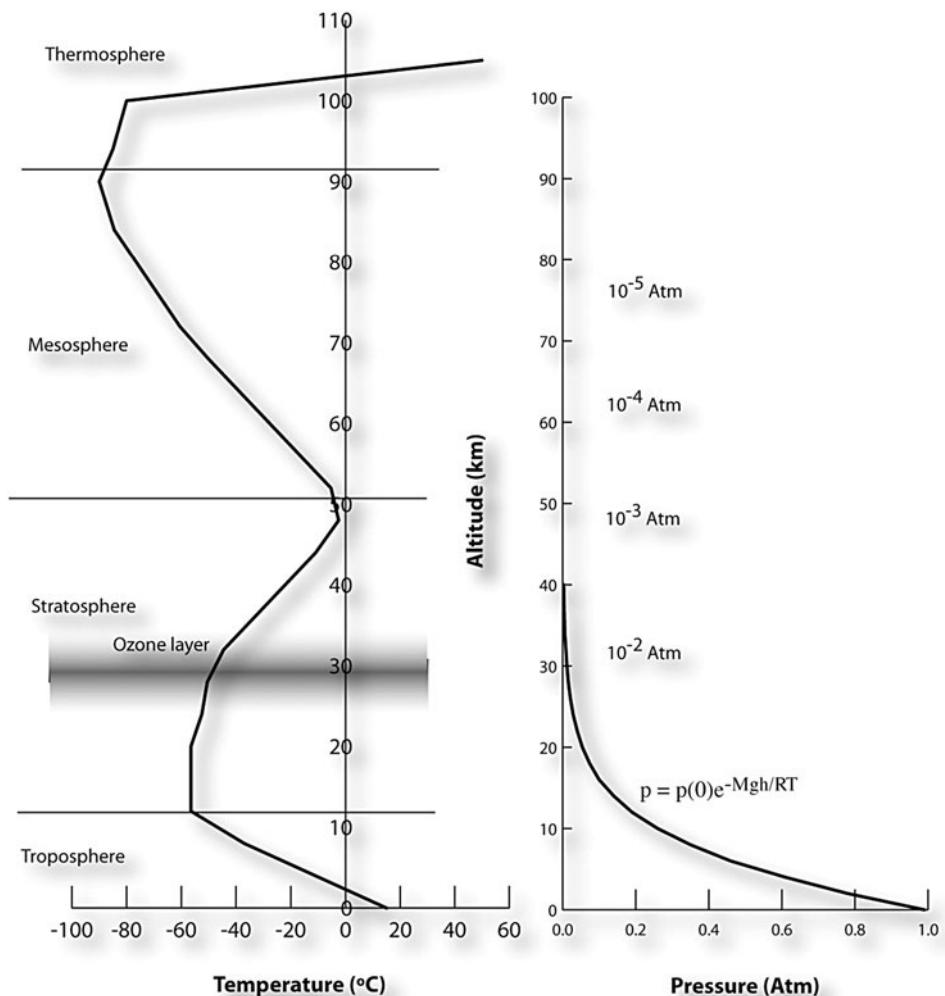


Figure 10.2 The actual state of the Earth's atmosphere is not in thermal equilibrium. The temperature varies with height as shown. At thermal equilibrium, the concept of a chemical potential that includes a field leads to the well-known barometric formula $p(h) = p(0)e^{-Mgh/RT}$.

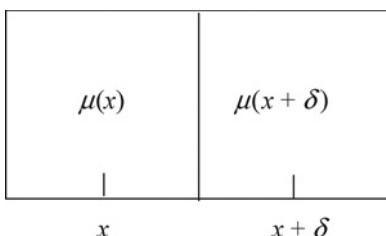


Figure 10.3 An expression for the entropy production in a continuous system can be obtained by considering two adjacent cells separated by a small distance δ . The entropy in the region between x and $x + \delta$ is equal to $s(x)\delta$. The affinity, which is the difference in the chemical potential is given by Equation (10.1.11).

10.1.2 Entropy Production Due to Electrical Conduction and Ohm's Law

To understand the physical meaning of expression (10.1.13), let us consider the flow of electrons in a conductor. In a conductor in which the electron density and temperature are uniform, the chemical potential of the electron μ_e (which is a function of the electron density and T) is constant. Also, for electrons, $z_k = -1$. Therefore, the derivative of the electrochemical potential is

$$\frac{\partial \tilde{\mu}_e}{\partial x} = \frac{\partial}{\partial x}(\mu_e - F\phi) = -\frac{\partial}{\partial x}(F\phi) \quad (10.1.14)$$

Since the electric field $E = -\partial\phi/\partial x$ and the conventional electric current $I = -FJ_e$, using (10.1.14) in expression (10.1.13) we obtain the following expression for the entropy production:

$$\frac{d_i s}{dt} = F \left(\frac{\partial \phi}{\partial x} \right) \frac{J_e}{T} = \frac{EI}{T} \quad (10.1.15)$$

Since the electric field is the change of potential per unit length, it follows that the integral of E over the entire length L of the system is the potential difference V across the entire system. The total entropy production from $x = 0$ to $x = L$ is

$$\frac{dS}{dt} = \int_0^L \left(\frac{d_i s}{dt} \right) dx = \int_0^L \frac{EI}{T} dx = \frac{VI}{T} \quad (10.1.16)$$

Now it is well known that the product VI , of potential difference and the current, is the heat generated per unit time, called the **ohmic heat**. The flow of an electric current through a resistor is a dissipative process that converts electrical energy into heat. For this reason we may write $VI = dQ/dt$. Thus, for a flow of electric current, we have

$$\frac{d_i S}{dt} = \frac{VI}{T} = \frac{1}{T} \frac{dQ}{dt}$$

(10.1.17)

This shows that the entropy production is equal to the dissipative heat divided by the temperature.

We noted in Chapter 3 that the entropy production due to each irreversible process is a product of a thermodynamic force and the flow it drives (see Equation (3.4.7)). In the above case, the flow is the electric current; the corresponding force is the term V/T . Now it is generally true that, when a system is close to thermodynamic equilibrium, the flow is proportional to the force. Hence, based on thermodynamic reasoning, we arrive at the conclusion

$$I = L_e \frac{V}{T} \quad (10.1.18)$$

in which L_e is a constant of proportionality for the electric current. L_e is called the **linear phenomenological coefficient**. Relations such as (10.1.18) are the basis of linear nonequilibrium thermodynamics, which we shall consider in more detail in Chapter 16. We see at once that this corresponds to the familiar **Ohm's law**, $V = IR$, where R is the resistance, if we identify

$$L_e = \frac{T}{R} \quad (10.1.19)$$

This is an elementary example of how the expression for entropy production can be used to obtain linear relations between thermodynamic forces and flows, which often turn out to be empirically discovered laws such as the Ohm's law. In Section 10.3 we shall see that a similar consideration of entropy production due to diffusion leads to another empirically discovered law called Fick's law of diffusion. *Modern thermodynamics enables us to incorporate many such phenomenological laws into one unified formalism.*

10.2 Membranes and Electrochemical Cells

10.2.1 Membrane Potentials

Just as equilibrium with a semipermeable membrane resulted in a difference in pressure (the osmotic pressure) between the two sides of the membrane, equilibrium of ions across a membrane that is permeable to one ion but not another results in an electric potential difference. As an example, consider a membrane separating two solutions of KCl of *unequal* concentrations (Figure 10.4). We assume that the membrane is permeable to K^+ ions but is impermeable to the larger Cl^- ions. Since the concentrations of the K^+ ions on the two sides of the membrane are unequal, K^+ ions will begin to flow to the region of lower concentration from the region of higher concentration. Such a flow of positive charge, without a counterbalancing flow of negative charge, will cause a change in the potential difference that will oppose the flow. Equilibrium is reached when the electrochemical potentials of K^+ on the two sides become equal, at which point the flow will stop. We shall denote the two sides with superscripts α and β . Then the equilibrium of the K^+ ion is established when

$$\tilde{\mu}_{K^+}^\alpha = \tilde{\mu}_{K^+}^\beta \quad (10.2.1)$$

Since the electrochemical potential of an ion k is $\tilde{\mu}_k = \mu_k + z_k F\phi = \mu_k^0 + RT \ln a_k + z_k F\phi$, in which a_k is the activity and z_k the ion number (which is +1 for K^+), the above equation can be written as

$$\mu_{K^+}^0 + RT \ln a_{K^+}^\alpha + F\phi^\alpha = \mu_{K^+}^0 + RT \ln a_{K^+}^\beta + F\phi^\beta \quad (10.2.2)$$

From this equation it follows that the potential difference, i.e. the **membrane potential** $\phi^\alpha - \phi^\beta$ across the membrane, can now be written as

$$\phi^\alpha - \phi^\beta = \frac{RT}{F} \ln \left(\frac{a_{K^+}^\beta}{a_{K^+}^\alpha} \right) \quad (10.2.3)$$

In electrochemistry, the concentrations are generally measured using the molality scale, as was discussed in Chapter 8. In the simplest approximation, the activities may be replaced by molalities m_{K^+} , i.e. the activity coefficients are assumed to be unity. Hence, one may estimate the membrane potential with the formula $\phi^\alpha - \phi^\beta = (RT/F) \ln(m_{K^+}^\beta / m_{K^+}^\alpha)$.

10.2.2 Electrochemical Affinity and Electromotive Force

In an electrochemical cell, the reactions at the electrodes that transfer electrons can generate an electromotive force (EMF). An electrochemical cell generally has different phases that separate the two electrodes

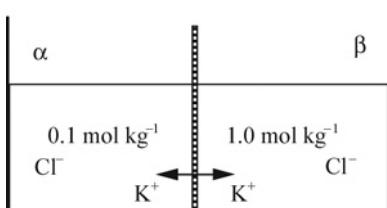


Figure 10.4 A membrane potential is generated when a membrane permeable to K^+ but not to Cl^- separates two solutions of KCl of unequal concentrations. In this case, the flow of the permeable K^+ ions is counterbalanced by the membrane potential.

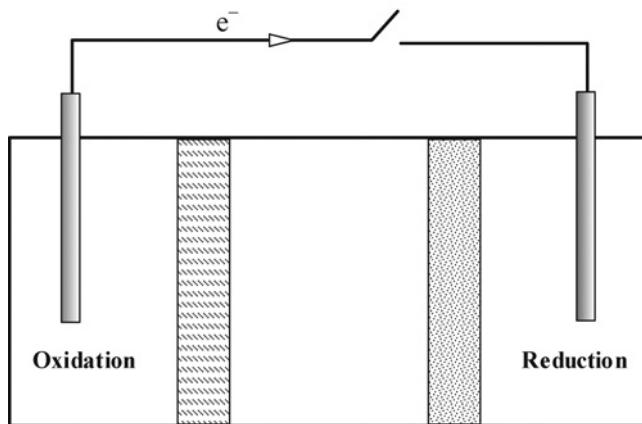


Figure 10.5 An electrochemical cell consisting of many phases that generate an EMF due to half-reactions at the electrodes. The electrode reactions are as given in Equations (10.2.4) and (10.2.5). Upon closing the circuit, chemical reactions occurring within the cell will generate an EMF that will drive a current. Cells such as this are represented by a cell diagram denoting the various phases and junctions. In a cell diagram, the reduction reaction is on the right.

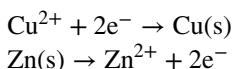
(Figure 10.5). By considering entropy production due to the overall reaction and the electric current flowing through the system we can derive a relationship between the activities and the EMF. In an electrochemical cell, the reactions at the two electrodes can be generally written as



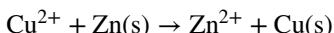
Each is called a **half-reaction**; the overall reaction is



For example, the half-reactions



at the two electrodes result in the overall reaction



(Thus, a zinc rod placed in an aqueous solution of CuSO_4 will dissolve and metallic copper will be deposited.)

Reactions at the electrodes may be more complicated than those indicated above, but the main idea is the same: at one electrode, electrons are transferred *from* the electrode; at the other electrode, electrons are transferred *to* the electrode. In representing electrochemical cells diagrammatically, it has become a convention to place the **'reduction' half-reaction on the right**. Thus, the electrode on the right-hand side of the diagram supplies the electrons that reduce the reactants.

Since the reactions at the electrodes may occur at different electrical potentials, we must use the electrochemical affinity to formulate the thermodynamics of an electrochemical cell. If \tilde{A} is the electrochemical affinity and ξ is the extent of reaction, the entropy production due to such a reaction is

$$\frac{d_i S}{dt} = \frac{\tilde{A}}{T} \frac{d\xi}{dt} \quad (10.2.7)$$

Since each mole of reacting X transfers n moles of electrons (see Equation (10.2.4)), and since $d\xi/dt$ is the velocity of the reaction, the relation between the current I (which is the amount of charge transferred per second) is

$$I = nF \frac{d\xi}{dt} \quad (10.2.8)$$

in which F is the Faraday constant (the amount of charge carried by a mole of electrons). Substituting Equation (10.2.8) in Equation (10.2.7) we find

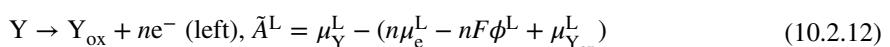
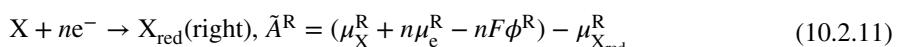
$$\frac{d_i S}{dt} = \frac{1}{T} \frac{\tilde{A}}{nF} I \quad (10.2.9)$$

Comparing this expression with Equation (10.1.17) we obtain the following relation between the voltage and the associated electrochemical affinity:

$$V = \boxed{\frac{\tilde{A}}{nF}} \quad (10.2.10)$$

in which n is the number of electrons transferred in the oxidation–reduction reaction. For a given \tilde{A} , the larger the number of electrons transferred, the smaller the potential difference.

Using the electrode reactions (10.2.4) and (10.2.5), the above expression can be more explicitly written in terms of the chemical potentials:



in which the superscripts indicate the reactions at the right and left electrodes. The electrochemical affinity of the electron in the left electrode is written as $\tilde{\mu}_e = \mu_e^L - F\phi^L$, and similarly for the electrons in the right electrode. The overall electrochemical affinity \tilde{A} , which is the sum of the two affinities, can now be written as

$$\tilde{A} = \tilde{A}^R + \tilde{A}^L = (\mu_X^R + \mu_Y^L - \mu_{X_{\text{red}}}^R - \mu_{Y_{\text{ox}}}^L) + n(\mu_e^R - \mu_e^L) - nF(\phi^R - \phi^L) \quad (10.2.13)$$

If the two electrodes are identical, then $\mu_e^R = \mu_e^L$ and the only difference between the two electrodes is in their electrical potential ϕ . By virtue of Equation (10.2.10), we can now write the voltage V associated with the above electrochemical affinity as

$$V = \frac{\tilde{A}}{nF} = \frac{1}{nF} (\mu_X^R + \mu_Y^L - \mu_{X_{\text{red}}}^R - \mu_{Y_{\text{ox}}}^L) - (\phi^R - \phi^L) \quad (10.2.14)$$

Now let us consider the ‘terminal voltage’ $V_{\text{cell}} = \phi^R - \phi^L$, the potential difference between the terminals for which $\tilde{A} = 0$. It is the open-circuit condition with zero current, similar to the osmotic pressure difference

at zero affinity. This terminal voltage V_{cell} is called the **EMF of the cell**. From Equation (10.2.14) we see that

$$V_{\text{cell}} = \frac{1}{nF}(\mu_X^R + \mu_Y^L - \mu_{X_{\text{red}}}^R - \mu_{Y_{\text{ox}}}^L) \quad (10.2.15)$$

For a nonzero \tilde{A} , i.e. for nonzero current, the terminal voltage is less than the EMF. On the other hand, if the potentials of the two electrodes are equalized by shorting the two terminals, then $\phi^R - \phi^L = 0$, and the flow of current $I = nF(d\xi/dt)$ is limited only by the rate of electron transfer at the electrodes. Under these conditions the voltage in Equation (10.2.14), $V = \tilde{A}/nF$ is also equal to the right-hand side of Equation (10.2.15).

It is more convenient to write the cell EMF (Equation (10.2.15)) in terms of the activities by using the general expression $\mu_k = \mu_k^0 + RT \ln a_k$ for the reactants and products. This leads to the well-known **Nernst equation**

$$V = V_0 - \frac{RT}{nF} \ln \left(\frac{a_{X_{\text{red}}}^R a_{Y_{\text{ox}}}^L}{a_X^R a_Y^L} \right) \quad (10.2.16)$$

where

$$V_0 = \frac{1}{nF}(\mu_{X0}^R + \mu_{Y0}^L - \mu_{X_{\text{red}}0}^R - \mu_{Y_{\text{ox}}0}^L) = \frac{-\Delta G_r^0}{nF} \quad (10.2.17)$$

Equation (10.2.16) relates the cell potential to the activities of the reactants. As we expect, V is zero at equilibrium and the equilibrium constant of the electrochemical reaction can be written as

$$\ln K = \frac{-\Delta G_r^0}{RT} = \frac{nFV_0}{RT} \quad (10.2.18)$$

10.2.3 Galvanic and Electrolytic Cells

A cell in which a chemical reaction generates an electric potential difference is called a **galvanic cell**; if an external source of electric voltage drives a chemical reaction, then it is called an **electrolytic cell**. Such electrochemical cells are represented by cell diagrams, as described in Box 10.1.

Box 10.1 Electrochemical cells and cell diagrams

When there is an external flow of current, there must be a compensating current within the cell. This can be accomplished in many ways, each defining a type of electrochemical cell. The choice of electrodes is also decided by the experimental conditions and the need to use an electrode without undesirable side reactions. Electrochemical cells often incorporate **salt bridges** and **liquid junctions**.

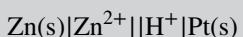
Liquid junctions. When two different liquids are in contact, usually through a porous wall, it is called a liquid junction. The concentrations of ions and their electrochemical potentials on either side of a liquid junction are generally not equal; the electrochemical potential difference causes a diffusional flow of ions. If the rates of flow of the different ions are unequal, then a potential difference will be generated across the liquid junction. Such a potential is called the **liquid junction potential**. The liquid junction potential may be reduced by the use of a **salt bridge**, in which the flows of the positive and negative ions are nearly equal.

Salt bridge. A commonly used salt bridge consists of a solution of KCl in agarose gel. In this medium, the flow of K^+ and Cl^- are nearly equal.

Cell diagrams. An electrochemical cell diagram is drawn adopting the following conventions:

- Reduction reaction occurs at the electrode on the right.
- The symbol | indicates a phase boundary, such as the boundary between a solid electrode and a solution.
- The symbol ‘:’ indicates a liquid junction, such as a porous wall separating a solution of $CuSO_4$ and $CuCl$.
- The symbol || or : : indicates a salt bridge, such as KCl in agarose gel.

For example, the cell in Figure 10.6 is represented by the following cell diagram:



Let us consider a simple reaction. When Zn reacts with an acid, H_2 is evolved. It is a simple electron-transfer reaction:



The reason why the electrons migrate from one atom to another is a difference in electrical potential; that is, in the above reaction, when an electron moves from a Zn atom to an H^+ ion, it is moving to a location of lower potential energy. An interesting possibility now arises: if the reactants are placed in a ‘cell’ such that the only way an electron transfer can occur is through a conducting wire, then we have a situation in which a chemical affinity drives an electric current. Such a cell would be a **galvanic cell**, as shown in Figure 10.6, in which the sum of the electrode half-reactions is Equations (10.2.19) and the flow of electrons occurs through an external circuit. Conversely, through an external EMF, the electron transfer can be reversed, which is the case in an **electrolytic cell**.

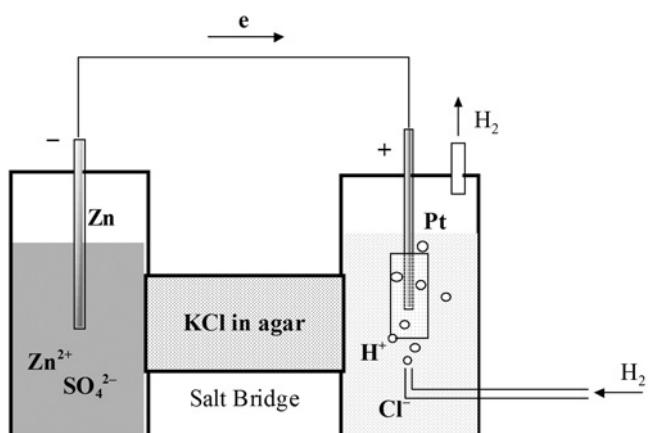


Figure 10.6 An example of a galvanic cell that is driven by the reaction $Zn(s) + 2H^+ \rightarrow Zn^{2+} + H_2$. The two electrode chambers are connected through a salt bridge that allows for the flow of current without introducing a liquid junction potential.

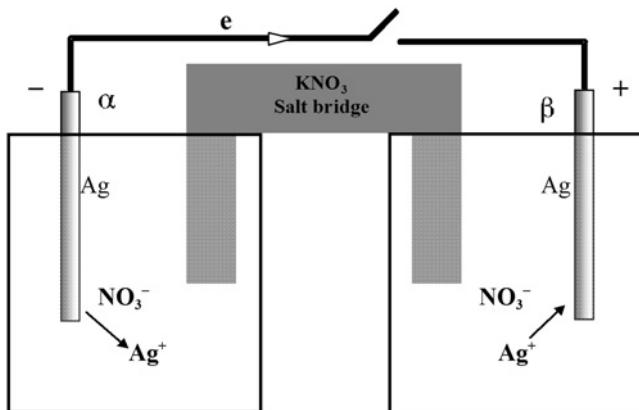


Figure 10.7 A concentration difference can generate an EMF. Two beakers containing AgNO_3 solutions at different concentrations are connected by a KNO_3 salt bridge. A silver electrode is placed in each cell. The difference in concentrations generates an EMF.

The EMF generated by a galvanic cell, as shown above, is given by the Nernst equation. In the above example, the cell EMF is given by

$$V = V_0 - \frac{RT}{nF} \ln \left(\frac{a_{\text{H}_2} a_{\text{Zn}^{2+}}}{a_{\text{Zn(s)}} a_{\text{H}^+}^2} \right) \quad (10.2.20)$$

10.2.4 Concentration Cell

The affinity generated by a concentration difference can also generate an EMF. A simple example of an AgNO_3 concentration cell in which a concentration-driven EMF can be realized is shown in Figure 10.7. The two beakers are linked by a KNO_3 salt bridge (a gel containing KNO_3 solution). A silver electrode is placed in each beaker. If the two electrodes are connected by a wire, the difference in electrochemical potential of Ag^+ ions causes a flow of electrons from one silver electrode to another, absorbing Ag^+ in the beaker that has a higher concentration and releasing them in the beaker that has a lower concentration.

The reactions at the two electrodes are



which amounts to transfer of Ag^+ ions from a higher concentration to a lower concentration. Electroneutrality is maintained in both beakers by the migration of K^+ and NO_3^- ions through the salt bridge. For such a cell V_0 in the Nernst equation equals zero because the reaction at one electrode is the reverse of the reaction at the other and the standard states of reactants and products are the same. Thus, for a concentration cell:

$$V_{\text{cell}} = -\frac{RT}{nF} \ln \left(\frac{a_{\text{Ag}^+}^\beta}{a_{\text{Ag}^+}^\alpha} \right) \quad (10.2.22)$$

10.2.5 Standard Electrode Potentials

Just as the tabulation of the Gibbs energies of formation facilitates the computation of equilibrium constants, the tabulation of **standard electrode potentials** facilitates the computation of equilibrium constants for electrochemical reactions. A voltage is assigned to each electrode half-reaction with the convention that the voltage of the hydrogen–platinum electrode, $\text{H}^+|\text{Pt}$, is zero. That is, the electrode reaction $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g})$ at a Pt electrode is taken to be the reference and the voltages associated with all other electrode reactions are measured with respect to it. *The standard electrode potentials are the potentials when activities of all the reactants and products equal one at $T = 298.15\text{ K}$.* For any cell, the voltages of the corresponding standard potentials are added to obtain the cell potentials. Since these potentials correspond to the situation when all the activities are equal to one, it follows from the Nernst equation that the standard cell voltage is equal to V_0 .

Example 10.3 shows how an equilibrium constant may be computed using the standard electrode potentials. A list of some of the commonly used standard electrode potentials is given in Table 10.1. In using the standard potentials, one must note that: (a) changing the stoichiometry does not change V_0 and (b) if the reaction is reversed, then the sign of V_0 also reverses.

Table 10.1 Standard electrode potentials.

Electrode reaction	V_0 (V)	Electrode
$\frac{1}{3}\text{Au}^{3+} + \text{e}^- \rightarrow \frac{1}{3}\text{Au}$	1.50	$\text{Au}^{3+} \text{Au}$
$\frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-$	1.360	$\text{Cl}^- \text{Cl}_2(\text{g}) \text{Pt}$
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.799	$\text{Ag}^+ \text{Ag}$
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.521	$\text{Cu}^+ \text{Cu}$
$\frac{1}{2}\text{Cu}^{2+} + \text{e}^- \rightarrow \frac{1}{2}\text{Cu}(\text{s})$	0.339	$\text{Cu}^{2+} \text{Cu}$
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.222	$\text{Cl}^- \text{AgCl}(\text{s}) \text{Ag}$
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.153	$\text{Cu}^{2+} \text{Cu}^+ \text{Pt}$
$\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g})$	0.0	$\text{H}^+ \text{H}_2 \text{Pt}$
$\frac{1}{2}\text{Pb}^{2+} + \text{e}^- \rightarrow \frac{1}{2}\text{Pb}(\text{s})$	-0.126	$\text{Pb}^{2+} \text{Pb}(\text{s})$
$\frac{1}{2}\text{Sn}^{2+} + \text{e}^- \rightarrow \frac{1}{2}\text{Sn}(\text{s})$	-0.140	$\text{Sn}^{2+} \text{Sn}(\text{s})$
$\frac{1}{2}\text{Ni}^{2+} + \text{e}^- \rightarrow \frac{1}{2}\text{Ni}(\text{s})$	-0.250	$\text{Ni}^{2+} \text{Ni}(\text{s})$
$\frac{1}{2}\text{Cd}^{2+} + \text{e}^- \rightarrow \frac{1}{2}\text{Cd}(\text{s})$	-0.402	$\text{Cd}^{2+} \text{Cd}(\text{s})$
$\frac{1}{2}\text{Zn}^{2+} + \text{e}^- \rightarrow \frac{1}{2}\text{Zn}(\text{s})$	-0.763	$\text{Zn}^{2+} \text{Zn}(\text{s})$
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.714	$\text{Na}^+ \text{Na}(\text{s})$
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.045	$\text{Li}^+ \text{Li}(\text{s})$

Note. (a) Changing the stoichiometry does not change V_0 . (b) If the reaction is reversed, the sign of V_0 also reverses.

10.3 Isothermal Diffusion

We have already seen in Section 4.3 that the flow of particles from a region of high concentration to a region of lower concentration is a flow driven by unequal chemical potentials. For a discrete system consisting of two parts of equal temperature T , one with chemical potential μ_1 and molar amount N_1 and the other with chemical potential μ_2 and molar amount N_2 we have the following relation:

$$-dN_1 = dN_2 = d\xi \quad (10.3.1)$$

The entropy production that results from unequal chemical potentials is

$$d_i S = -\left(\frac{\mu_2 - \mu_1}{T}\right) d\xi = \frac{A}{T} d\xi > 0 \quad (10.3.2)$$

The positivity of this quantity, required by the Second Law, implies that particle transport is from a region of higher chemical potential to a region of lower chemical potential. It is the diffusion of particles from a region of higher chemical potential to a region of lower chemical potential. In most situations this is a flow of a component from a higher concentration to a lower concentration. At equilibrium, the concentrations become uniform, but this need not be so in every case. For example, when a liquid is in equilibrium with its vapor or when a gas reaches equilibrium in the presence of a gravitational field, the chemical potentials becomes uniform, not the concentrations. *The tendency of the thermodynamic forces that drive matter flow is to equalize the chemical potential, not the concentrations.*

10.3.1 Diffusion in a Continuous System and Fick's Law

Expression (10.3.2) can be generalized to describe a continuous system, as was done for the general case of a field in Section 10.1 (Figure 10.3). Let us consider a system in which the variation of the chemical potential is along one direction only, say x . We shall also assume that T is uniform and does not change with position. Then, as in Equation (10.1.13), the rate of entropy production for diffusion is

$$\frac{d_i s(x)}{dt} = -\sum_k \frac{1}{T} \left(\frac{\partial \mu_k}{\partial x} \right) J_{Nk} \quad (10.3.3)$$

For simplicity, let us consider the flow of a single component k :

$$\frac{d_i s(x)}{dt} = -\frac{1}{T} \left(\frac{\partial \mu_k}{\partial x} \right) J_{Nk} \quad (10.3.4)$$

We note, once again, that the entropy production is the product of a thermodynamic flow J_{Nk} and the force, $-(1/T)(\partial \mu_k / \partial x)$, that drives it. The identification of a thermodynamic force and the corresponding flow enables us to relate the two. Near equilibrium, the flow is linearly proportional to the force. In the above case, we can write this linear relation as

$$J_{Nk} = -L_k \frac{1}{T} \left(\frac{\partial \mu_k}{\partial x} \right) \quad (10.3.5)$$

The constant of proportionality, L_k , is the linear phenomenological coefficient for diffusional flow. We saw earlier that, in an ideal fluid mixture, the chemical potential can be written as $\mu(p, T, x_k) = \mu(p, T) + RT \ln x_k$, in which x_k is the mole fraction, which in general is a function of position. If n_{tot} is the total molar density and n_k is the molar density of component k , then the mole fraction $x_k = n_k/n_{\text{tot}}$. We shall assume that the change of n_{tot} due to diffusion is insignificant, so that $\partial \ln x_k / \partial x = \partial \ln n_k / \partial x$. Then, substituting

Table 10.2 Diffusion coefficients of molecules in gases and liquids.

Compound, in air ($p = 101.325 \text{ kPa}$, $T = 293.15 \text{ K}$)	$D (10^{-4} \text{ m}^2 \text{ s}^{-1})$	Solute, in water ($T = 298.15 \text{ K}$)	$D (10^{-9} \text{ m}^2 \text{ s}^{-1})$
CH_4	0.106	Sucrose	0.52
Ar	0.148	Glucose	0.67
CO_2	0.160	Alanine	0.91
CO	0.208	Ethylene glycol	1.16
H_2O	0.242	Ethanol	1.24
He	0.580	Acetone	1.28
H_2	0.627		

Source: D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 75th edition, 1994, CRC Press: Ann Arbor, MI.

$\mu(p, T, x_k) = \mu(p, T) + RT \ln x_k$ into Equation (10.3.5), we obtain the following thermodynamic relation between the diffusion current J_{Nk} and the concentration:

$$J_{Nk} = -L_k R \frac{1}{n_k} \frac{\partial n_k}{\partial x} \quad (10.3.6)$$

Empirical studies of diffusion have led to what is called Fick's law. According to **Fick's law**:

$$J_{Nk} = -D_k \frac{\partial n_k}{\partial x} \quad (10.3.7)$$

in which D_k is the diffusion coefficient of the diffusing component k . Typical values of the diffusion coefficients for gases and liquids are given in Table 10.2. Clearly, this expression is the same as Equation (10.3.6) if we make the identification

$$D_k = \frac{L_k R}{n_k} \quad (10.3.8)$$

This gives us a relation between the thermodynamic phenomenological coefficient L_k and the empirical diffusion coefficient.

An important point to note is that the thermodynamic relation (10.3.5) is valid in all cases, whereas Fick's law (10.3.7) is not. For example, in the case of a liquid in equilibrium with its vapor, since the chemical potential is uniform, $(\partial \mu_k / \partial x) = 0$ and (10.3.5) correctly predicts $J_{Nk} = 0$; but (10.3.7) does not predict $J_{Nk} = 0$ because $(\partial n_k / \partial x) \neq 0$. In general, if we write (10.3.5) as $J_{Nk} = -(L_k/T)(\partial \mu_k / \partial n_k)(\partial n_k / \partial x)$, then we see that, depending on the sign of $(\partial \mu_k / \partial n_k)$, J_{Nk} can be positive or negative when $(\partial n_k / \partial x) > 0$. Thus, the flow is toward the region of lower concentration when $(\partial \mu_k / \partial n_k) > 0$, but the flow can be to the region of higher concentration when $(\partial \mu_k / \partial n_k) < 0$. The latter situation arises when a mixture of two components is separating into two phases: each component flows from a region of lower concentration to a region of higher concentration. As we shall see in later chapters, the system is 'unstable' when $(\partial \mu_k / \partial n_k) < 0$.

10.3.2 The Diffusion Equation

In the absence of chemical reactions, the only way the molar density $n_k(x, t)$ can change with time is due to the flow J_{Nk} . Consider a small cell of size δ at a location x (Figure 10.8). The molar amount in this cell is equal to $n_k(x, t)\delta$. The rate of change of the molar amount in this cell is $\partial(n_k(x, t)\delta)/\partial t$. This change is due to

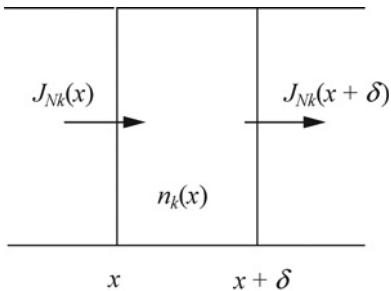


Figure 10.8 In the absence of chemical reactions, the change in the molar amount of a substance in a small cell of size δ , at a location x , equals the net flow, the difference in the flow J_{Nk} into and out of the cell. The number of moles in the cell of size δ is $n_k\delta$. The net flow into the cell of size δ is given by Equation (10.3.9). This difference in the flow will cause a net rate of change in the mole amount $\partial(n_k(x, t)\delta)/\partial t$. On equating the net flow to the rate of change of the molar amount, we obtain the equation $\partial n_k(x, t)/\partial t = -\partial J_{Nk}/\partial x$.

the net flow, i.e. the difference between the inflow and the outflow of component k in the cell. The net flow into the cell of size δ is equal to

$$J_{Nk}(x) - J_{Nk}(x + \delta) = J_{Nk}(x) - \left(J_{Nk}(x) + \frac{\partial J_{Nk}}{\partial x} \delta \right) = -\frac{\partial J_{Nk}}{\partial x} \delta \quad (10.3.9)$$

Equating the net flow to the rate of change of the molar amount, we obtain the equation

$$\frac{\partial n_k(x, t)}{\partial t} = -\frac{\partial J_{Nk}}{\partial x} \quad (10.3.10)$$

Using Fick's law (10.3.7), we can write this equation entirely in terms of $n_k(x, t)$ as

$$\frac{\partial n_k(x, t)}{\partial t} = D_k \frac{\partial^2 n_k(x, t)}{\partial x^2}$$

(10.3.11)

This partial differential equation for $n_k(x)$ is the **diffusion equation** for the component k . It is valid in a homogeneous system. In a homogeneous system, diffusion tends to eliminate concentration differences and equalize the concentrations throughout the system. However, it must be borne in mind that, in general, the thermodynamic force tends to equalize the chemical potential, not the concentrations.

10.3.3 The Stokes–Einstein Relation

The viscous force on a particle in a fluid and its diffusive motion are both results of random molecular collisions. A particle diffuses due to random collisions it undergoes with the fluid molecules, and it can also transfer its momentum to the fluid molecules during these collisions. The latter process appears as the viscous force on a macro level. Through thermodynamics one can see that the diffusion coefficient and the coefficient of viscous force or ‘friction’ must be related – a reflection of the fact that both are the result of molecular collisions. This relation is called the **Stokes–Einstein relation**.

Fick's law gives us the diffusion current in the presence of a concentration gradient. In the presence of a field, there is also a current, which is proportional to the strength of the field. For example, in the presence of an electric field \mathbf{E} , an ion carrying a charge $e z_k$ will drift at constant speed proportional to the magnitude of the force $e z_k |\mathbf{E}|$. This happens because the force due to the field F_{field} (whose magnitude equals $e z_k |\mathbf{E}|$ for

ions) accelerates the ion till the opposing viscous or frictional force, which is proportional to the velocity, balances F_{field} . When the ion moves at a speed v , the viscous force equals $\gamma_k v$, in which γ_k is the coefficient of viscous force. When the two forces balance, $\gamma_k v = F_{\text{field}}$ and the ion will drift with a **terminal velocity** v . Hence, the terminal or **drift velocity** can be written as

$$v = \frac{F_{\text{field}}}{\gamma_k} \quad (10.3.12)$$

Since the number of ions that drift is proportional to the concentration n_k , the ionic drift gives rise to the following particle current density I_k due to the component k along the x axis:

$$I_k = vn_k = \frac{ez_k}{\gamma_k} n_k E_x = -\Gamma_k n_k \frac{\partial \phi}{\partial x} \quad (10.3.13)$$

in which the constant $\Gamma_k = ez_k/\gamma_k$ is called the **ionic mobility** of the ion k and E_x is the x -component of \mathbf{E} . (Note that the total electric current density due to all the ions $I = \sum_k ez_k I_k$.) Similarly, a molecule of mass m_k , falling freely in the atmosphere, or any fluid, will reach a ‘terminal velocity’ $v = gm_k/\gamma_k$, where g is the acceleration due to gravity. In general, for any potential ψ associated with a conservative field, the mobility of a component k is defined by

$$J_{\text{field}} = -\Gamma_k n_k \frac{\partial \psi}{\partial x} \quad (10.3.14)$$

Linear phenomenological laws of nonequilibrium thermodynamics lead to a general relation between mobility Γ_k and the diffusion coefficient D_k . This relation can be obtained as follows. The general expression for the chemical potential in a field with potential ψ is given by $\tilde{\mu}_k = \mu_k + \tau_k \psi$, in which τ_k is the interaction energy per mole due to the field (10.1.5). In the simplest approximation of an ideal system, if we write the chemical potential in terms of the concentration n_k , then we have

$$\tilde{\mu}_k = \mu_k^0 + RT \ln(n_k) + \tau_k \psi \quad (10.3.15)$$

A gradient in this chemical potential will result in a thermodynamic flow

$$J_{Nk} = -L_k \frac{1}{T} \left(\frac{\partial \tilde{\mu}_k}{\partial x} \right) = -\frac{L_k}{T} \left(\frac{RT}{n_k} \frac{\partial n_k}{\partial x} + \tau_k \frac{\partial \psi}{\partial x} \right) \quad (10.3.16)$$

where we have used $\partial \ln x_k / \partial x = \partial \ln n_k / \partial x$. In Equation (10.3.16), the first term on the right-hand side is the familiar diffusion current and the second term is the drift current due to the field. Comparing this expression with Fick’s law (10.3.7) and expression (10.3.14) that defines mobility, we see that

$$\frac{L_k R}{n_k} = D_k, \frac{L_k \tau_k}{T} = \Gamma_k n_k \quad (10.3.17)$$

From these two relations it follows that the diffusion coefficient D_k and the mobility Γ_k have the following general relation:

$$\boxed{\frac{\Gamma_k}{D_k} = \frac{\tau_k}{RT}} \quad (10.3.18)$$

This relation was first obtained by Einstein and is sometimes called the **Einstein relation**. For ionic systems, as we have seen in Section 10.1 (see Equation (10.1.5)), $\tau_k = F z_k = e N_A z_k$ and $\Gamma_k = e z_k / \gamma_k$. Since $R = k_B N_A$,

in which k_B is the Boltzmann constant and N_A the Avogadro number, Equation (10.1.18) for **ionic mobility** Γ_k becomes

$$\frac{\Gamma_k}{D_k} = \frac{ez_k}{\gamma_k D_k} = \frac{z_k F}{RT} = \frac{ez_k}{k_B T} \quad (10.3.19)$$

which leads to the following general relation between the diffusion coefficient D_k and the friction coefficient γ_k of a molecule or ion k , called the **Stokes–Einstein relation**:

$$D_k = \frac{k_B T}{\gamma_k}$$

(10.3.20)

10.4 Chemical Potential for an Internal Degree of Freedom

The notion of a chemical potential can also be extended to transformations in an internal degree of freedom of molecules such as orientation of a polar molecule with respect to an external field (Figure 10.9) or deformation of a macromolecule due to flow and similar phenomena [2]. This can be done by defining an internal coordinate θ just as we define an ‘external coordinate’ such as the position x . In this section, we shall only consider the orientation of an electric dipole of a polar molecule with respect to an electric field (generalization to other situations being straightforward). In this case, θ is the angle between the direction of the field and the dipole, as shown in Figure 10.9. Just as we defined a concentration as a function of position, we can also define a concentration $n(\theta)$ as a function of θ . Just as electrochemical potential is a function of position and the potential of a field, for an internal coordinate θ , the chemical potential of component k is a function of θ and the potential:

$$\tilde{\mu}_k(\theta, T) = \tilde{\mu}_k(\theta, T) + g_k \phi(\theta) \quad (10.4.1)$$

in which $g_k \phi(\theta)$ is the interaction energy per mole between the field and the dipole. If the dipole moment per mole is \mathbf{p}_k and the electric field \mathbf{E} , then

$$g_k \phi(\theta) = -|\mathbf{p}| |\mathbf{E}| \cos(\theta) \quad (10.4.2)$$

in which we may identify $g_k = |\mathbf{p}|$ and $\phi(\theta) = -|\mathbf{E}| \cos(\theta)$.

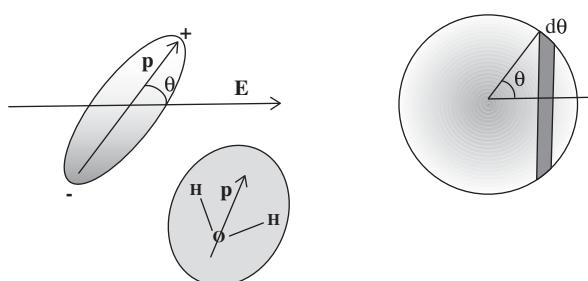


Figure 10.9 Chemical potential $\mu(\theta)$ can be defined for an internal degree of freedom such as the orientation of a polar molecule with respect to an electric field \mathbf{E} . The electric dipole moment is denoted by \mathbf{p} . The energy of an electric dipole in field \mathbf{E} is given by $-\mathbf{p} \cdot \mathbf{E}$. A water molecule is an example of a molecule with a dipole moment. Since the oxygen atom tends to accumulate negative charge, there is a slight charge separation giving rise to an electric dipole moment.

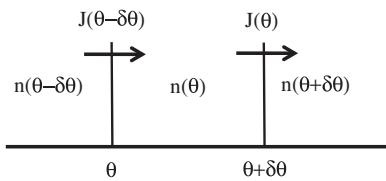


Figure 10.10 Reaction scheme for a continuous internal degrees of freedom.

Other quantities, such as concentration $n_k(\theta)$, entropy density $s(\theta)$, and the ‘flow’ in the θ space can be defined as a function of θ , just as they were defined as functions of x . However, in spherical coordinates, on a unit sphere, since the area of the segment between θ and $\theta + d\theta$ is equal to $2\pi \sin \theta d\theta d\phi$, we use the following definitions:

$s(\theta) 2\pi \sin \theta d\theta$ = entropy of molecules with an internal coordinate between θ and $\theta + d\theta$

$n(\theta) 2\pi \sin \theta d\theta$ = molar amount of molecules with an internal coordinate between θ and $\theta + d\theta$

$J_\theta 2\pi \sin \theta d\theta$ = the molar amount of molecules whose orientation is changing from θ to $\theta + d\theta$ per unit time (see Figure 10.10)

For simplicity we consider a unit volume and only one species and drop the subscript k of n .

With these definitions it is clear that all the formalism that was developed in Section 10.1 for the position x can be directly converted to θ by formally replacing x with θ . Accordingly, we are led to the equation:

$$\frac{d_i s(\theta)}{dt} = -\frac{1}{T} \left(\frac{\partial \tilde{\mu}(\theta)}{\partial \theta} \right) J_N(\theta) > 0 \quad (10.4.3)$$

which is similar to Equation (10.1.13). In the above equation we can identify the affinity as

$$\tilde{A}(\theta) = -\frac{\partial \tilde{\mu}(\theta)}{\partial \theta} \quad (10.4.4)$$

for the ‘reaction’ $n(\theta) \rightleftharpoons n(\theta + \delta\theta)$ with the corresponding extent of reaction $\xi(\theta)$. The velocity of this reaction $J_N(\theta) = d\xi(\theta)/dt$ (see Figure 10.10) is the number of molecules being transformed from θ to $\theta + d\theta$. With these definitions, the rate of entropy production can also be written as

$$\frac{d_i s(\theta)}{dt} = -\frac{1}{T} \left(\frac{\partial \tilde{\mu}(\theta)}{\partial \theta} \right) \frac{d\xi(\theta)}{dt} > 0 \quad (10.4.5)$$

For a system with an internal coordinate such as θ , the total rate of entropy change is given by

$$\begin{aligned} \frac{dS}{dt} &= \frac{1}{T} \frac{dU}{dt} + \frac{p}{T} \frac{dV}{dt} - \frac{1}{T} \int_{\theta} \frac{\partial \mu(\theta)}{\partial \theta} \frac{d\xi(\theta)}{dt} d\theta \\ &= \frac{1}{T} \frac{dU}{dt} + \frac{p}{T} \frac{dV}{dt} - \frac{1}{T} \int_{\theta} \frac{\partial \mu(\theta)}{\partial \theta} J_N(\theta) d\theta \end{aligned} \quad (10.4.6)$$

For the total entropy production the Second Law implies that

$$\frac{d_i S}{dt} = -\frac{1}{T} \int_{\theta} \frac{\partial \mu(\theta)}{\partial \theta} J_N(\theta) d\theta > 0 \quad (10.4.7)$$

In the formalism presented above, we have a more restrictive statement of the Second Law expressed in Equation (10.4.5). When the system reaches equilibrium, since the affinity becomes zero, we have

$$\tilde{A}(\theta) = \frac{\partial[\mu(\theta) + g\phi(\theta)]}{\partial\theta} = 0 \quad (10.4.8)$$

Writing the chemical potential more explicitly, we may then conclude that at equilibrium:

$$\tilde{\mu}(\theta) = \mu_0(T) + RT \ln[a(\theta)] + g\phi(\theta) = C \quad (10.4.9)$$

in which C is a constant and $a(\theta)$ is the activity for the molecules with orientation θ with respect to the field \mathbf{E} (see Figure 10.9). Also note that, in the absence of a field, since all orientations are equivalent, μ_0 should be independent of θ . As we have noted before, the activity of an ideal mixture can be approximated by the mole fraction. For an internal degree of freedom, each value of θ may be taken as a species and, by analogy, we may define an ideal activity by $a(\theta) = n(\theta)/n_{\text{tot}}$ in which n_{tot} is the total number of dipoles. It is now a matter of elementary calculation to show that, at equilibrium:

$$n(\theta) = n_{\text{tot}} F(T) e^{-g\phi(\theta)/RT} = n_{\text{tot}} F(T) e^{|\mathbf{p}||\mathbf{E}| \cos \theta / RT} \quad (10.4.10)$$

in which $F(T)$ is a function of T , expressed in terms of $\mu_0(T)$ and C (Exercise 10.8), and in which we have used Equation (10.4.2). Note also that $F(T)$ should be such that $\int_0^\pi n(\theta) \sin(\theta) d\theta = n_{\text{tot}}$.

10.4.1 The Debye Equation for Electric Dipole Relaxation

Since the only possible way in which $n(\theta)$ can change is due to the current $J_N(\theta)$, we have a situation analogous to diffusion, as illustrated in Figure 10.10. As noted earlier, in spherical coordinates we use the following definitions:

$$\begin{aligned} n(\theta) 2\pi \sin \theta d\theta &= \text{molar amount of molecules with internal coordinate between } \theta \text{ and } \theta + d\theta \\ J_\theta 2\pi \sin \theta d\theta &= \text{molar amount of molecules whose orientation is changing from } \theta \text{ to } \theta + d\theta \text{ per unit time} \end{aligned}$$

From these definitions, it follows that the conservation equation for the dipoles is

$$\frac{\partial n(\theta) \sin(\theta)}{\partial t} = - \frac{\partial J_N(\theta) \sin(\theta)}{\partial \theta} \quad (10.4.11)$$

As we did in the case of diffusion, by looking at the entropy production (10.4.3), we can identify the force corresponding to the flow $J_N(\theta)$ as $-1/T(\partial\tilde{\mu}(\theta)/\partial\theta)$. When the system is near equilibrium, there exists a linear relation between the flow and the force, which can be written as

$$J_N(\theta) = -\frac{L_\theta}{T} \frac{\partial\tilde{\mu}(\theta)}{\partial\theta} \quad (10.4.12)$$

in which L_θ is the linear phenomenological coefficient. In the approximation of an ideal mixture:

$$\tilde{\mu}(\theta) = \mu_0(T) + RT \ln(n(\theta)/n_{\text{tot}}) - |\mathbf{p}||\mathbf{E}| \cos \theta \quad (10.4.13)$$

Substituting Equation (10.4.13) into Equation (10.4.12), we obtain

$$J_N(\theta) = -\frac{L_\theta R}{n(\theta)} \frac{\partial n(\theta)}{\partial \theta} + \frac{L_\theta}{T} |\mathbf{p}| |\mathbf{E}| \frac{\partial}{\partial \theta} \cos \theta \quad (10.4.14)$$

In analogy with ordinary diffusion, we may define a rotational diffusion in the θ -space, for which expression (10.4.14) corresponds to Fick's law. A rotational diffusion coefficient D_θ may now be identified as

$$D_\theta = \frac{L_\theta R}{n(\theta)} \quad (10.4.15)$$

With this identification, the flow $J_N(\theta)$ given by Equation (10.4.14) can be written as

$$J_N(\theta) = -D_\theta \frac{\partial n(\theta)}{\partial \theta} - \left[\frac{D_\theta}{TR} |\mathbf{p}| |\mathbf{E}| \sin \theta \right] n(\theta) \quad (10.4.16)$$

Finally, substituting this expression in Equation (10.4.11) gives

$$\frac{\partial n(\theta)}{\partial t} = \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \left(D_\theta \frac{\partial n(\theta)}{\partial \theta} + \left[\frac{D_\theta}{TR} |\mathbf{p}| |\mathbf{E}| \sin \theta \right] n(\theta) \right) \quad (10.4.17)$$

This is the **Debye equation** for the relaxation of dipoles in an electric field. It has been used for analyzing the relaxation of dipoles in an oscillating electric field.

References

1. Guggenheim, E.A., *Modern Thermodynamics*. 1933, Methuen: London.
2. Prigogine, I., Mazur, P., Sur l'extension de la thermodynamique aux phénomènes irreversibles liés aux degrés de liberté internes. *Physica*, **19** (1953), 241.

Examples

Example 10.1 Use the barometric formula to estimate the pressure at an altitude of 3.0 km. The temperature of the atmosphere is not uniform (so it is not in equilibrium). Assume an average temperature $T = 270.0$ K.

Solution The pressure at an altitude h is given by the barometric formula $p(h) = p(0)e^{-gMh/RT}$. For the purpose of estimating, since 78% of the atmosphere consists of N₂, we shall use the molar mass of N₂ for M . The pressure at an altitude of 3.0 km will be

$$\begin{aligned} p(3 \text{ km}) &= (1 \text{ atm}) \exp \left[-\frac{(9.8 \text{ m s}^{-2})(28.0 \times 10^{-3} \text{ kg mol}^{-1})3.0 \times 10^3 \text{ m}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(270 \text{ K})} \right] \\ &= (1 \text{ atm}) \exp(-0.366) \\ &= 0.69 \text{ atm} \end{aligned}$$

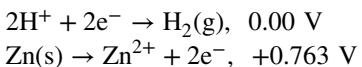
Example 10.2 Calculate the membrane potential for the setup shown in Figure 10.4.

Solution In this case, the expected potential difference across the membrane is

$$\begin{aligned} V &= \phi^\alpha - \phi^\beta = \frac{RT}{F} \ln \left(\frac{1.0}{0.1} \right) = 0.0257 \ln(10) \\ &= 0.0592 \text{ V} \end{aligned}$$

Example 10.3 Calculate the standard cell potential V_0 for the cell shown in Figure 10.6. Also calculate the equilibrium constant for the reaction $\text{Zn(s)} + 2\text{H}^+ \rightarrow \text{H}_2(\text{g}) + \text{Zn}^{2+}$.

Considering the two electrode reactions, we have



The total cell potential is

$$V_0 = 0 + 0.763 \text{ V} = 0.763 \text{ V}$$

and the equilibrium constant is

$$\begin{aligned} K &= \exp\left(\frac{2FV_0}{RT}\right) \\ &= \exp\left(\frac{2 \times 9.648 \times 10^4 \times 0.763}{8.314 \times 298.15}\right) \\ &= 6.215 \times 10^{25} \end{aligned}$$

Exercises

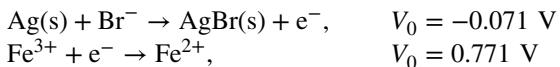
10.1 Use the chemical potential of an ideal gas in Equation (10.1.9) and obtain the barometric formula (10.1.10). Use the barometric formula to estimate the boiling point of water at an altitude of 2.50 km above sea level. Assume an average $T = 270 \text{ K}$.

10.2 A heater coil is run at a voltage of 110 V and it draws 2.0 A current. If its temperature is equal to 200 °C, what is the rate of entropy production due to this coil?

10.3 Calculate the equilibrium constants at $T = 25.0 \text{ }^\circ\text{C}$ for the following electrochemical reactions using the standard potentials in Table 10.1:

- (a) $\text{Cl}_2(\text{g}) + 2\text{Li(s)} \rightarrow 2\text{Li}^+ + 2\text{Cl}^-$
- (b) $\text{Cd(s)} + \text{Cu}^{2+} \rightarrow \text{Cd}^{2+} + \text{Cu(s)}$
- (c) $2\text{Ag(s)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{Ag}^+ + 2\text{Cl}^-$
- (d) $2\text{Na(s)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{Na}^+ + 2\text{Cl}^-$

10.4 If the reaction $\text{Ag(s)} + \text{Fe}^{3+} + \text{Br}^- \rightarrow \text{AgBr(s)} + \text{Fe}^{2+}$ is not in equilibrium it can be used generate an EMF. The ‘half-cell’ reactions that correspond to the oxidation and reduction in this cell are



- (a) Calculate V_0 for this reaction.
- (b) What is the EMF for the following activities at $T = 298.15 \text{ K}$: $a_{\text{Fe}^{3+}} = 0.98$; $a_{\text{Br}^-} = 0.30$; $a_{\text{Fe}^{2+}} = 0.01$.
- (c) What will be the EMF at $T = 0.0 \text{ }^\circ\text{C}$?

10.5 The K^+ concentration inside a nerve cell is much larger than the concentration outside it. Assume that the potential difference across the cell membrane is 90 mV. Assuming that the system is in equilibrium, estimate the ratio of concentration of K^+ inside and outside the cell.

10.6 Verify that

$$n(x, t) = \frac{n(0)}{2\sqrt{\pi D t}} e^{-x^2/4Dt}$$

is the solution of the diffusion equation (10.3.11). Using *Mathematica* or *Maple*, plot this solution for various values of t for one of the gases listed in Table 10.2, assuming $n(0) = 1$. This gives you an idea of how far a gas will diffuse in a given time. Obtain a simple expression to estimate the distance a molecule will diffuse in a time t , given its diffusion coefficient D .

10.7 Compute the diffusion current corresponding to the barometric distribution

$$n(x) = n(0)e^{-gMx/RT}.$$

- 10.8** Using Equation (10.4.9) and the ideal activity $a(\theta) = n(\theta)/n_{\text{tot}}$ for the dipole orientation, obtain the equilibrium expression (10.4.10). Give an explicit expression for the function $F(T)$ in terms of μ_0 and C .
- 10.9** The electric dipole moment of water molecules is 6.14×10^{-30} C m. In an electric field of 10.0 V m $^{-1}$, find the fraction of molecules oriented with respect to the field in the range $10^\circ < \theta < 20^\circ$ when $T = 298$ K.

11

Thermodynamics of Radiation

Introduction

Electromagnetic radiation, which interacts with matter, also reaches the state of thermal equilibrium with a definite temperature. This state of electromagnetic radiation is called **thermal radiation**, also called *heat radiation* in earlier literature. In fact, today we know that our universe is filled with thermal radiation at a temperature of about 2.73 K.

It has long been observed that heat transfer can take place from one body to another in the form of radiation with no material contact between the two bodies. This form of heat was called ‘heat radiation’. When it was discovered that motion of charges produced electromagnetic radiation, the idea that heat radiation was a form of electromagnetic radiation was taken up, especially in the works of Gustav Kirchhoff (1824–1887), Ludwig Boltzmann (1844–1906), Joseph Stefan (1835–1893) and Wilhelm Wien (1864–1928), and its thermodynamic consequences were investigated [1].

11.1 Energy Density and Intensity of Thermal Radiation

We begin by defining basic quantities required to study the properties of thermal radiation (here we follow the classic work of Planck on thermal radiation [1]). Radiation is associated with **energy density** u , which is the energy per unit volume, and **specific intensity** or **radiance**, I , which is defined as follows (Figure 11.1a): the energy incident per unit time on a small area, $d\sigma$, due to radiation from a solid angle $d\Omega$ ($=\sin \theta d\theta d\varphi$), which makes an angle θ with the surface normal and equals $I \cos \theta d\Omega d\sigma$. The total amount of radiation incident on one side of the area $d\sigma$ (Figure 11.1b) is equal to $\int_{\theta=0}^{\pi/2} \int_{\varphi=0}^{2\pi} I \cos \theta d\Omega = \int_{\theta=0}^{\pi/2} \int_{\varphi=0}^{2\pi} I \cos \theta \sin \theta d\theta d\varphi = \pi I$. The quantity πI is called the **radiation intensity** or **irradiance** or **radiant flux density**. Electromagnetic radiation has two independent states of polarization. The above quantities can be defined for each independent state of polarization. For unpolarized light, as in the case of thermal radiation, the total intensity is the sum of the intensities of the two independent states of polarization. A similar definition can be used for radiation emitted from a small surface area $d\sigma$, in which case πI is the per unit area of the surface, called **radiation intensity** or **irradiance**.

The energy density u and radiance I could also be defined as functions of frequency for *each independent state of polarization* as:

$$u(v) dv = \text{spectral energy density of radiation in the frequency range } v \text{ and } v + dv \text{ (J m}^{-3} \text{ Hz}^{-1}\text{)}$$

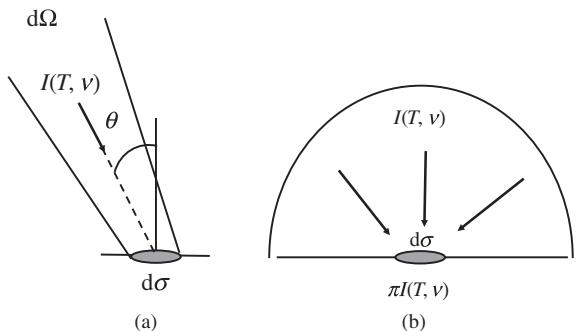


Figure 11.1 (a) Definition of spectral radiance $I(T, v)$. The energy flux incident on the area element $d\sigma$, from a solid angle $d\Omega = \sin \theta d\theta d\phi$, is given by $I(T, v) \cos \theta d\Omega d\sigma$. Here θ is the angle between the normal to $d\sigma$ and the incident radiation. (b) The total amount of radiation incident on $d\sigma$ from one side, the intensity of radiation, equals $\pi I(T, v)$. For electromagnetic radiation, the spectral intensity $\pi I(T, v)$ contains two independent states of polarization.

$I(v) dv$ = **spectral radiance** in the frequency range v and $v + dv$ ($\text{W Hz}^{-1} \text{ sr}^{-1} \text{ m}^{-2}$)

$\pi I(v) dv$ = **spectral intensity or spectral irradiance** in the frequency range v and $v + dv$ ($\text{W Hz}^{-1} \text{ m}^{-2}$)

There is a simple relationship between the spectral radiance $I(v)$ of radiation propagating at a velocity c and its energy density [1]:

$$\boxed{u(v) = \frac{4\pi I(v)}{c}} \quad (11.1.1)$$

This relation is not particular to electromagnetic radiation; it is valid for any quantity that fills space homogeneously and propagates with velocity c in all directions. In addition to intensity, electromagnetic radiation has two independent states of polarization. For each independent state of polarization (11.1.1) is valid. For unpolarized thermal radiation, the specific intensity $I(v)$ consists of two independent states of polarization.



Gustav Kirchhoff (1824–1887).

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As noted by Gustav Kirchhoff (1824–1887), thermal radiation that is simultaneously in equilibrium with several substances should not change with the introduction or removal of a substance.

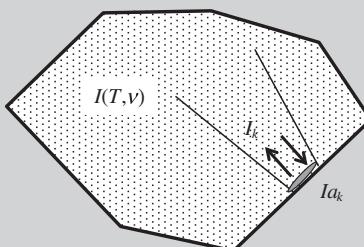
Hence $I(v)$ and $u(v)$ associated with thermal radiation must be functions only of the temperature T , independent of the substances with which it is in equilibrium. We shall therefore write thermal spectral energy density and radiance as $u(T, v)$ and $I(T, v)$ respectively.

A body in thermal equilibrium with radiation is continuously emitting and absorbing radiation. **Spectral absorptivity**, $a_k(T, v)$, of a body k is defined as the fraction of the incident thermal spectral radiance $I(T, v)$ that is absorbed by the body k in the frequency range v and $v + dv$ at a temperature T . The thermal radiation absorbed by the body in the solid angle $d\Omega$ equals $a_k(T, v)I(T, v)d\Omega$. Let $I_k(T, v)$ be the spectral radiance of the body k . Then the power emitted per unit area into a solid angle $d\Omega$ equals $I_k(T, v)d\Omega$. At thermal equilibrium, the radiation absorbed by the body k in the solid angle $d\Omega$ must equal the radiation it emits in that solid angle. It then follows that

$$\frac{I_k(T, v)}{a_k(T, v)} = I(T, v) \quad (11.1.2)$$

As noted above, $I(T, v)$ thermal spectral radiance must be independent of substances with which it is in equilibrium. Hence the ratio of a body's radiance to its absorptivity, $I_k(T, v)/a_k(T, v)$, is independent of the substance k and function only of temperature T and frequency v . This fundamental observation is called **Kirchoff's law** (see Box 11.1).

Box 11.1 Kirchhoff's law



Kirchhoff's law states that, at thermal equilibrium, the ratio, $I_k(T, v)/a_k(T, v)$, of emissive radiance $I_k(T, v)$ of a body k to its absorptivity $a_k(T, v)$ is independent of the body and is equal to the radiance of thermal radiation $I(T, v)$:

$$\frac{I_k(T, v)}{a_k(T, v)} = I(T, v)$$

For a perfectly absorbing body, $a_k(T, v) = 1$. Such a body is called a **blackbody**; its spectral radiance is equal to the thermal spectral radiance $I(T, v)$. **Emissivity**, e_k , of a body k is defined as the ratio of its spectral radiance to that of a blackbody: $e_k = I_k(T, v)/I(T, v)$. Thus **Kirchoff's law** can also be stated as: at thermal equilibrium,

$$\text{Emissivity } e_k = \text{Absorptivity } a_k$$

The **emissive power** of a body k is the power emitted per unit area into all directions in a hemisphere. It equals $\pi I_k(T)$. Emissivities of some materials are shown below:

Material	Emissivity
Lampblack	0.84
Polished copper	0.023
Cast iron	0.60–0.70
Polyethylene black plastic	0.92

For a perfectly absorbing body, $a_k(T, \nu) = 1$. Such a body is called a **blackbody**; *spectral radiance is equal to the thermal spectral radiance $I(T, \nu)$* . In this context, another parameter called **emissivity**, e_k , of a body k is defined as the ratio of its spectral radiance, $I_k(T, \nu)$, to that of a black body, i.e. $e_k = I_k(T, \nu)/I(T, \nu)$. Thus **Kirchoff's law** (11.1.2) can also be stated as: at thermal equilibrium

$$\text{Emissivity } e_k = \text{Absorptivity } a_k$$

At the end of the nineteenth century, classical thermodynamics faced the challenge of determining the exact functional form of $u(T, \nu)$ or $I(T, \nu)$. None of the deductions based on the laws of physics that were known at that time agreed with experimental measurements of $u(T, \nu)$. This fundamental problem remained unsolved until Max Planck (1858–1947) introduced his revolutionary quantum hypothesis. With the quantum hypothesis, according to which matter absorbed and emitted radiation in discrete bundles or ‘quanta’, Planck was able to derive the following expression, which agreed well with the observed frequency distribution $u(T, \nu)$:

$$u(T, \nu) d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{(e^{h\nu/k_B T} - 1)} \quad (11.1.3)$$

Here h ($= 6.626 \times 10^{-34}$ J s) is the Planck’s constant and k_B ($= 1.381 \times 10^{-23}$ J K $^{-1}$) is the Boltzmann constant. The expression for the energy density includes the two independent states of polarization. The derivation of this formula, which requires the principles of statistical mechanics, can be found in Chapter 20. Finally, we note that total energy density of thermal radiation is

$$u(T) = \int_0^\infty u(T, \nu) d\nu \quad (11.1.4)$$

When functions $u(\nu, T)$ obtained using classical electromagnetic theory were used in this integral, the total energy density, $u(T, \nu)$, turned out to be infinite. The Planck formula (11.1.3), however, gives a finite value for $u(T, \nu)$.



Max Planck (1858–1947).
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11.2 The Equation of State

It was clear, even from the classical electromagnetic theory, that a field which interacts with matter and imparts energy and momentum must itself carry energy and momentum. Classical expressions for the energy and momentum associated with the electromagnetic field can be found in texts on electromagnetic theory. For the purposes of understanding the thermodynamic aspects of radiation, we need an equation of state, i.e. an equation that gives the pressure exerted by thermal radiation and its relation to the temperature.

Using classical electrodynamics it can be shown [1] that the pressure exerted by electromagnetic radiation is related to the energy density u by

$$p = \frac{u}{3} \quad (11.2.1)$$

This relation follows from purely mechanical considerations of force exerted by electromagnetic radiation when it is reflected by the walls of a container. Though it was originally derived using the classical electrodynamics, Equation (11.2.1) can be more easily derived by treating electromagnetic radiation filling a container as a gas of photons (shown in Box 11.2). We shall presently see that when this equation of state is combined with the equations of thermodynamics, we arrive at the conclusion that the *energy density* $u(T, v)$ (*and hence $I(T, v)$*) is proportional to the fourth power of the temperature, a result that is credited to Joseph Stefan (1835–1893) and Ludwig Boltzmann (1844–1906) and called the **Stefan–Boltzmann law**. The fact that energy density $u(T) = \int_0^\infty u(T, v)dv$ of thermal radiation is only a function of temperature, independent of the volume, implies that in a volume V the total energy is

$$U = Vu(T) \quad (11.2.2)$$

Though thermal radiation is a gas of photons, it has features that are different from that of an ideal gas. At a fixed temperature T , as the volume of thermal radiation expands, the total energy increases (unlike in the case of an ideal gas in which it remains constant). As the volume increases, the ‘heat’ that must be supplied to such a system to keep its temperature constant is thermal radiation entering the system. This heat keeps the energy density constant. The change in entropy due to this heat flow is given by

$$d_e S = dQ/T = (dU + p dV)/T \quad (11.2.3)$$

Once we assign an entropy to the system in this fashion, all the thermodynamic consequences follow. Consider, for example, the Helmholtz equation (5.2.11) (which follows from the fact that entropy is a state function and therefore $\partial^2 S/\partial T \partial V = \partial^2 S/\partial V \partial T$):

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \left[\frac{\partial}{\partial T} \left(\frac{p}{T}\right)\right]_V \quad (11.2.4)$$

Using Equation (11.2.2) and the equation of state, $p = u/3$, in this equation we can obtain (Exercise 11.1):

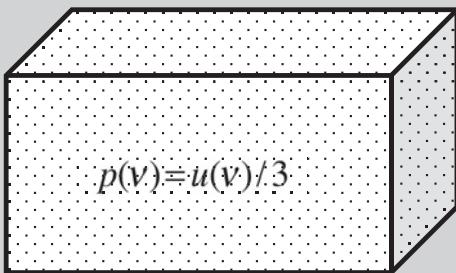
$$4u(T) = T \left(\frac{\partial u(T)}{\partial T}\right) \quad (11.2.5)$$

Upon integrating this equation, we arrive at the **Stefan–Boltzmann law**:

$$u(T) = \beta T^4 \quad (11.2.6)$$

in which β is a constant. The value of $\beta = 7.56 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$ is obtained by measuring the intensity of radiation emitted by a blackbody at a temperature T . The above energy density includes the two independent states of polarization.

Box 11.2 Photon gas pressure: a heuristic derivation



For a heuristic derivation of the pressure of a photon gas, let $n(v)$ be the number of photons per unit volume with frequency v . The momentum of each photon is (hv/c) . The radiation pressure on the walls is due to photon collisions. Each collision imparts a momentum $2(hv/c)$ to the wall upon reflection. Since the photons are in random motion, at any instant the fraction of the photons that will be moving in the direction of the wall equals $1/6$. Hence the number of photons that will collide with a unit area of the wall in one second is $(n(v)c/6)$. The total momentum imparted to an unit area of the wall per second is the pressure. Hence we have:

$$p(v) = \left(\frac{n(v)c}{6} \right) \frac{2hv}{c} = \frac{n(v)hv}{3}$$

Now, since the energy density $u(v) = n(v)hv$, we arrive at the result:

$$p(v) = \frac{u(v)}{3}$$

A more rigorous derivation, taking all the directions of the photon momentum into consideration, also gives the same result. For photons of all frequencies we can integrate over the frequency v :

$$p = \int_0^{\infty} p(v)dv = \int_0^{\infty} \frac{u(v)}{3} dv = \frac{u}{3}$$

where u is the total energy due to photons of all frequencies and p is the total pressure. Note that a similar derivation for the ideal gas gives $p = 2u/3$, in which $u = n(mv_{\text{avg}}^2/2)$, where n is the number of molecules per unit volume and $(mv_{\text{avg}}^2/2)$ is the average kinetic energy of a molecule.

The Stefan–Boltzmann law can also be written in terms of irradiance of a blackbody. By integrating Equation (11.1.1) over all frequencies v , we arrive at $u(T) = 2 \times 4\pi I(T)c$, where we have explicitly indicated that the intensity $I(T)$ is the intensity due to each independent state of polarization. *In this notation, experimentally measured total radiance equals $2I(T)$.* The corresponding irradiance $\pi 2I(T)$ (which is the power emitted per unit area in all directions in a hemisphere) can now be written as

$$\pi(2I) = u(T)c/4 = (\beta c/4)T^4 = \sigma T^4 \quad (11.2.7)$$

in which the constant $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is called the **Stefan–Boltzmann constant**.

Using Equation (11.2.6), we can now write the pressure, $p = u/3$, as function of temperature:

$$p(T) = \beta T^4/3 \quad (11.2.8)$$

Equations (11.2.6) and (11.2.8) are the equations of state for thermal radiation. For temperatures of order 10^3 K or less, the radiation pressure is small, but it can be quite large for stellar temperatures. In the interior of stars, where the temperatures can be 10^7 K, we find, using Equation (11.2.8), that the pressure due to thermal radiation is about 2.52×10^{12} Pa $\approx 2 \times 10^7$ atm!

11.3 Entropy and Adiabatic Processes

For thermal radiation, the change in entropy is entirely due to heat flow:

$$dS = d_e S = \frac{dU + p dV}{T} \quad (11.3.1)$$

Considering U as a function of V and T , this equation can be written as

$$dS = \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] dV + \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT \quad (11.3.2)$$

Since $U = Vu = V\beta T^4$ and $p = \beta T^4/3$ we can obtain the explicit differential expression

$$dS = \left(\frac{4}{3} \beta T^3 \right) dV + (4\beta VT^2) dT \quad (11.3.3)$$

This expression enables us to identify the derivatives of S with respect to T and V :

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{4}{3} \beta T^3 \quad \left(\frac{\partial S}{\partial T} \right)_V = 4\beta VT^2 \quad (11.3.4)$$

By integrating these two equations and setting $S = 0$ at $T = 0$ and $V = 0$, it is easy to see (Exercise 11.3) that

$$S = \frac{4}{3} \beta VT^3 \quad (11.3.5)$$

The above expression for entropy and the equations of state (11.2.6) and (11.2.8) are basic; all other thermodynamic quantities for thermal radiation can be obtained from them. Unlike other thermodynamic systems we have studied so far, the temperature T is sufficient to specify all the thermodynamic quantities of thermal radiation; the energy density $u(T)$, the entropy density $s(T) = S(T)/V$ and all other thermodynamic quantities are entirely determined by T . There is no term involving a chemical potential in the expressions for S or U . If we consider the particle nature of thermal radiation, i.e. a gas of photons, the *chemical potential must be assumed to equal zero* – a point that we will discuss in detail in Section 11.5.

In an adiabatic process the entropy remains constant. From the expression for entropy, Equation (11.3.5), the relation between the volume and temperature in an adiabatic process immediately follows:

$$VT^3 = \text{constant} \quad (11.3.6)$$

The radiation filling the universe is currently at about 2.7 K. The effect of the expansion of the universe on the radiation that fills it can be approximated as an adiabatic process. (During the evolution of the universe its total entropy is not a constant. Irreversible processes generate entropy, but the increase in entropy of radiation due to these irreversible processes is small.) Using Equation (11.3.6) and the current value of T , one can compute the temperature when the volume, for example, is one millionth of the present volume. Thus thermodynamics gives us the relation between the volume of the universe and the temperature of the thermal radiation that fills it.

In a manner similar to the total entropy S of thermal radiation, entropy density $s(T)$ can also be obtained using the fact that the energy density $u(T)$ is entirely heat. We can thus write:

$$ds(T) = \frac{du(T)}{T} = \frac{4\beta T^3 dT}{T} \quad (11.3.7)$$

in which we have used expression $u(T) = \beta T^4$ for the energy density that was obtained earlier. Integrating this equation, and noting that $s(T) = 0$ at $T = 0$ K, we obtain

$$s(T) = \frac{4}{3}\beta T^3 \quad (11.3.8)$$

which is in agreement with the expression for the total entropy of thermal radiation obtained above.

As was noted by Max Planck [1, p. 89], the expression (11.3.7) is also valid for every frequency component of thermal radiation. This observation enables us to obtain the entropy density, $s(v, T)$, as a function of the frequency v and temperature T , an expression analogous to the Planck energy distribution $u(v, T)$. Writing the fundamental expression (11.3.7) for each frequency component of thermal radiation, we have

$$ds(T, v) = \frac{du(T, v)}{T} = \frac{1}{T} \frac{\partial u(T, v)}{\partial T} dT \quad (11.3.9)$$

The partial derivative $\partial u(v, T)/\partial T$ can be evaluated using the Planck distribution (11.1.3). Upon substituting this derivative in Equation (11.3.9) and integrating, we obtain the expression

$$s(T, v) = \frac{8\pi h v^3}{c^3} a \int \frac{e^{a/T}}{(e^{a/T} - 1)^2} \frac{1}{T^3} dT \text{ in which } a = hv/k_B$$

The integral can be evaluated (analytically or using *Mathematica*) and we obtain the expression

$$s(T, v) = \frac{8\pi v^2 k_B}{c^3} \left[\frac{hv}{k_B T} \left(1 + \frac{1}{(e^{hv/k_B T} - 1)} \right) - \ln(e^{hv/k_B T} - 1) \right] \quad (11.3.10)$$

The Planck distribution for energy density and the above analogous expression for the entropy density are the fundamental equations of thermal radiation.

It is clear that thermal radiation not only carries energy, it also carries entropy. Just as we can associate specific intensity or spectral intensity, $I(v)$, with thermal radiation, we can also associate a **specific spectral entropy intensity**, $L(v)$. The definition of $L(v)$ is similar to $I(v)$, only it is in the context of entropy flow:

The entropy incident per unit time on a small area, $d\sigma$, in the frequency range v and $v + dv$, due to linearly polarized radiation from a solid angle, $d\Omega = \sin\theta d\theta d\phi$, which makes an angle θ with the surface normal equals $L(v) \cos\theta d\Omega d\sigma dv$.

Following the same line of reasoning that leads to the relation $u(v) = 2 \times 4\pi I(v)/c$ for thermal radiation at a given T (in which the factor 2 takes into consideration two independent states of polarization), we can arrive at the relation

$$s(v) = 2 \frac{4\pi}{c} L(v) \quad (11.3.11)$$

We note that this relation is valid whenever the entropy intensity, $L(v)$, is isotropic and the entropy density, $s(v)$, is uniform, for thermal as well as nonthermal or nonequilibrium radiation, i.e. radiation not in equilibrium with matter. For nonthermal radiation, expression (11.3.10) is not valid. In Section 11.8 expressions for the entropy density and intensity for nonequilibrium radiation are obtained.

11.4 Wien's Theorem

At the end of the nineteenth century, one of the most outstanding problems was the frequency dependence of the spectral energy density $u(T, v)$. Wilhelm Wien (1864–1928) made an important contribution in his attempt to obtain $u(T, v)$. Wien developed a method with which he could analyze what may be called the *microscopic consequences* of the laws of thermodynamics. He began by considering adiabatic compression of thermal radiation. Adiabatic compression keeps the system in thermal equilibrium but changes the temperature so that $VT^3 = \text{constant}$ (Equation (11.3.6)). On a microscopic level, he analyzed the shift of each frequency v to a new frequency v' due to its interaction with the compressing piston. Since this frequency shift corresponds to a change in temperature such that $VT^3 = \text{constant}$, he could obtain a relation between how $u(T, v)$ changed with v and T . This led Wien to the conclusion that $u(T, v)$ must have the following functional form (for more details see Reference [1]):

$$u(T, v) = v^3 f(v/T) = T^3 (v/T)^3 f(v/T) \quad (11.4.1)$$

i.e. $u(T, v)$ is a function of the *ratio* (v/T) multiplied by T^3 . This conclusion follows from the laws of thermodynamics. We shall refer to Equation (11.4.1) as **Wien's theorem**. Note that Equation (11.4.1) is in agreement with Planck's formula (11.1.3).

Experimentally it was found that, for a given T , as a function of v , $u(T, v)$ has a maximum. Let v_{\max} be the value of v at which $u(T, v)$ reaches its maximum value. Then, because $u(T, v)/T^3$ is a function of the ratio (v/T) , it follows that $u(v/T)$ reaches its maximum at a particular value of the ratio $(v/T) = C_1$. So for a given T , $u(T, v)$ reaches its maximum at v_{\max} when $(v_{\max}/T) = C_1$. In other words,

$$\frac{T}{v_{\max}} = C_1 \quad (11.4.2)$$

The spectral energy density $u(T, v)$ can be expressed as a function of the wavelength λ by noting that $v = c/\lambda$ and $dv = -(c/\lambda^2)d\lambda$. Using Equation (11.4.1) we can write $u(T, v)dv = -T^3(c/\lambda T)^3 f(c/\lambda T)(c/\lambda^2)d\lambda$. By combining all terms except T^5 as a function, $g(\lambda T)$, we can replace the right-hand side of the equation with $T^5 g(\lambda T)d\lambda$. Now we can identify the expression $T^5 g(\lambda T)d\lambda = u(T, \lambda)d\lambda$ as the spectral energy density as a function λ . It is a function of the product λT multiplied by T^5 . The function $u(T, \lambda)/T^5$ reaches its maximum for a particular value of the product $\lambda T = C_2$. Hence, for a given T , if $u(T, \lambda)$ is plotted as a function of λ , its maximum will occur at λ_{\max} such that $\lambda_{\max}T = C_2$. The values of the constants C_1 and C_2 can be obtained using Planck's formula (11.1.3). Generally the value of C_2 is used. We thus have what is called **Wein's displacement law**. It tells us how the maximum of $u(T, \lambda)$ is displaced by changes in T :

$$T\lambda_{\max} = 2.8979 \times 10^{-3} \text{ m K} \quad (11.4.3)$$

As T increases, λ_{\max} decreases proportionately. This conclusion is entirely a consequence of the laws of thermodynamics.

The above method of Wien is general and can be applied, for example, to an ideal gas. Here the objective would be to obtain the energy density u as a function of the velocity v and the temperature. It can be shown that (see Reference [2]) $u(T, v) = v^4 f(v^2/T)$, which shows us that using thermodynamics we can arrive at the conclusion that the velocity distribution is a function of (v^2/T) . This is consistent with the Maxwell velocity distribution (1.6.13). Wien's approach shows us how thermodynamics can be used to investigate microscopic aspects of systems such as energy or velocity distributions.

Wien's analysis and all other classical attempts to obtain the form of $u(T, v)$ for thermal radiation gave results that not only did not agree with experiments but also gave infinite values for $u(T, v)$ when all frequencies

ν (0 to ∞) were included. It is now well known that it was to solve this problem that Planck introduced his quantum hypothesis in 1900.

11.5 Chemical Potential of Thermal Radiation

The equations of state for thermal radiation are

$$p = \frac{u}{3}, \quad u = \beta T^4 \quad (11.5.1)$$

where u is the energy density and p is the pressure.

If all the material particles in a volume are removed, what was classically thought to be a vacuum is not empty but filled with thermal radiation at the temperature of the walls of the container. There is no distinction between heat and such radiation in the following sense. If we consider a volume filled with thermal radiation in contact with a heat reservoir (Figure 11.2), then if the volume is enlarged, the temperature, T , and hence the energy density, u , of the system are maintained constant by the flow of heat into the system from the reservoir. The heat that flows into the system is thermal radiation.

From the particle point of view, thermal radiation consists of photons, which we shall refer to as *thermal photons*. Unlike in an ideal gas, the total number of thermal photons is not conserved during isothermal changes of volume. The change in the total energy, $U = uV$, due to the flow of thermal photons from or to the heat reservoir must be interpreted as the flow of heat. Thus, for thermal radiation, in a reversible expansion at constant T we have $dS = d_e S = dQ/T$:

$$dU = dQ - p dV = T dS - p dV \quad (11.5.2)$$

This equation remains valid even though the number of photons in the system is changing. Comparing this equation with the equation introduced by Gibbs, $dU = dQ - p dV + \mu dN$, we conclude that the chemical potential $\mu = 0$. *The state in which $\mu = 0$ is a state in which the partial pressure or the particle density is a function only of the temperature.* Indeed, in the expression for the chemical potential, $\mu_k = \mu_k^0(T) + RT \ln[p_k/p_0]$, if we set $\mu_k = 0$ we see that the partial pressure p_k is only a function of T .

11.5.1 Two Level Atom in Equilibrium with Radiation

With the above observations that the chemical potential of thermal radiation is zero, the interaction of a two-level atom with blackbody radiation (which Einstein used to obtain the ratio of the rates of spontaneous

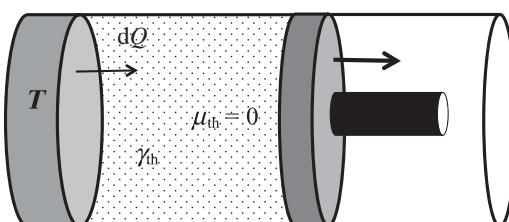


Figure 11.2 Heat radiation in contact with a heat reservoir. The energy entering or leaving such a system is thermal radiation. Though the number of photons is changing, $dU = dQ - p dV$.

and stimulated radiation) can be analyzed in a somewhat different light. If A and A* are the two states of the atom and γ_{th} is a thermal photon, then the spontaneous and stimulated emission of radiation can be written as



From the point of view of equilibrium of a chemical reaction, the above two reactions are the same. The condition for chemical equilibrium is

$$\mu_{A^*} = \mu_A + \mu_\gamma \quad (11.5.5)$$

Since $\mu_\gamma = 0$, we have $\mu_{A^*} = \mu_A$. As we have seen in Chapter 9, if we use the expression $\mu_k = \mu_k^0(T) + RT \ln(p_k/p_0)$ for the chemical potential, and note that the concentration is proportional to the partial pressure, the law of mass action takes the form:

$$\frac{[A]}{[A^*]} = K(T) \quad (11.5.6)$$

On the other hand, looking at the reactions (11.5.3) and (11.5.4) as elementary chemical reactions, we may write

$$\frac{[A][\gamma_{\text{th}}]}{[A^*]} = K'(T) \quad (11.5.7)$$

However, because $[\gamma_{\text{th}}]$ is a function of temperature only, it can be absorbed in the definition of the equilibrium constant so that if we define $K(T) \equiv K'(T)/[\gamma_{\text{th}}]$ we recover the equation (11.5.6), which follows from thermodynamics.

Similarly, we may consider any exothermic reaction,



from the viewpoint of thermal photons, and write this reaction as



The condition for equilibrium can now be written as

$$\mu_A + \mu_B = 2\mu_C + \mu_\gamma \quad (11.5.10)$$

Since $\mu_\gamma = 0$, we recover the condition for chemical equilibrium derived in Chapter 9. For this reaction also, one can obtain $K'(T)$ similar to that defined in Equation (11.5.7).

11.6 Matter–Antimatter in Equilibrium with Thermal Radiation: The State of Zero Chemical Potential

When we consider interconversion of matter and radiation, as in the case of particle–antiparticle pair creation and annihilation, the chemical potential of thermal photons becomes more significant (see Figure 11.3). Similar thermodynamic analysis could be done for electron–hole pair production by radiation. Consider thermal photons in thermal equilibrium with electron–positron pairs:



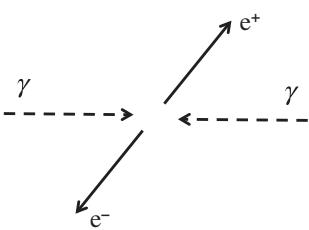


Figure 11.3 Creation of particle–antiparticle pairs by thermal photons.

At thermal equilibrium we have

$$\mu_{e^+} + \mu_{e^-} = 2\mu_\gamma \quad (11.6.2)$$

For reasons of symmetry between particles and antiparticles, we may assert that $\mu_{e^+} = \mu_{e^-}$. Since $\mu_\gamma = 0$ we must conclude that for particle–antiparticle pairs that can be created by thermal photons $\mu_{e^+} = \mu_{e^-} = 0$.

It is interesting to further discuss this state of matter for which $\mu = 0$. For simplicity, let us consider $\mu = 0$ state in an ideal monatomic gas mixture for which

$$\begin{aligned} \mu_k &= \frac{U_k - TS_k + p_k V}{N_k} \\ &= \frac{N_k[(3/2)RT + W_k] - TN_kR[(3/2)\ln T + \ln(V/N_k) + s_0] + N_kRT}{N_k} \end{aligned} \quad (11.6.3)$$

in which we used the internal energy $U_k = N_k[(3/2)RT + W_k]$ of component k of the ideal gas mixture and its entropy $S_k = N_kR[(3/2)\ln T + \ln(V/N_k) + s_0]$ and the ideal gas equation $p_k V = N_k RT$. As we have already noted in Chapter 2, the theory of relativity gives us the absolute value of energy $E^2 = p^2 c^2 + m^2 c^4$. The momentum $p = 0$ at $T = 0$ leaves the rest energy as $E = mc^2$. The term W_k is the rest energy of one mole of the particles: $W_k = M_k c^2$, in which M_k is the molar mass of component k . (Quantum theory gives us the entropy constant s_0 in the expression for entropy.) Using Equation (11.6.3) we can write the molar density (N_k/V) as

$$\frac{N_k}{V} = z(T)e^{(\mu - M_k c^2)/RT} \quad (11.6.4)$$

in which $z(T)$ is a function of temperature only (in Chapter 20 we can see that it is closely related to the partition function of an ideal gas). When the process of particle-antiparticle pair production is in thermal equilibrium, since $\mu = 0$ the thermal particle density is given by

$$\left(\frac{N_k}{V} \right)_{\text{th}} = z(T)e^{-M_k c^2/RT} \quad (11.6.5)$$

The corresponding partial pressure is given by

$$p_{k,\text{th}} = RTz(T)e^{-M_k c^2/RT} \quad (11.6.6)$$

The physical meaning of the above equations can be understood as follows: just as photons of energy $h\nu$ are excitations of the electromagnetic field, particles of energy $E = \sqrt{m^2 c^4 + p^2 c^2}$ are also excitations of a quantum field. In the nonrelativistic approximation, $E \approx mc^2 + p^2/2m$. According to the Boltzmann principle, in a field the probability $P(E)$ of an excitation of energy E is given by the proportionality:

$$P(E) \propto \rho(E)e^{-E/kT} = \rho(E)e^{-[mc^2 + (p^2/2m)]/k_B T} \quad (11.6.7)$$

where $\rho(E)$ is the density of states of energy E (see Chapter 20). If we approximate the statistics of these excitations by classical Boltzmann statistics, the density of particles of mass m can be obtained by integrating Equation (11.6.7) over all momenta p . We then obtain an expression of the form (11.6.5) in which the molar mass $M_k = N_A m_k$. Thus Equations (11.6.5) and (11.6.6) give the density and partial pressure due to particles that appear spontaneously at temperature T as thermal excitations of quantum fields. In this state, in which $\mu = 0$, there is no distinction between heat and matter; just as it is for thermal photons, the particle density is entirely determined by the temperature.

At ordinary temperatures, the thermal particle density obtained above is extremely small. Nevertheless, from the point of view of thermodynamic formalism after the advent of quantum field theory, it is important to consider this state in which the chemical potential vanishes. It is a state of thermal equilibrium that matter could reach; indeed matter was in such a state during the early part of the universe. Had matter stayed in thermal equilibrium with radiation, at the current temperature of the universe, 2.73 K, the density of protons and electrons, given by Equation (11.6.5) or its modifications, would be virtually zero. Indeed, the very existence of particles in the universe at the present temperatures implies that the universe is in a nonequilibrium state. As a result of the particular way in which the universe has evolved, matter was not able to convert to radiation and stay in thermal equilibrium with it.

From Equation (11.6.4) we see that assigning a nonzero value for the chemical potential is a way of fixing the particle density at a given temperature. Since we have an understanding of the **absolute zero of chemical potential**, we can write the chemical potential of an ideal gas particle as

$$\mu_k = RT \ln \left(\frac{p_k}{p_{k,\text{th}}} \right) \quad (11.6.8)$$

in which $p_{k,\text{th}}$ is the thermal pressure defined above. In principle, one may adopt this scale of chemical potential for all ideal systems.

11.7 Chemical Potential of Radiation not in Thermal Equilibrium with Matter

From the above discussion we see how a nonzero chemical potential may be associated with ‘nonthermal’ electromagnetic radiation, i.e. radiation that is not in thermal equilibrium with matter with which it is interacting. In discussing thermal and nonthermal radiation, one must keep in mind the distinction between *thermal energy density*, given by Planck’s formula (11.1.3), and the *thermal spectrum* of the radiation emitted by the an object at temperature T . Consider a hollow sphere at a temperature T that is well above the ambient temperature. The radiation filling the space within the sphere and in thermal equilibrium with the sphere will have an energy density given by the Planck formula. If we now make a small hole in the sphere through which this thermal radiation can propagate to the space outside the sphere, that radiation will have a thermal spectrum whose shape is given by the Planck formula, but the energy density of this radiation depends on the location at which the radiation is received and it will not equal the Planck energy density. It is not uncommon to refer to radiation emitted by an object at temperature T as ‘thermal radiation’, by which it is meant that the radiation has a thermal spectrum but it is clear that its energy density is not the thermal energy density given by the Planck formula. Thus the radiation from the Sun reaching the Earth has a thermal spectrum corresponding Sun’s surface temperature, T_{sun} , but its energy density at the Earth’s surface will not be equal to Planck’s energy density at T_{sun} . Such radiation may be referred to as ‘thermal radiation’ but one must keep in mind that it is not in thermal equilibrium with matter on the Earth, which is at a different temperature T_{earth} .

Let us consider matter at a temperature T , interacting with radiation whose energy distribution is not the Planck distribution (11.1.3) at the same temperature T . For electromagnetic radiation of frequency ν , whether it is in thermal equilibrium or not, the pressure associated with the energy density $u(\nu)$ is

$$p(\nu) = u(\nu)/3 \quad (11.7.1)$$

Also, as noted in Section 11.1, for any radiation that homogeneously fills space, for each independent state of polarization, the spectral energy density $u(\nu)$ is related to the spectral radiance $I(\nu)$:

$$u(\nu) = 4\pi I(\nu)/c \quad (11.7.2)$$

As before, we shall refer to $u(\nu)$ as ‘nonthermal’ or ‘nonequilibrium’ radiation and, to distinguish thermal radiation density from it, we shall write Planck energy density as, $u_{\text{th}}(T, \nu)$ and the associated pressure and intensity as $p_{\text{th}}(T, \nu)$ and $I_{\text{th}}(T, \nu)$ respectively, with a subscript ‘th’ emphasizing that it is thermal radiation. Following Equation (11.6.8), we can write the chemical potential of nonthermal or nonequilibrium radiation as

$$\mu(\nu) = RT \ln \left(\frac{p(\nu)}{p_{\text{th}}(T, \nu)} \right) = RT \ln \left(\frac{u(\nu)}{u_{\text{th}}(T, \nu)} \right) = RT \ln \left(\frac{I(\nu)}{I_{\text{th}}(T, \nu)} \right) \quad (11.7.3)$$

When the radiation reaches equilibrium with matter at temperature T , $u(\nu) = u_{\text{th}}(T, \nu)$ and the chemical potential will equal zero.

An example of nonequilibrium or nonthermal radiation is the solar radiation that reaches the Earth. As discussed above, solar radiation is sometimes said to be ‘thermal’ by which it is meant it has a thermal spectrum. The radiation has the Planck energy density, $u_{\text{th}}(T_{\text{sun}}, \nu)$, at the solar surface, corresponding to the solar surface temperature $T_{\text{sun}} \approx 5800$ K. As radiation propagates through space from the Sun’s surface, the energy density decreases by a factor $(r_{\text{sun}}/r)^2$ in which r is the distance from the center of the Sun and r_{sun} is the radius of the Sun. When solar radiation arrives at the Earth’s surface, which is at an average temperature, $T_{\text{earth}} \approx 287$, its spectrum is that of T_{sun} but the energy density is much smaller than $u_{\text{th}}(T_{\text{sun}}, \nu)$. This radiation is not in thermal equilibrium with matter on the surface of the Earth. Using (11.7.3) its chemical potential can be written as

$$\mu(\nu) = RT \ln \left(\frac{(r_{\text{sun}}/r)^2 u_{\text{th}}(T_{\text{sun}}, \nu)}{u_{\text{th}}(T_{\text{earth}}, \nu)} \right) \quad (11.7.4)$$

in which r is the radius of Earth’s orbit. This nonzero chemical potential drives photosynthesis. Ultimately solar radiation absorbed by the Earth reaches thermal equilibrium with matter at the Earth’s temperature T_{earth} and is radiated back into space as thermal radiation at T_{earth} .

11.8 Entropy of Nonequilibrium Radiation

For nonequilibrium radiation, the spectral radiance $I(\nu)$ is not derived from Planck’s distribution; it is arbitrary. However, we can still associate a temperature, $T(\nu)$, to each frequency, ν , such that the thermal spectral intensity of each independent state of polarization at that temperature equals $I(\nu)$, i.e. we choose T such that

$$I(\nu) = \frac{c}{8\pi} u(\nu, T) = \frac{h\nu^3}{c^2} \frac{1}{(e^{h\nu/k_B T} - 1)} \quad (11.8.1)$$

In other words, we assume that each frequency component of the nonequilibrium radiation is at a different temperature; in contrast, for thermal radiation with Planck’s energy density or thermal spectrum, all the

frequency components of the radiation are at the same temperature. We assume that the nonequilibrium radiation is in a cavity with homogeneous energy distribution and isotropic intensity. A small hole in this cavity will emit radiation with spectral intensity $I(\nu)$. The temperature associated with each frequency of nonequilibrium radiation is thus defined by [3]

$$I(\nu) \frac{c^2}{h\nu^3} = \frac{1}{(e^{h\nu/k_B T} - 1)}$$

We can now write T explicitly in terms of the frequency ν and the nonequilibrium intensity $I(\nu)$ by inverting the above equation:

$$\frac{1}{T(\nu)} = \frac{k_B}{h\nu} [\ln(\beta I(\nu) + 1) - \ln(\beta I(\nu))] \quad \text{in which } \beta = \frac{c^2}{h\nu^3} \quad (11.8.2)$$

Now the specific spectral entropy intensity associated with this radiation may be defined as

$$dL(\nu) = \frac{dI(\nu)}{T} = \frac{k_B}{h\nu} [\ln(\beta I(\nu) + 1) - \ln(\beta I(\nu))] dI(\nu) \quad (11.8.3)$$

in which we have used Equation (11.8.2) for $1/T$. By defining $x = \beta I(\nu)$, the above equation can be integrated to obtain, for each independent state of polarization, the following specific entropy intensity $L(\nu)$ in terms of $I(\nu)$, which we assume is given:

$$L(\nu) = \frac{k_B \nu^2}{c^2} [(x + 1) \ln(x + 1) - x \ln x] \quad (11.8.4)$$

in which

$$x = \frac{c^2}{h\nu^3} I(\nu)$$

As before, taking the two independent states of polarization into consideration, the associated total entropy density can be written as

$$s(\nu) = 2 \frac{4\pi}{c} L(\nu) \quad (11.8.5)$$

The above result can also be obtained using quantum statistics of Bosons [4]. With this expression, given $I(\nu)$, we can compute the entropy flux associated with nonequilibrium radiation. For example, the solar radiation arriving at the Earth's surface has a spectral distribution given by the Planck distribution at the solar surface temperature T_{sun} , which is close to 5800. However, only at the surface of the Sun is the intensity $I(\nu) = (c/8\pi)u(5800, \nu)$. As the solar radiation propagates through space, the intensity decreases in proportion to the inverse square of the distance from its origin. If $I_{\text{sun}}(\nu)$ is the intensity at the surface of the Sun and r_{sun} is the radius of the Sun, then from the conservation of energy we see that the intensity $I(\nu)$ at a distance r from the center of the Sun are related by $I_{\text{sun}}(\nu) r_{\text{sun}}^2 = I(\nu)r^2$ (we assume $r > r_{\text{sun}}$). Thus

$$I(\nu) = (r_{\text{sun}}^2/r^2)I_{\text{sun}}(\nu) = (r_{\text{sun}}^2/r^2)(c/8\pi)u(5800, \nu)$$

This expression for $I(\nu)$ can be used in Equation (11.8.4) to compute the specific entropy intensity at a distance r from the center of the Sun. Finally, we note that the expression for the entropy density of thermal radiation, Equation (11.3.10), can also be written in the more general form of Equation (11.8.4) using the substitution

$$x = \frac{1}{(e^{h\nu/k_B T} - 1)}$$

References

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Example

Example 11.1 Using the equation of state, calculate the energy density and pressure of thermal radiation at 6000 K (which is approximately the temperature of the radiation from the Sun). Also calculate the pressure at $T = 10^7$ K.

Solution The energy density is given by the Stefan–Boltzmann law, $u = \beta T^4$, in which $\beta = 7.56 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$ (see Equation (11.2.6)). Hence the energy density is at 6000 K is

$$u(6000 \text{ K}) = 7.56 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4} (6000 \text{ K})^4 = 0.98 \text{ J m}^{-3}$$

The pressure due to thermal radiation is given by $p = u/3 = (0.98/3) \text{ J m}^{-3} = 0.33 \text{ Pa} \approx 3 \times 10^{-6} \text{ atm}$.

At $T = 10^7$ K the energy density and pressure are

$$u = 7.56 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4} (10^7 \text{ K})^4 = 7.56 \times 10^{12} \text{ J m}^{-3}$$

$$p = u/3 = 2.52 \times 10^{12} \text{ Pa} = 2.5 \times 10^7 \text{ atm}$$

Exercises

- 11.1 Obtain Equation (11.2.5) using Equations (11.2.1) and (11.2.2) in the Helmholtz equation (11.2.4).
- 11.2 Using Planck's formula (11.1.3) for $u(v, T)$ in Equation (11.1.4), obtain the Stefan–Boltzmann law (11.2.6) and an expression for the Stefan–Boltzmann constant β .
- 11.3 Show that Equation (11.3.5) follows from Equation (11.3.4).
- 11.4 At an early stage of its evolution, the universe was filled with thermal radiation at a very high temperature. As the universe expanded adiabatically, the temperature of the radiation decreased. Using the current value of $T = 2.73 \text{ K}$, obtain the ratio of the present volume to the volume of the universe when $T = 10^{10} \text{ K}$.
- 11.5 The thermal spectral radiance $I(T, \lambda)d\lambda$ is defined as the radiance in the wavelength range λ and $\lambda + d\lambda$ of thermal radiation at temperature T .
 - (a) Show that:

$$I(T, \lambda)d\lambda = \frac{2hc^2}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k_B T} - 1}$$

- (b) The surface temperature of the Sun is 6000 K. Plot $I(6000, \lambda)$, a function of λ , and verify that $\lambda_{\max} \approx 483 \text{ nm}$ for the solar thermal radiation.
- (c) What will λ_{\max} be if the Sun's surface temperature is 10 000 K?

- 11.6** The total energy of the Earth is in a steady state. It means the flux of solar radiation absorbed by the Earth equals that emitted as thermal radiation. (a) Assuming that the average surface temperature of the Earth is about 288 K, estimate the amount of thermal radiation emitted by the Earth per second. (b) Assuming that the temperature of the solar radiation is 6000 K, estimate the total rate of entropy due to the thermal radiation flux through the Earth.
- 11.7** Estimate the chemical potential of solar radiation at the surface of the Earth where matter is at temperature $T = 295$ K.

Part III

Fluctuations and Stability

12

The Gibbs Stability Theory

12.1 Classical Stability Theory

The random motion of molecules causes all thermodynamic quantities such as temperature, concentration and partial molar volume to fluctuate. In addition, due to its interaction with the exterior, the state of a system is subject to constant perturbations. The state of equilibrium must remain stable in the face of all fluctuations and perturbations. In this chapter we shall develop a theory of stability for isolated systems in which the total energy U , volume V and molar amounts N_k are constant. The stability of the equilibrium state leads us to conclude that certain physical quantities, such as heat capacities, must have a definite sign. This chapter is an introduction to the theory of stability as developed by Gibbs. Chapter 13 contains some elementary applications of this stability theory. In Chapter 14, we shall present a more general theory of stability and fluctuations based on the entropy production associated with fluctuations. The more general theory is applicable to a wide range of systems, including nonequilibrium systems.

For an isolated system, the entropy reaches its maximum value at equilibrium; thus, any fluctuation can only reduce the entropy. In response to a fluctuation, entropy-producing irreversible processes spontaneously drive the system back to equilibrium. Hence, *the state of equilibrium is stable to any perturbation that results in a decrease in entropy*. Conversely, if fluctuations can grow, the system is not in equilibrium. The fluctuations in temperature, volume, etc., are quantified by their magnitudes, such as δT and δV . The entropy of the system is a function of these parameters. In general, the entropy can be expanded as a power series in these parameters, so we have

$$S = S_{\text{eq}} + \delta S + \frac{1}{2} \delta^2 S + \dots \quad (12.1.1)$$

In such an expansion, the term δS represents the *first-order* terms containing δT , δV , etc., the term $\delta^2 S$ represents the *second order* terms containing $(\delta T)^2$, $(\delta V)^2$, etc., and so on. This notation will be made explicit in the examples that follow. Also, as we shall see below, since the entropy is a maximum, the first-order term δS vanishes. The change in entropy is due to the second- and higher-order terms, the leading contribution coming from the second-order term $\delta^2 S$.

We shall look at the stability conditions associated with fluctuations in different quantities such as temperature, volume and molar amounts in an isolated system in which U , V and N_k are constant.

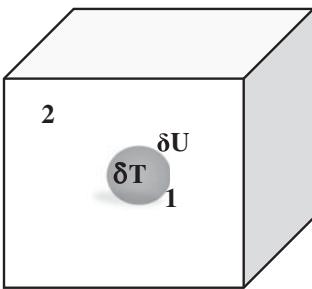


Figure 12.1 Thermal fluctuations in the equilibrium state. We consider a fluctuation that results in a flow of energy δU from one part to the other, causing the temperatures to change by a small amount δT .

12.2 Thermal Stability

For the fluctuations in temperature, we shall consider a simple situation without loss of generality. Let us assume that the fluctuation occurs in a small part of the system (Figure 12.1). Due to the fluctuation there is a flow of energy, δU , from one part to the other, resulting in a small temperature fluctuation, δT , in the smaller part. The subscripts 1 and 2 identify the two parts of the system. The total entropy of the system is

$$S = S_1 + S_2 \quad (12.2.1)$$

Here entropy S_1 is a function of U_1, V_1 , etc., and S_2 is a function of U_2, V_2 , etc. If we express S as a Taylor series about its equilibrium value, S_{eq} , we can express the change in entropy, ΔS , from its equilibrium value as

$$\begin{aligned} S - S_{\text{eq}} = \Delta S &= \left(\frac{\partial S_1}{\partial U_1} \right) \delta U_1 + \left(\frac{\partial S_2}{\partial U_2} \right) \delta U_2 + \left(\frac{\partial^2 S_1}{\partial U_1^2} \right) \frac{(\delta U_1)^2}{2} \\ &\quad + \left(\frac{\partial^2 S_2}{\partial U_2^2} \right) \frac{(\delta U_2)^2}{2} + \dots \end{aligned} \quad (12.2.2)$$

where all the derivatives are evaluated at the equilibrium state.

Since the total energy of the system remains constant, $\delta U_1 = -\delta U_2 = \delta U$. Also, recall that $(\partial S/\partial U)_{V, N} = 1/T$. Hence Equation (12.2.2) can be written as

$$\Delta S = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta U + \left[\frac{\partial}{\partial U_1} \frac{1}{T_1} + \frac{\partial}{\partial U_2} \frac{1}{T_2} \right] \frac{(\delta U)^2}{2} + \dots \quad (12.2.3)$$

We can now identify the first and second variations of entropy, δS and $\delta^2 S$, and write them explicitly in terms of the perturbation δU :

$$\delta S = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta U \quad (12.2.4)$$

$$\frac{1}{2} \delta^2 S = \left[\frac{\partial}{\partial U_1} \frac{1}{T_1} + \frac{\partial}{\partial U_2} \frac{1}{T_2} \right] \frac{(\delta U)^2}{2} \quad (12.2.5)$$

At equilibrium, since all thermodynamic forces must vanish, the entire system should be at the same temperature. Hence $T_1 = T_2$ and the first variation of entropy $\delta S = 0$. (If it is taken as a postulate that entropy

is a maximum at equilibrium, then the first variation should vanish. One then concludes that $T_1 = T_2$.) The changes in entropy due to fluctuations in the equilibrium state are due to the second variation $\delta^2 S$ (the smaller higher-order terms in the Taylor series are neglected). At equilibrium, since S is a maximum, fluctuations can only decrease S , i.e. $\delta^2 S < 0$, and spontaneous, entropy-increasing irreversible processes drive the system back to the state of equilibrium. Now let us write Equation (12.2.5) explicitly in terms of the physical properties of the system and see what the condition for stability implies. First we note that, at constant V ,

$$\frac{\partial}{\partial U} \frac{1}{T} = -\frac{1}{T^2} \frac{\partial T}{\partial U} = -\frac{1}{T^2} \frac{1}{C_V} \quad (12.2.6)$$

in which C_V is the heat capacity. We shall use C_{V_1} for the heat capacity of the smaller part and C_{V_2} for the heat capacity of the larger part. If the change in the temperature of the smaller is δT then we have $\delta U_1 = C_{V_1}(\delta T)$. Using Equation (12.2.6) for the two parts in Equation (12.2.5), writing $\delta U = C_{V_1}(\delta T)$ and noting that all the derivatives are evaluated at equilibrium, so that $T_1 = T_2 = T$, we obtain

$$\frac{1}{2} \delta^2 S = -\frac{C_{V_1}(\delta T)^2}{2T^2} \left(1 + \frac{C_{V_1}}{C_{V_2}} \right) \quad (12.2.7)$$

If system 1 is small compared to system 2, $C_{V_1} \ll C_{V_2}$ so that the second term in the parentheses can be ignored. In general, then, for stability of the equilibrium state of a subsystem imbedded in a much larger system, we have

$$\frac{1}{2} \delta^2 S = -\frac{C_V(\delta T)^2}{2T^2} < 0 \quad (12.2.8)$$

This condition requires that the heat capacity $C_V > 0$. *Thus, the state of equilibrium is stable to thermal fluctuations because the heat capacity at constant volume is positive.* Conversely, if the heat capacity is negative, the system is an unstable nonequilibrium state.

12.3 Mechanical Stability

We now turn to stability of the system with respect to fluctuations in its volume with N remaining constant, i.e. fluctuations in the molar volume. As in the previous case, consider a system divided into two parts (Figure 12.2), but this time assume there is a small change in volume δV_1 of system 1 and a consequent small change

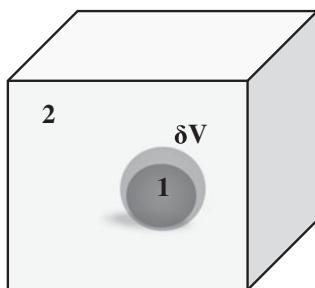


Figure 12.2 Fluctuation in volume V of a subsystem with a fixed N .

δV_2 of system 2. Since the total volume of the system remains fixed, $\delta V_1 = -\delta V_2 = \delta V$. To compute the change in entropy associated with such a fluctuation, we can write an equation similar to (12.2.3), with V taking the place of U . Since $(\partial S/\partial V)_{U,N} = p/T$, a calculation similar to that in Section 12.2 (Exercise 12.2) leads to

$$\delta S = \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) \delta V \quad (12.3.1)$$

$$\frac{1}{2} \delta^2 S = \left[\frac{\partial}{\partial V_1} \frac{p_1}{T_1} + \frac{\partial}{\partial V_2} \frac{p_2}{T_2} \right] \frac{(\delta V)^2}{2} \quad (12.3.2)$$

Because the derivatives are evaluated at equilibrium $p_1/T_1 = p_2/T_2 = p/T$. The first variation δS vanishes (as it must if S is a maximum at equilibrium). To understand the physical meaning of the conditions for stability, $\delta^2 S < 0$, the second variation can be written in terms of the isothermal compressibility. The isothermal compressibility κ_T is defined by $\kappa_T = -(1/V) (\partial V/\partial p)$. We assume that T remains unchanged when the fluctuation in V occurs. With these observations it is easy to see that Equation (12.3.2) can be written as

$$\delta^2 S = -\frac{1}{T\kappa_T} \frac{(\delta V)^2}{V_1} \left[1 + \frac{V_1}{V_2} \right] \quad (12.3.3)$$

As before, if one part is much larger than another, $V_2 \gg V_1$, this expression can be simplified and the condition for stability can be written as

$$\delta^2 S = -\frac{1}{T\kappa_T} \frac{(\delta V)^2}{V} < 0 \quad (12.3.4)$$

where we have used V for the arbitrary volume V_1 . This is valid when $\kappa_T > 0$. *Thus the state of equilibrium is stable to volume or mechanical fluctuations because the isothermal compressibility is positive. If $\kappa_T < 0$, the system is in an unstable nonequilibrium state.*

12.4 Stability and Fluctuations in N_k

Fluctuations in the molar amounts, N_k , of the various components of a system occur due to chemical reactions and due to transport, such as diffusion. We shall consider each case separately.

12.4.1 Chemical Stability

These fluctuations can be identified as the fluctuations in the extent of reaction ξ about its equilibrium value. Considering a fluctuation $\delta\xi$, the change in entropy is

$$S - S_{\text{eq}} = \Delta S = \delta S + \frac{1}{2} \delta^2 S = \left(\frac{\partial S}{\partial \xi} \right)_{U,V} \delta \xi + \frac{1}{2} \left(\frac{\partial^2 S}{\partial \xi^2} \right)_{U,V} (\delta \xi)^2 \quad (12.4.1)$$

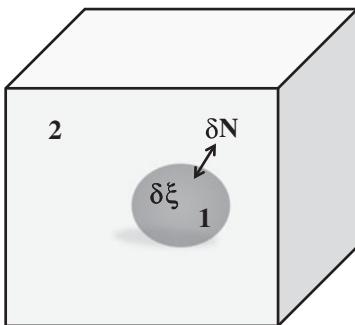


Figure 12.3 Fluctuations in N_k of a subsystem can occur due to chemical reactions (change in ξ) and exchange of molecules with the rest of the system. The state of equilibrium is stable if the entropy change associated with fluctuations is negative.

We have seen in Chapter 4 that $(\partial S / \partial \xi)_{U, V} = A/T$. Hence Equation (12.4.1) can be written as

$$\Delta S = \delta S + \frac{1}{2} \delta^2 S = \left(\frac{A}{T} \right)_{\text{eq}} \delta \xi + \frac{1}{2T} \left(\frac{\partial A}{\partial \xi} \right)_{\text{eq}} (\delta \xi)^2 \quad (12.4.2)$$

(T is constant). In this equation the identification of the first and second variations of entropy are obvious. At equilibrium, the affinity A vanishes, so that once again $\delta S = 0$. For the stability of the equilibrium state, we then require the second variation $\delta^2 S$ to be negative:

$$\frac{1}{2} \delta^2 S = \frac{1}{2T} \left(\frac{\partial A}{\partial \xi} \right)_{\text{eq}} (\delta \xi)^2 < 0 \quad (12.4.3)$$

Since $T > 0$, the condition for stability of the equilibrium state is

$$\boxed{\left(\frac{\partial A}{\partial \xi} \right)_{\text{eq}} < 0}^1 \quad (12.4.4)$$

When many chemical reactions take place simultaneously, condition (12.4.3) can be generalized to the following statement [1, 2]:

$$\frac{1}{2} \delta^2 S = \sum_{i,j} \frac{1}{2T} \left(\frac{\partial A_i}{\partial \xi_j} \right)_{\text{eq}} \delta \xi_i \delta \xi_j < 0 \quad (12.4.5)$$

12.4.2 Stability to Fluctuations Due to Diffusion

The fluctuations in N_k considered so far were only due to chemical reactions. The fluctuation in mole number can also occur due to the exchange of matter between a part of a system and the rest (Figure 12.3). As in the

¹This condition can be used to derive the Le Chatelier–Braun principle discussed in Section 9.3.

case of exchange of energy, we consider the total change in entropy of the two parts of the system (indicated as before by subscripts 1 and 2):

$$S = S_1 + S_2 \quad (12.4.6)$$

$$\begin{aligned} S - S_{\text{eq}} &= \Delta S \sum_k \left[\left(\frac{\partial S_1}{\partial N_{1k}} \right) \delta N_{1k} + \left(\frac{\partial S_2}{\partial N_{2k}} \right) \delta N_{2k} \right] \\ &\quad + \sum_{ij} \left[\left(\frac{\partial^2 S_1}{\partial N_{1i} \partial N_{1j}} \right) \frac{\delta N_{1i} \delta N_{1j}}{2} + \left(\frac{\partial^2 S_2}{\partial N_{2i} \partial N_{2j}} \right) \frac{\delta N_{2i} \delta N_{2j}}{2} \right] + \dots \end{aligned} \quad (12.4.7)$$

Now we note that $\delta N_{1k} = -\delta N_{2k} = \delta N_k$ and $(\partial S/\partial N_k) = -\mu_k/T$. Equation (12.4.7) can then be written so that the first and second variations of the entropy can be identified:

$$\Delta S = \delta S + \frac{\delta^2 S}{2} = \sum_k \left(\frac{\mu_{2k}}{T} - \frac{\mu_{1k}}{T} \right) \delta N_k - \sum_{ij} \left(\frac{\partial}{\partial N_j} \frac{\mu_{1i}}{T} + \frac{\partial}{\partial N_j} \frac{\mu_{2i}}{T} \right) \frac{\delta N_i \delta N_j}{2} \quad (12.4.8)$$

As before, if the derivatives are evaluated at the state of equilibrium, the chemical potentials of the two parts must be equal. Hence the first term vanishes. Furthermore, if system 1 is small compared to system 2, the change in the chemical potential (which depends on the concentrations) with respect to N_k of system 2 will be small compared to the corresponding change in system 1. That is,

$$\left(\frac{\partial}{\partial N_j} \frac{\mu_{1i}}{T} \right) \gg \left(\frac{\partial}{\partial N_j} \frac{\mu_{2i}}{T} \right)$$

if system 1 is much smaller than system 2. We then have

$$\boxed{\delta^2 S = - \sum_{ij} \left(\frac{\partial}{\partial N_j} \frac{\mu_{1i}}{T} \right) \delta N_i \delta N_j < 0} \quad (12.4.9)$$

as the condition for the stability of an equilibrium state when fluctuations in N_k are considered.

In fact, this condition is general and can be applied to fluctuations due to chemical reactions as well. By assuming the fluctuations $\delta N_k = v_k \delta \xi$, in which v_k is the stoichiometric coefficient, we can obtain (Exercise 12.4) condition (12.4.5). *Thus a system that is stable to diffusion is also stable to chemical reactions.* This is called the **Duhem–Jougeut theorem** [3, 4]. A more detailed discussion of this theorem and many other aspects of stability theory can be found in the literature [2].

In summary, the general condition for the stability of the equilibrium state to thermal, volume and mole number fluctuations can be expressed by combining Equations (12.2.8), (12.3.4) and (12.4.9):

$$\boxed{\delta^2 S = - \frac{C_V(\delta T)^2}{T^2} - \frac{1}{T \kappa_T} \frac{(\delta V)^2}{V} - \sum_{ij} \left(\frac{\partial}{\partial N_j} \frac{\mu_i}{T} \right) \delta N_i \delta N_j < 0} \quad (12.4.10)$$

Here C_V is the heat capacity of the system with arbitrary volume V and chemical potential μ_i .

Though we have derived the above results by assuming S to be a function of U , V and N_k , and a system in which U , V and N are constant, the results derived have a more general validity in that they are also valid for other situations in which p and/or T are maintained constant. The corresponding results are expressed in

terms of the enthalpy H , Helmholtz free energy F and Gibbs free energy G . In fact, a more general theory of stability that is valid for a wide range of conditions can be developed using the entropy production $d_i S$ as the basis. This more general approach will be presented in Chapter 14. The Gibbs stability theory is valid only for well-defined boundary conditions such as $T = \text{constant}$. In contrast, the approach of Chapter 14 is independent of such conditions; it depends on irreversible processes inside the system.

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4. Duhem, P., *Traité Élémentaire de Mécanique Chimique*, 4 Vols. 1899, Gauthiers-Villars: Paris.

Exercises

- 12.1** For N_2 at equilibrium at $T = 300 \text{ K}$ and $p = 1.0 \text{ atm}$, using the ideal gas approximation, calculate the change in entropy due to a fluctuation of $\delta T = 1.0 \times 10^{-3} \text{ K}$ in a volume $V = 1.0 \times 10^{-6} \text{ mL}$.
- 12.2** Obtain expressions (12.3.1) and (12.3.2) for the first- and second-order entropy changes due to fluctuations of volume at constant N .
- 12.3** Explain the physical meaning of condition (12.4.4) for stability with respect to a chemical reaction.
- 12.4** In expression (12.4.9) assume that the change in mole number is due to a chemical reaction and obtain expression (12.4.3) and generalize it to (12.4.5).

13

Critical Phenomena and Configurational Heat Capacity

Introduction

In this chapter we shall consider applications of stability theory to critical phenomena of liquid–vapor transitions and the separation of binary mixtures. When the applied pressure and temperature are altered, systems can become unstable, causing their physical state to transform into another distinct state. When the pressure on a gas is increased, for example, it may lose its stability and make a transition to a liquid. Similarly, when the temperature of a two-component liquid mixture (such as hexane and nitrobenzene) changes, the mixture may become unstable to changes in its composition; the mixture then separates into two phases, each rich in one of the components. In Chapters 18 and 19 we shall see that, in far-from-equilibrium systems, loss of stability can lead to a wide variety of complex nonequilibrium states. In equilibrium systems, loss of stability leads to phase separation. In this chapter, we shall also look at the response of a system that can undergo internal transformations to quick changes in temperature. This leads us to the concept of **configurational heat capacity**.

13.1 Stability and Critical Phenomena

In Chapters 1 and 7 we looked briefly at the critical behavior of a pure substance. If its temperature is above the critical temperature T_c then there is no distinction between the gas and the liquid states, regardless of the pressure. Below the critical temperature, at low pressures the substance is in the form of a gas, but liquid begins to form as the pressure is increased. We can understand this transformation in terms of stability.

As shown in Figure 13.1 by the arrows, by using an appropriate path it is possible to go from a gaseous state to a liquid state in a continuous fashion. This was noted by James Thomson, who also suggested that the isotherms below the critical point were also continuous, as shown in Figure 13.2 by the curve IAJKLB_M. This suggestion was pursued by van der Waals, whose equation, as we saw in Chapter 1, indeed gives the curve shown. However, the region JKL in Figure 13.2 cannot be physically realized because it is an unstable region, i.e. it is not mechanically stable. In Section 12.3 we saw that the condition for mechanical stability

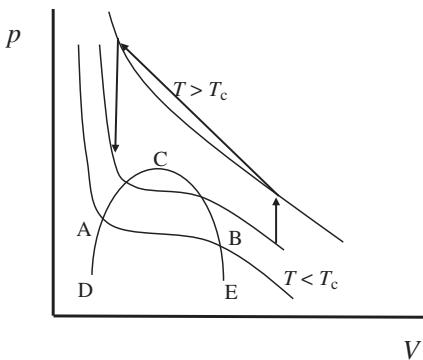


Figure 13.1 The critical behavior of a pure substance. Below the critical temperature, at a fixed temperature, a decrease in volume results in a transition to a liquid state in the region AB in which the two phases coexist. The envelope of the segments AB for the family of isotherms has the shape ECD. Above the critical temperature T_c there is no gas–liquid transition. The gas becomes more and more dense, there being no distinction between the gas and the liquid phases. By following the path shown by the arrows, it is possible to go from a gas to a liquid state without going through a transition.

is that the compressibility $\kappa_T \equiv -(1/V)(\partial V/\partial p) > 0$. In Figure 13.2, this implies that the system is stable only if

$$\left(\frac{\partial p}{\partial V} \right)_T < 0 \quad (13.1.1)$$

a condition that is satisfied for the segments IA and BM and for all the isotherms above the critical temperature. These regions represent stable regions. For the segment JKL we see that $(\partial p/\partial V)_T > 0$, which means that this state is unstable. In this unstable state, if the volume of the system is kept fixed, then small fluctuations in

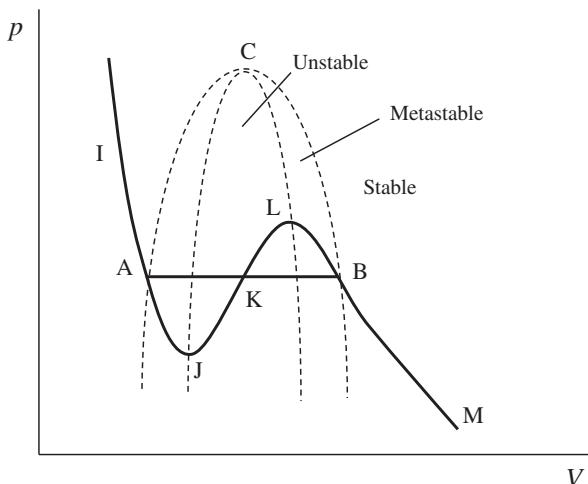


Figure 13.2 The stable, metastable and unstable regions for a liquid–vapor transition are indicated. In the region JKL, $(\partial p/\partial V)_T > 0$, which shows that the system is unstable.

pressure, depending on the initial state, will cause either the vapor to condense or the liquid to evaporate. The system will collapse to a point in the segment AB, where liquid and vapor coexist. As shown in Section 7.4, the amount of the substance in the two phases is given by the ‘lever rule’.

In region BL of Figure 13.2, the system is a supersaturated vapor and may begin to condense if nucleation can occur. This is a **metastable state**. Similarly, in the region AJ we have a superheated liquid that will vaporize if there is nucleation of the vapor phase. The stable, metastable and unstable regions are indicated in Figure 13.2. Finally, at the critical point C, both the first and second derivatives of p with respect to V equal zero. Here, the stability is determined by the higher-order derivatives. For stable mechanical equilibrium at the critical point we have

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = 0, \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0, \quad \left(\frac{\partial^3 p}{\partial V^3}\right)_{T_c} < 0 \quad (13.1.2)$$

which is an inflection point. The inequality $(\partial^3 p / \partial V^3) < 0$ is obtained by considering terms of higher order than $\delta^2 S$.

13.2 Stability and Critical Phenomena in Binary Solutions

In solutions, depending on the temperature, the various components can segregate into separate phases. For simplicity, we shall only consider binary mixtures. This is a phenomenon similar to the critical phenomenon in a liquid–vapor transition, in that in one range of temperature the system is in one homogeneous phase (solution), but in an another range of temperature the system becomes unstable and the two components separate into two phases. The **critical temperature** that separates these two ranges depends on the composition of the mixture. This can happen in three ways, as illustrated by the following examples.

At atmospheric pressure, liquids *n*-hexane and nitrobenzene are miscible in all proportions when the temperature is above 19 °C. Below 19 °C, the mixture separates into two distinct phases, one rich in nitrobenzene and the other in *n*-hexane. The corresponding phase diagram is shown in Figure 13.3a. At about 10 °C, for example, in one phase the mole fraction of nitrobenzene is 0.18, but in the other phase the mole fraction is about 0.75. As the temperature increases, at $T = T_c$, the two liquid layers become identical in composition, indicated by the point C. Point C is called the **critical solution point** or **consolute point** and its location depends on the applied pressure. In this example, above the critical temperature the two liquids are miscible in all proportions. Hence, the system is said to have an **upper critical temperature**. However, this is not always the case, as shown in Figure 13.3b and c. The critical temperature can be such that below T_c the two components become miscible in all proportions. An example of such a mixture is that of diethylamine and water. Such a mixture is said to have a **lower critical solution temperature**. A binary system can have both an upper and a lower critical solution temperature, as shown in Figure 13.3c. An example of such a system is a mixture of *m*-toluidine and glycerol.

Let us now look at the phase separation of binary mixtures from the point of view of stability. The separation of phases occurs when the system becomes unstable with respect to diffusion of the two components; that is, if the separation of the two components results in an increase in entropy, then the fluctuations in N_k due to diffusion in a given volume grow, resulting in the separation of the two components. As we saw in Section 12.4, the condition for stability against diffusion of the components is

$$\delta^2 S = - \sum_{i,k} \frac{\partial}{\partial N_k} \left(\frac{\mu_i}{T} \right) \delta N_k \delta N_i < 0 \quad (13.2.1)$$

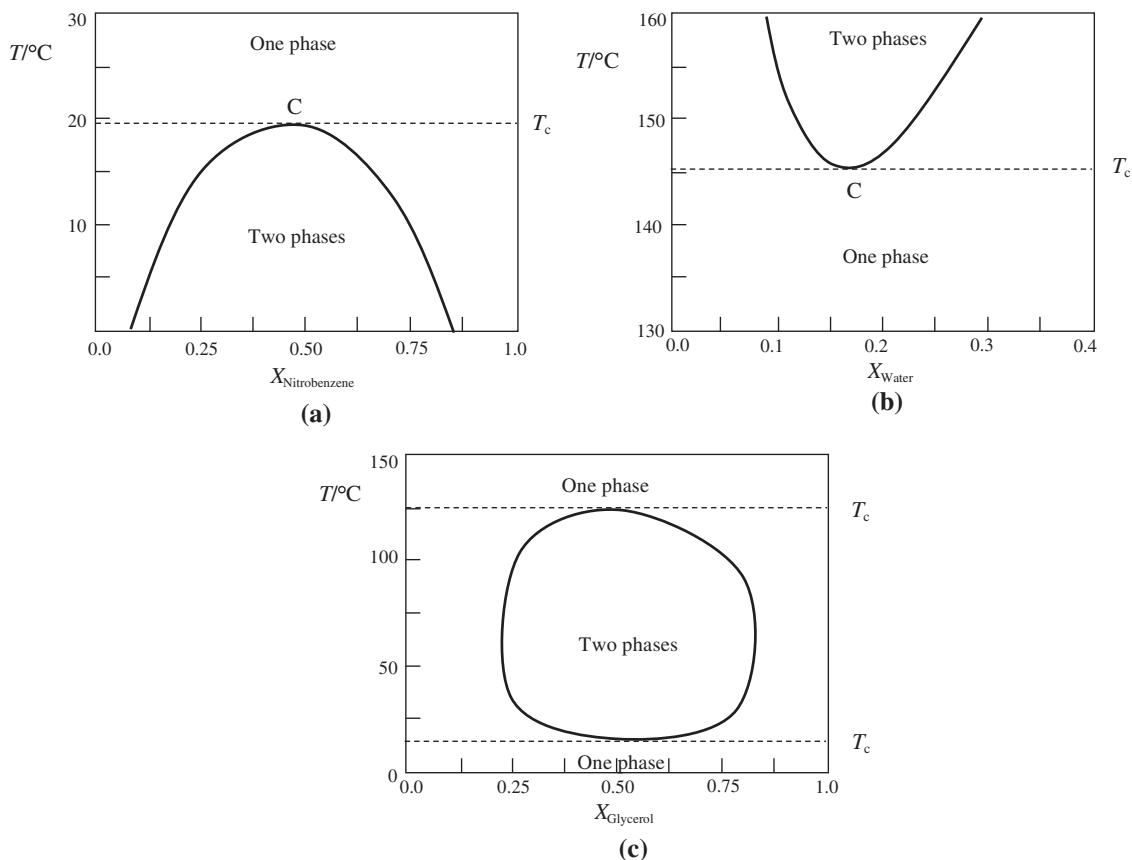


Figure 13.3 Three types of phase diagram showing the critical phenomenon in binary solutions: (a) a mixture of hexane and nitrobenzene; (b) a mixture of diethylamine and water; (c) a mixture of *m*-toluidine and glycerol.

At a fixed T , for binary mixtures this can be written in the explicit form

$$\mu_{11}(\delta N_1)^2 + \mu_{22}(\delta N_2)^2 + \mu_{21}(\delta N_1)(\delta N_2) + \mu_{12}(\delta N_1)(\delta N_2) > 0 \quad (13.2.2)$$

in which

$$\mu_{11} = \frac{\partial \mu_1}{\partial N_1}, \quad \mu_{22} = \frac{\partial \mu_2}{\partial N_2}, \quad \mu_{21} = \frac{\partial \mu_2}{\partial N_1}, \quad \mu_{12} = \frac{\partial \mu_1}{\partial N_2} \quad (13.2.3)$$

Condition (13.2.2) is mathematically identical to the statement that the matrix with elements μ_{ij} is *positive definite*. Also, because

$$\mu_{21} = \frac{\partial \mu_2}{\partial N_1} = \frac{\partial}{\partial N_1} \frac{\partial G}{\partial N_2} = \frac{\partial}{\partial N_2} \frac{\partial G}{\partial N_1} = \mu_{12} \quad (13.2.4)$$

this matrix is symmetric. The stability of the system is assured if the symmetric matrix

$$\begin{bmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{bmatrix} \quad (13.2.5)$$

is positive definite. The necessary and sufficient conditions for the positivity of (13.2.5) are

$$\mu_{11} > 0, \quad \mu_{22} > 0, \quad \mu_{11}\mu_{22} - \mu_{21}\mu_{12} > 0 \quad (13.2.6)$$

If these are not satisfied, then condition (13.2.2) will be violated and the system becomes unstable. Note that (13.2.4) and (13.2.6) imply that $\mu_{12} = \mu_{21} < 0$ to assure stability for all positive values of μ_{11} and μ_{22} .

If we have an explicit expression for the chemical potential, then the conditions (13.2.6) can be related to the activity coefficients of the system. This can be done, for example, for a class of solutions called **strictly regular solutions**, which were studied by Hildebrandt and by Fowler and Guggenheim in 1939. The two components of strictly regular solutions interact strongly and their chemical potentials are of the form

$$\mu_1(T, p, x_1, x_2) = \mu_1^0(T, p) + RT \ln(x_1) + \alpha x_2^2 \quad (13.2.7)$$

$$\mu_2(T, p, x_1, x_2) = \mu_2^0(T, p) + RT \ln(x_2) + \alpha x_1^2 \quad (13.2.8)$$

in which

$$x_1 = \frac{N_1}{N_1 + N_2}, \quad x_2 = \frac{N_2}{N_1 + N_2} \quad (13.2.9)$$

are mole fractions. The factor α is related to the difference in interaction energy between two similar molecules (two molecules of component 1 or two molecules of component 2) and two dissimilar molecules (one molecule of component 1 and one of component 2). For solutions that are nearly perfect, α is nearly zero. From these expressions it follows that activity coefficients are given by $RT \ln \gamma_1 = \alpha x_2^2$ and $RT \ln \gamma_2 = \alpha x_1^2$. We can now apply the stability conditions (13.2.6) to this system. By evaluating the derivative we see that the condition $\mu_{11} = (\partial\mu_1/\partial N_1) > 0$ becomes (Exercise 13.5)

$$\frac{RT}{2\alpha} - x_1(1 - x_1) > 0 \quad (13.2.10)$$

For nearly perfect solutions, since $\alpha \rightarrow 0$, this inequality is always satisfied.

For a given composition specified by x_1 , if $R/2\alpha$ is positive, then for sufficiently large T this condition will be satisfied. However, it can be violated for smaller T . The maximum value of $x_1(1 - x_1)$ is 0.25. Thus, for $RT/2\alpha < 0.25$ there must be a range of x_1 in which the inequality (13.2.10) is not valid. When this happens, the system becomes unstable and separates into two phases. In this case we have an upper critical solution temperature. From (13.2.10), it follows that the relation between the mole fraction and the temperature below which the system becomes unstable is

$$\frac{RT_c}{2\alpha} - x_1(1 - x_1) = 0 \quad (13.2.11)$$

This gives us the plot of T_c as a function of x_1 , shown in Figure 13.4. It is easy to see that the maximum of T_c occurs at $x_1 = 0.5$. Thus, the critical temperature and mole fractions are

$$(x_1)_c = 0.5, \quad T_c = \frac{\alpha}{2R} \quad (13.2.12)$$

The equation $T = (2\alpha/R)x_1(1 - x_1)$ gives the boundary between the metastable region and the unstable region. The boundary between the stable region and the metastable region is the coexistence curve. The coexistence curve of the two phases can be obtained by writing the chemical potentials μ_1 and μ_2 in both phases and equating them. This is left as an exercise.

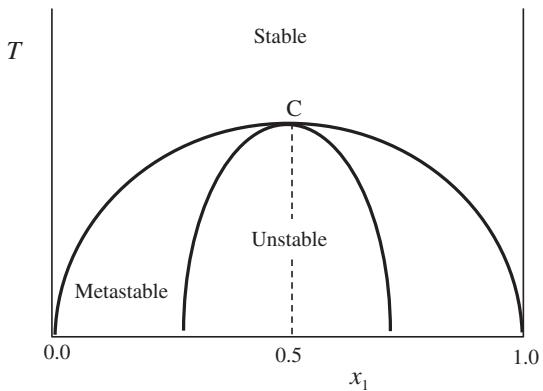


Figure 13.4 The phase diagram for strictly regular solutions.

13.3 Configurational Heat Capacity

The thermodynamic state of chemically reacting systems may be specified by p , T and the extent of reaction ξ . For such a system, the heat capacity must also involve changes in ξ due to the change in temperature. For example, we may consider a compound that may exist in two isomeric forms. Then the extent of reaction ξ specifies the molar amounts of each form given the initial amounts. The heat absorbed by such a system may change not only p and T but also ξ , because the system will relax to its equilibrium with respect to the transformation when p and T change. If the system is in equilibrium with respect to the extent of reaction ξ , then the corresponding affinity $A = 0$. Now, since the heat exchanged $dQ = dU - p \, dV = dH - V \, dp$, we can write

$$dQ = (h_{T,\xi} - V) \, dp + C_{p,\xi} \, dT + h_{T,p} \, d\xi \quad (13.3.1)$$

in which

$$h_{T,\xi} = \left(\frac{\partial H}{\partial p} \right)_{T,\xi}, \quad C_{p,\xi} = \left(\frac{\partial H}{\partial T} \right)_{p,\xi}, \quad h_{T,p} = \left(\frac{\partial H}{\partial \xi} \right)_{T,p} \quad (13.3.2)$$

At constant pressure, we can write the heat capacity $C_p = C_{p,\text{pm}} N$ as

$$C_p = \left(\frac{dQ}{dT} \right)_p = C_{p,\xi} + h_{T,p} \left(\frac{d\xi}{dT} \right)_p \quad (13.3.3)$$

Now for an equilibrium transformation, it can be shown (Exercise 13.6) that

$$\left(\frac{\partial \xi}{\partial T} \right)_{p,A=0} = - \frac{h_{T,p}}{T \left(\frac{\partial A}{\partial \xi} \right)_{T,p}} \quad (13.3.4)$$

By substituting Equation (13.3.4) into Equation (13.3.3) we obtain the following result for a system that remains in equilibrium as it is receiving heat:

$$C_{p,A=0} = C_{p,\xi} - T \left(\frac{\partial A}{\partial \xi} \right)_{T,p} \left(\frac{\partial \xi}{\partial T} \right)_{p,A=0}^2 \quad (13.3.5)$$

However, we have seen in Section 12.4 that the condition for the stability of a system with respect to chemical reactions is $(\partial A / \partial \xi) < 0$. Hence, the second term on the right-hand side of Equation (13.3.5) is positive.

The term $C_{p,\xi}$ is the heat capacity at constant composition. There may be situations, however, in which the relaxation of the transformation represented by ξ is very slow. In this case, we measure the heat capacity at a constant composition. This leads us to the following general conclusion:

The heat capacity at a constant composition is always less than the heat capacity of a system that remains in equilibrium with respect to ξ as it receives heat.

The term $h_{T,p}(d\xi/dT)$ is called the configurational heat capacity, because it refers to the heat capacity due to the relaxation of the system to the equilibrium configuration. The configurational heat capacity can be observed in systems such as glycerin near its crystalline state, where the molecules can vibrate but not rotate freely as they do in the liquid state. This restricted motion is called *libration*. As the temperature is increased, a greater fraction of the molecules begin to rotate. For this system, ξ is the extent of reaction for the libration–rotation transformation. For glycerin, there exists a state called the *vitreous state* in which the libration–rotation equilibrium is reached rather slowly. If such a system is heated rapidly, the equilibrium is not maintained and the measured heat capacity will be $C_{p,\xi}$, which is lower than the heat capacity measured through slow heating during which the system remains in equilibrium.

Further Reading

Hildebrandt, J.M., Prausnitz, J.M., Scott, R.L., *Regular and Related Solutions*. 1970, Van Nostrand-Reinhold: New York.
 Prigogine, I., Defay, R., *Chemical Thermodynamics*, fourth edition. 1967, Longmans: London.
 Van Ness, H.C., Abbott, M.M., *Classical Thermodynamics of Nonelectrolyte Solutions*. 1982, McGraw-Hill, New York.

Exercises

- 13.1** Using the Gibbs–Duhem equation at constant p and T , and the relation $d\mu_k = \sum_i (\partial\mu_k/\partial N_i)_{p,T} dN_i$, show that

$$\sum_i \left(\frac{\partial\mu_k}{\partial N_i} \right)_{p,T} N_i = 0$$

This equation implies that the determinant of the matrix with elements $\mu_{ki} = (\partial\mu_k/\partial N_i)$ is equal to zero. Consequently, one of the eigenvalues of the matrix (13.2.5) is zero.

- 13.2** Show that, if the 2×2 matrix (13.2.5) has a negative eigenvalue, then the inequality (13.2.2) can be violated.
- 13.3** Show that if the matrix (13.2.5) has positive eigenvalues, then $\mu_{11} > 0$ and $\mu_{22} > 0$.
- 13.4** In a strictly binary solution, assuming that the two phases are symmetric, i.e. the dominant mole fraction in both phases is the same, obtain the coexistence curve by equating the chemical potentials in the two phases.
- 13.5** Using Equations (13.2.7) and (13.2.9), show that the condition $m_{11} = \partial m_1 / \partial N_1 > 0$ leads to Equation (13.2.10).
- 13.6** For an equilibrium transformation, show that

$$\left(\frac{\partial \xi}{\partial T} \right)_{p,A=0} = - \frac{h_{T,p}}{T \left(\frac{\partial A}{\partial \xi} \right)_{T,p}}$$

14

Entropy Production, Fluctuations and Small Systems

14.1 Stability and Entropy Production

In Chapter 12 we considered fluctuations in an isolated system in which U , V and N_k are constant and we obtained conditions for the stability of the equilibrium state. These conditions, in fact, have a more general validity in that they remain valid when other types of boundary condition are imposed on the system. For example, instead of constant U and V , we may consider systems maintained at constant T and V , constant p and S or constant T and p . The main reason for the general validity of the stability conditions is that all of these conditions are a direct consequence of the fact that for all natural processes $d_i S > 0$. As we have seen in Chapter 5, when each of these three pairs of variables is held constant, one of the thermodynamic potentials F , H or G is minimized. In each case we have shown that, in accordance with the Second Law,

$$dF = -T d_i S \leq 0 \quad (T, V = \text{constant}) \quad (14.1.1)$$

$$dG = -T d_i S \leq 0 \quad (T, p = \text{constant}) \quad (14.1.2)$$

$$dH = -T d_i S \leq 0 \quad (S, p = \text{constant}) \quad (14.1.3)$$

Through these relations, the change of the thermodynamic potentials ΔF , ΔG or ΔH due to a fluctuation can be related to the entropy production $\Delta_i S$. The system is stable to all fluctuations that result in $\Delta_i S < 0$, because irreversible processes that arise as a result of the fluctuation increasing the entropy restore the system to its equilibrium state. From the above relations it is clear how one could also characterize stability of the equilibrium state by stating that the system is stable to fluctuations for which $\Delta F > 0$, $\Delta G > 0$ or $\Delta H > 0$. For fluctuations in the equilibrium state, these conditions can be written more explicitly in terms of the second-order variations $\delta^2 F > 0$, $\delta^2 G > 0$ and $\delta^2 H > 0$, which in turn can be expressed using the second-order derivatives of these potentials. The conditions for stability obtained in this way are identical to those obtained in Chapter 12.

A theory of stability that is based on the positivity of entropy production in natural processes is more general than the classical Gibbs–Duhem theory of stability [1, 2], which is limited to the constraints expressed in Equations (14.1.1) to (14.1.3) and the associated thermodynamic potentials. In addition, stability theory based on entropy production can also be used to obtain conditions for the stability of nonequilibrium states.

In our more general approach, the main task is to obtain an expression for the entropy production, $\Delta_i S$, associated with a fluctuation. A system is stable to fluctuations if the associated $\Delta_i S < 0$. In Chapter 3 we have seen that the rate of entropy production due to irreversible processes takes the quadratic form

$$\frac{d_i S}{dt} = \sum_k F_k \frac{dX_k}{dt} = \sum_k F_k J_k \quad (14.1.4)$$

in which the F_k are the ‘thermodynamic forces’ and where we have represented dX_k/dt as the ‘flow’ or ‘current’ J_k . Thermodynamic forces arise when there is nonuniformity of temperature, pressure or chemical potential. If we denote the equilibrium state by E and the state to which a fluctuation has driven the system by I , then the change in entropy in going from E to I is

$$\Delta_i S = \int_E^I d_i S = \int_E^I \sum_k F_k dX_k \quad (14.1.5)$$

In this section we shall present simple examples of the calculation of $\Delta_i S$ and defer the more general theory to later chapters in which we consider the stability of nonequilibrium states.

14.1.1 Chemical Stability

Let us look at entropy production associated with a fluctuation in a chemical reaction specified by a change $\delta\xi$ in the extent of reaction (Figure 14.1). In Chapter 4 we have seen that entropy production due to a chemical reaction is

$$d_i S = \frac{A}{T} d\xi \quad (14.1.6)$$

At equilibrium, the affinity $A_{eq} = 0$. For a small change $\alpha = (\xi - \xi_{eq})$ in the extent of reaction from the equilibrium state, we may approximate A by

$$A = A_{eq} + \left(\frac{\partial A}{\partial \xi} \right)_{eq} \alpha = \left(\frac{\partial A}{\partial \xi} \right)_{eq} \alpha \quad (14.1.7)$$

The entropy production $\Delta_i S$ due to the fluctuation can be calculated by noting that $d\xi = d\alpha$:

$$\Delta_i S = \int_0^{\delta\xi} d_i S = \int_0^{\delta\xi} \frac{A}{T} d\xi = \frac{1}{T} \int_0^{\delta\xi} \left(\frac{\partial A}{\partial \xi} \right)_{eq} \alpha d\alpha = \left(\frac{\partial A}{\partial \xi} \right)_{eq} \frac{(\delta\xi)^2}{2T} \quad (14.1.8)$$

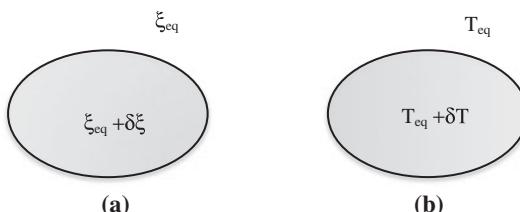


Figure 14.1 (a) A local fluctuation in the extent of reaction; the entropy change associated with such a fluctuation can be calculated using Equation (14.1.9a). (b) A local fluctuation in temperature; the associated entropy change can be calculated using Equation (14.1.11).

The **stability condition** $\Delta_i S < 0$ now takes the form

$$\boxed{\Delta_i S = \left(\frac{\partial A}{\partial \xi} \right)_{eq} \frac{(\delta \xi)^2}{2T} < 0} \quad (14.1.9a)$$

which is identical to Equation (12.4.3). If we consider r chemical reactions, we have

$$\boxed{\Delta_i S = \sum_{i,j}^r \frac{1}{2T} \left(\frac{\partial A_i}{\partial \xi_j} \right)_{eq} \delta \xi_i \delta \xi_j < 0} \quad (14.1.9b)$$

Using the relation between the affinities A_i and the corresponding chemical potentials μ_k and the relation between ξ_j and the molar amounts N_k , the above equation can be written as (Exercise 12.4)

$$\Delta_i S = - \sum_{i,j}^r \frac{1}{T} \left(\frac{\partial \mu_i}{\partial N_j} \right)_{eq} \frac{\delta N_i \delta N_j}{2} < 0 \quad (14.1.9c)$$

It is important to note that we arrived at this condition for stability by only assuming that for spontaneous processes $\Delta_i S > 0$; consequently, it is independent of the boundary conditions imposed on the system.

14.1.2 Thermal Stability

As a second example, let us consider thermal fluctuations. Let the temperature of a local region of interest be $T_{eq} + \alpha$, where T_{eq} is the equilibrium temperature and α is a small deviation. As we have seen in Chapter 3, the entropy production due to heat flow is

$$\begin{aligned} \frac{d_i S}{dt} &= \left(\frac{1}{T_{eq} + \alpha} - \frac{1}{T_{eq}} \right) \frac{dQ}{dt} \\ &\simeq - \frac{\alpha}{T_{eq}^2} \frac{dQ}{dt} \end{aligned} \quad (14.1.10)$$

For small changes in temperature, we can write $dQ = C_V d\alpha$ where C_V is the heat capacity at constant volume. Then for a temperature change of δT , we have

$$\Delta_i S = \int_0^{\delta T} d_i S = \int_0^{\delta T} -\frac{C_V}{T_{eq}^2} \alpha d\alpha = -\frac{C_V}{T_{eq}^2} \frac{(\delta T)^2}{2} \quad (14.1.11)$$

The condition for thermal stability can now be written as

$$\boxed{\Delta_i S = - \frac{C_V}{T_{eq}^2} \frac{(\delta T)^2}{2} < 0} \quad (14.1.12)$$

which is identical to condition (12.2.8). As before, we conclude that this condition is satisfied only if $C_V > 0$.

Similarly, the probability of entropy production associated with the fluctuation of the volume of a subsystem at a fixed pressure and molar amount N_k of its constituents can be shown to be equal to

$\Delta_i S = -(1/T_{\text{eq}}\kappa_T)(\delta V^2/2V_{\text{eq}})$ in which $\kappa_T = -(1/V)(\partial V/\partial p)_T$ is the isothermal compressibility. Combining the above results, for fluctuations in T , N_k and V we arrive at

$$\begin{aligned}\Delta_i S &= \int_E^I d_i S = \int_E^I \sum_k F_k dX_k \\ &= -\frac{C_V(\delta T)^2}{2T^2} - \frac{1}{T\kappa_T} \frac{(\delta V)^2}{2V} - \sum_{i,j} \left(\frac{\partial}{\partial N_j} \frac{\mu_i}{T} \right) \frac{\delta N_i \delta N_j}{2} < 0\end{aligned}\quad (14.1.13)$$

Finally, we note that this entropy term is second order in the perturbations δT , δV and δN_k , consistent with the theory of Chapter 12.

In expression (14.1.13), the independent variables are T , V and N . The following more general expression through which the entropy change is due to any other set of independent variables can be derived from (14.1.13):

$$\Delta_i S = \frac{\delta^2 S}{2} = \frac{-1}{2T} \left[\delta T \delta S - \delta p \delta V + \sum_i \delta \mu_i \delta N_i \right] < 0 \quad (14.1.14)$$

In Equation (14.1.13) in the first term $C_V \delta T/T = \delta Q/T = \delta S$; similarly, in the second term $\delta V/\kappa_T V = -\delta p$; and in the third term $\sum_j (\partial \mu_i / \partial N_j) dN_j = \delta \mu_i$. Using these relations it is easy to see that (14.1.13) can be written in the form (14.1.14).

That the entropy production should be second order in the perturbation follows from the fact that the forces F_k and fluxes J_k vanish at equilibrium. If $\delta J_k = (dX_k/dt)$ and δF_k are forces and fluxes associated with the fluctuation close to equilibrium, entropy production takes the form

$$\frac{d\Delta_i S}{dt} = \frac{d_i S}{dt} = \sum_k \delta F_k \delta J_k = \sum_k F_k J_k > 0 \quad (14.1.15)$$

From this expression it is clear that the leading contribution to the entropy change due to a fluctuation in the equilibrium state is of second order and we may make this explicit by using $\delta^2 S/2$ in place of $\Delta_i S$. In terms of $\delta^2 S/2$, Equations (14.1.14) and (14.1.15) can be written as

$$\boxed{\delta^2 S < 0}, \boxed{\frac{1}{2} \frac{d\delta^2 S}{dt} = \sum_k \delta F_k \delta J_k > 0} \quad (14.1.16)$$

in which the second equation is the Second Law. These two equations express the essence of stability of the equilibrium state: *the fluctuations decrease the entropy whereas the irreversible processes restore the system to its initial state*. These equations are specific cases of a more general theory of stability formulated by Lyapunov, which we will discuss in Chapters 17 and 18.

14.2 Thermodynamic Theory of Fluctuations

14.2.1 The Probability Distribution

In the previous sections we have discussed the stability of a thermodynamic state in the face of fluctuations. However, the theory that we presented does not give us the probability of a fluctuation of a given magnitude. To be sure, our experience tells us that fluctuations in thermodynamic quantities are extremely small in macroscopic systems except near critical points; still we would like to have a theory that relates these fluctuations to thermodynamic quantities and gives us the conditions under which they become important.

In an effort to understand the relation between microscopic behavior of matter, which was in the realm of mechanics, and macroscopic laws of thermodynamics, Ludwig Boltzmann (1844–1906) introduced his famous relation that related entropy and probability (see Box 3.1):

$$S = k_B \ln W \quad (14.2.1)$$

in which $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant and W is the number of microscopic states corresponding to the macroscopic thermodynamic state. The variable W is called **thermodynamic probability** (as suggested by Max Planck) because, unlike the usual probability, it is a number larger than one – in fact it is a very large number. Thus, Boltzmann introduced the idea of probability into thermodynamics – a controversial idea whose true meaning could only be understood through the modern theories of unstable dynamical systems [3].

Albert Einstein (1879–1955) proposed a formula for the probability of a fluctuation in thermodynamic quantities by using Boltzmann's idea in reverse; whereas Boltzmann used 'microscopic' probability to derive thermodynamic entropy, Einstein used thermodynamic entropy to obtain the probability of a fluctuation through the following relation:

$$P(\Delta S) = Z^{-1} e^{\Delta S/k_B} \quad (14.2.2)$$

in which ΔS is the entropy change associated with the fluctuation from the state of equilibrium and Z is a normalization constant that ensures the sum of all probabilities equals one. Though relations (14.2.1) and (14.2.2) may be mathematically close, it is important to note that conceptually one is the opposite of the other. In Equation (14.2.1) the probability of a state is the fundamental quantity and entropy is derived from it; in Equation (14.2.2) entropy as defined in thermodynamics is the fundamental quantity and the probability of a fluctuation is derived from it. Einstein's formula shows that from thermodynamic entropy we can also obtain the probability of fluctuations.

To obtain the probability of a fluctuation, we must obtain the entropy change associated with it (Figure 14.2). The basic problem then is to obtain ΔS in terms of the fluctuations δT , δp , etc. However, this has

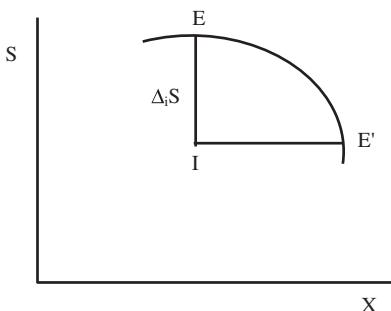


Figure 14.2 The entropy change ΔS associated with a fluctuation from an equilibrium state E to a nonequilibrium state I . Entropy S is shown as a function of a thermodynamic variable X . The fluctuation that decreases entropy drives the system to the state I . We compute the entropy change ΔS associated with such a fluctuation by computing the entropy produced, $\Delta_i S$, as the system relaxes back to the equilibrium state E from I . In classical formalisms that do not use $d_i S$, the entropy change ΔS is calculated by first determining an equilibrium state E' that has the same entropy as the state I and then by computing the entropy change along a reversible trajectory $E'E$ of equilibrium states.

already been done in the previous section. Expression (14.1.13) gives us the entropy associated with a fluctuation:

$$\Delta S = -\frac{C_V(\delta T)^2}{2T^2} - \frac{1}{2T\kappa_T} \frac{(\delta V)^2}{V} - \sum_{ij} \left(\frac{\partial}{\partial N_j} \frac{\mu_i}{T} \right) \frac{\delta N_i \delta N_j}{2} \quad (14.2.3)$$

This expression can be made more explicit if the derivative of the chemical potential is expressed in terms of the molar amounts N_k . For ideal gases this can easily be done because the chemical potential of a component k is

$$\begin{aligned} \mu_k &= \mu_{k0}(T) + RT \ln(p_k/p_0) \\ &= \mu_{k0}(T) + RT \ln(N_k RT / V p_0) \end{aligned} \quad (14.2.4)$$

in which p_0 is the standard pressure (usually 1 bar). Substituting this expression into Equation (14.2.3), we obtain

$$\boxed{\Delta S = -\frac{C_V(\delta T)^2}{2T^2} - \frac{1}{T\kappa_T} \frac{(\delta V)^2}{2V} - \sum_i \frac{R(\delta N_i)^2}{2N_i}} \quad (14.2.5)$$

Here C_V is the heat capacity of the ideal gas mixture. In this expression the N_i are expressed in moles. By multiplying them by the Avogadro number N_A , they can be converted to *numbers of molecules* \tilde{N}_i . The same expression can be derived for an ideal system for which $\mu_k = \mu_{k0}(T) + RT \ln x_k$, in which x_k is the mole fraction (Exercise 14.2). Now using the Einstein formula (14.2.2), the probability of a fluctuation in T , V and \tilde{N}_i can be written as

$$\begin{aligned} P(\delta T, \delta V, \delta \tilde{N}_i) &= Z^{-1} \exp(\Delta S/k_B) \\ &= Z^{-1} \exp \left[-\frac{C_V(\delta T)^2}{2k_B T^2} - \frac{1}{2k_B T \kappa_T} \frac{(\delta V)^2}{V} - \sum_i \frac{(\delta \tilde{N}_i)^2}{2\tilde{N}_i} \right] \end{aligned} \quad (14.2.6)$$

in which we have replaced R in Equation (14.2.5) by $k_B N_A$. In this expression the normalization factor Z is defined as

$$Z = \iiint P(x, y, z) dx dy dz \quad (14.2.7)$$

The probability distribution is a Gaussian in each of the independent variables δT , δV and $\delta \tilde{N}_k$. The integral of a Gaussian is given by

$$\int_{-\infty}^{\infty} e^{-x^2/a} dx = \sqrt{\pi a} \quad (14.2.8)$$

With this formula, the probability can be explicitly written and the root mean square value of the fluctuations can be obtained (Exercise 14.3). A more general form of the probability distribution can be obtained from Equation (14.1.14) in which the change of entropy due to fluctuation is expressed in terms of products of pairs of variables:

$$\boxed{P = Z^{-1} \exp \left[\frac{\delta^2 S}{2k_B} \right] = Z^{-1} \exp \left[\frac{-1}{2k_B T} (\delta T \delta S - \delta p \delta V + \sum_k \delta \mu_k \delta N_k) \right]} \quad (14.2.9)$$

in which Z is the normalization constant. For any set of independent variables Y_k , Equation (14.2.9) can be used to obtain the probability distribution for the fluctuation of these variables by expressing δT , δS , etc., in

terms of the fluctuations in Y_k . For notational convenience, let us denote the deviations of the independent variables Y_k from their equilibrium values by α_k . Then, in general, $\delta^2 S$ will be a quadratic function in α_k :

$$\frac{\delta^2 S}{2} = -\frac{1}{2} \sum_{i,j} g_{ij} \alpha_i \alpha_j \quad (14.2.10)$$

in which the g_{ij} are appropriate coefficients and $g_{ij} = g_{ji}$; the negative sign is introduced only to emphasize the fact that $\delta^2 S$ is a negative quantity. For a single α , the probability $P(\alpha) = \sqrt{(g/2\pi k_B)} \exp(-g\alpha^2/2k_B)$. In the more general case, the corresponding probability distribution can be written explicitly as

$$P(\alpha_1, \alpha_2, \dots, \alpha_m) = \sqrt{\frac{\det [\mathbf{g}]}{(2\pi k_B)^m}} \exp \left[-\frac{1}{2k_B} \sum_{i,j=1}^m g_{ij} \alpha_i \alpha_j \right] \quad (14.2.11)$$

in which $\det [\mathbf{g}]$ is the determinant of the matrix g_{ij} . In the rest of this section we shall derive some important general results that we will use in Chapter 16 for deriving a set of fundamental relations in nonequilibrium thermodynamics, the **Onsager reciprocal relations**.

14.2.2 Average Values and Correlations

In general, given a probability distribution for a set of variables α_k , one can compute average values and correlations between pairs of variables. We shall use the notation $\langle f \rangle$ to denote the average value of any function $f(\alpha_1, \alpha_2, \dots, \alpha_m)$ of the variables α_k ; it is computed using the integral

$$\langle f \rangle = \int f(\alpha_1, \alpha_2, \dots, \alpha_m) P(\alpha_1, \alpha_2, \dots, \alpha_m) d\alpha_1 d\alpha_2 \cdots d\alpha_m \quad (14.2.12)$$

The correlation between two variables f and g is defined as

$$\langle fg \rangle = \int f(\alpha_1, \alpha_2, \dots, \alpha_m) g(\alpha_1, \alpha_2, \dots, \alpha_m) P(\alpha_1, \alpha_2, \dots, \alpha_m) d\alpha_1 d\alpha_2 \cdots d\alpha_m \quad (14.2.13)$$

We shall soon give a general expression for the correlation $\langle \alpha_i \alpha_j \rangle$ between any two variables α_i and α_j , but first we shall calculate other correlation functions that will lead us to the result.

We have seen earlier that the entropy production (14.1.15) associated with a small fluctuation from equilibrium can be written as

$$\frac{d\Delta_i S}{dt} = \frac{1}{2} \frac{d\delta^2 S}{dt} = \sum_k F_k J_k \quad (14.2.14)$$

in which the F_k are thermodynamic forces that drive the flows $J_k = dX_k/dt$, both of which vanish at equilibrium. Now if we compute the time derivative of the general quadratic expression (14.2.10), since $g_{ij} = g_{ji}$, we obtain

$$\frac{1}{2} \frac{d\delta^2 S}{dt} = - \sum_{i,j} g_{ij} \alpha_i \frac{d\alpha_j}{dt} \quad (14.2.15)$$

If we identify the derivative ($d\alpha_j/dt$) as a ‘thermodynamic flow’ (δJ_j close to equilibrium), comparison of Equations (14.2.14) and (14.2.15) shows that the term

$$F_j \equiv - \sum_i g_{ij} \alpha_i \quad (14.2.16)$$

will be the corresponding thermodynamic force. Furthermore, due to the Gaussian form of the probability distribution (14.2.11), we also have the relation

$$F_i = k_B \frac{\partial \ln P}{\partial \alpha_i} \quad (14.2.17)$$

We will first show that

$$\langle F_i \alpha_j \rangle = -k_B \delta_{ij} \quad (14.2.18)$$

in which δ_{ij} is the ‘Kronecker delta’: $\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$. This shows that each fluctuation is correlated to its corresponding force but not to other forces. By definition

$$\langle F_i \alpha_j \rangle = \int F_i \alpha_j P d\alpha_1 d\alpha_2 \cdots d\alpha_m$$

Using Equation (14.2.17) this integral can be written as

$$\begin{aligned} \langle F_i \alpha_j \rangle &= \int k_B \left(\frac{\partial \ln P}{\partial \alpha_i} \right) \alpha_j P d\alpha_1 d\alpha_2 \cdots d\alpha_m \\ &= \int k_B \left(\frac{\partial P}{\partial \alpha_i} \right) \alpha_j d\alpha_1 d\alpha_2 \cdots d\alpha_m \end{aligned}$$

Which, on integration by parts, gives

$$\langle F_i \alpha_j \rangle = k_B P \alpha_j \Big|_{-\infty}^{+\infty} - k_B \int \left(\frac{\partial \alpha_j}{\partial \alpha_i} \right) P d\alpha_1 d\alpha_2 \cdots d\alpha_m$$

The first term vanishes because $\lim_{\alpha \rightarrow \pm\infty} \alpha_j P(\alpha_j) = 0$. The second term vanishes if $i \neq j$ and equals $-k_B$ if $i = j$. Thus we arrive at the result (14.2.18).

Also useful is the following general result. By substituting Equation (14.2.16) into Equation (14.2.18) we arrive at

$$\langle F_i \alpha_j \rangle = \left\langle - \sum_k g_{ik} \alpha_k \alpha_j \right\rangle = - \sum_k g_{ik} \langle \alpha_k \alpha_j \rangle = -k_B \delta_{ij}$$

which simplifies to

$$\sum_k g_{ik} \langle \alpha_k \alpha_j \rangle = k_B \delta_{ij} \quad (14.2.19)$$

This implies that the matrix $\langle \alpha_i \alpha_j \rangle / k_B$ is the inverse of the matrix g_{ik} :

$$\langle \alpha_i \alpha_j \rangle = k_B (g^{-1})_{ij} \quad (14.2.20)$$

One particularly interesting result is the average value of the entropy fluctuations associated with the m independent variables α_i :

$$\begin{aligned} \langle \Delta_i S \rangle &= \left\langle -\frac{1}{2} \sum_{i,j=1}^m g_{ij} \alpha_i \alpha_j \right\rangle = -\frac{1}{2} \sum_{i,j=1}^m g_{ij} \langle \alpha_i \alpha_j \rangle = -\frac{k_B}{2} \sum_{i,j=1}^m g_{ij} (g^{-1})_{ji} \\ &= -\frac{k_B}{2} \sum_{i=1}^m \delta_{ii} = -\frac{mk_B}{2} \end{aligned} \quad (14.2.21)$$

Thus, we see that the average value of entropy fluctuations due to m independent variables is given by the simple expression

$$\langle \Delta_i S \rangle = -\frac{mk_B}{2} \quad (14.2.22)$$

Each independent process that contributes to entropy is associated with a fluctuation $-k_B/2$ at equilibrium. This result is analogous to the equipartition theorem in statistical mechanics, which states that each degree of freedom carries with it an average energy of $k_B T/2$.

As a simple example, let us consider entropy fluctuations due to r chemical reactions. As was shown in Equation (14.1.9), we have

$$\Delta_i S_{\text{chem}} = \sum_{i,j}^r \frac{1}{2T} \left(\frac{\partial A_i}{\partial \xi_j} \right)_{\text{eq}} \delta \xi_i \delta \xi_j = -\frac{1}{2} \sum_{i,j}^r g_{ij} \delta \xi_i \delta \xi_j \quad (14.2.23)$$

in which we have made the identification $g_{ij} = -(1/T)(\partial A_i / \partial \xi_j)_{\text{eq}}$. From the general result (14.2.22) we see that the average value of the entropy fluctuations due to r chemical reactions is

$$\langle \Delta_i S_{\text{chem}} \rangle = -r \frac{k_B}{2} \quad (14.2.24)$$

This shows how fluctuations in ξ_i decrease entropy. In Chapter 16 we shall use Equations (14.2.16) and (14.2.20) to derive the Onsager reciprocal relations.

14.3 Small Systems

Fluctuations discussed in the above two sections are clearly important when considering small systems. However, thermodynamics of small systems has features not considered in previous chapters. We shall discuss them in this section.

Pioneering work in formulating the thermodynamics of small systems was done by Terrell Hill [4] in the early 1960s. It could be applied to many small systems that we encounter in nature: small particles in the atmosphere called aerosols (which include small droplets of water containing dissolved compounds), crystal nuclei in supersaturated solutions, colloids, small particles in interstellar space and ‘nanosystems’. Important as it was, thermodynamics of small systems has taken on a new significance due to the development of **nanoscience**, the production and study of particles in the size range 1–100 nm. Thermodynamics applied to particles in the ‘nano range’ is called **nanothermodynamics**, but, because we do not limit our discussion to this size range, we call this topic thermodynamics of small systems.

The laws of thermodynamics are universal, valid for all systems. However, depending on the system being considered, various approximations are made. Care is necessary in applying thermodynamics to systems that are very small. First, it must be ensured that thermodynamic variables that were used for large systems have a clear physical meaning when used to describe small systems. Due to random molecular motion, thermodynamic variables will fluctuate about their average values. We need a clear understanding of the magnitude of these fluctuations relative to the average values and if and why the system is stable when subjected to them. Second, quantities, such as interfacial energy, that could be neglected for large systems must be taken into consideration. In Chapter 5, we have already seen how interfacial energy could be included in the thermodynamic description of a system. We shall extend this formalism to understand why some properties, such as solubility and melting point, change with size. In general, properties of very fine powders

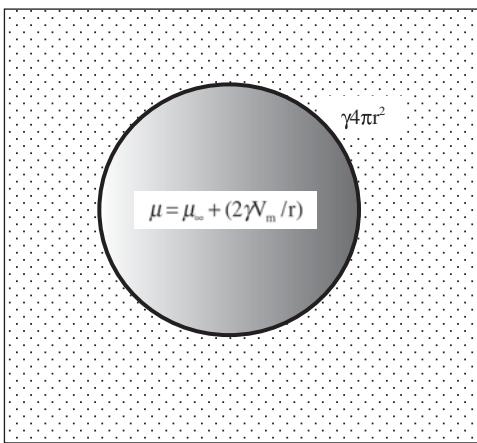


Figure 14.3 Chemical potential of a small spherical particle or liquid drop depends of the radius r , where γ is the interfacial energy or surface tension ($J m^{-2}$). The energy of the interface equals $4\pi r^2 \gamma$.

could be significantly different from those of a bulk substance – hence the current interest in nanotechnology. We shall begin by discussing the thermodynamic formalism that includes interfacial energy.

14.3.1 Chemical Potential of Small Systems

Chemical potential is an important variable that enables us to understand how the properties of a system may change as its size decreases to microscopic dimensions. In this section, we will derive an expression for the chemical potential as a function of size.

In Chapter 5 (Section 5.6) we noted that molecules at an interface have different energy and entropy compared to molecules in the bulk. This **interfacial energy** or **surface tension**, γ , is generally of the order of $10^{-1} - 10^{-2} J m^{-2}$. Whether interfacial energy can be neglected or not depends on the size of the system, more precisely on the area-to-volume ratio. If U_m is the molar energy, for a sphere of radius r , the ratio of interfacial energy to bulk energy is $4\pi r^2 \gamma / [(4\pi r^3 / 3V_m) U_m] = 3\gamma V_m / r U_m$, in which V_m is the molar volume. If this quantity is very small, the interfacial energy can be neglected and as $r \rightarrow \infty$ it becomes zero. If this ratio is not small, then we include the interfacial energy term in the expression for dU . For a pure substance:

$$dU = T dS - p dV + \mu dN + \gamma d\Sigma \quad (14.3.1)$$

in which Σ is the interfacial area. The last two terms can be combined to express the chemical potential as a function of the size of the system. For simplicity, we shall assume that the system is a sphere of radius r . Then the molar amount $N = (4\pi r^3 / 3V_m)$. The interfacial term $d\Sigma = d(4\pi r^2) = 8\pi r dr$ can be written in terms of dN by noting that $dN = 4\pi r^2 dr / V_m = (r / 2V_m) d\Sigma$. Thus we can substitute $(2V_m / r) dN$ for $d\Sigma$ in Equation (14.3.1) to obtain

$$dU = T dS - p dV + \left(\mu + \frac{2\gamma V_m}{r} \right) dN \quad (14.3.2)$$

Using this equation we see that, for a pure substance, we can assign an effective chemical potential that depends on the system's radius (Figure 14.3). We shall write this potential as

$$\mu = \mu_\infty + \frac{2\gamma V_m}{r}$$

(14.3.3)

in which μ_∞ is the chemical potential as $r \rightarrow \infty$; it is the ‘bulk chemical potential’ that has been used in the previous chapters when interfacial energy could be ignored. The Gibbs energy of the system is

$$G = \mu_\infty N + \gamma \Sigma \quad (14.3.4)$$

and simple calculation shows that $(\partial G/\partial N)_{p,T} = \mu = \mu_\infty + (2\gamma V_m/r)$.

The above equation can also be understood in terms of the excess pressure in a small system. In Chapter 5, we have seen that surface tension (or interfacial tension) increases the pressure in a small spherical system by an amount $\Delta p = 2\gamma/r$ (see Equation (5.6.6)). Expression (14.3.3) is the chemical potential under this higher pressure. This can be seen by noting that

$$\mu(p + \Delta p, T) = \mu(p, T) + \int_p^{p+\Delta p} \left(\frac{\partial \mu}{\partial p} \right)_T dp = \mu(p, T) + \int_p^{p+\Delta p} V_m dp, \quad \Delta p = \frac{2\gamma}{r}$$

where we have used the relation $(\partial G_m/\partial p)_T = (\partial \mu/\partial p)_T = V_m$. For solids and liquids the molar volume V_m does not change much with changes in pressure and hence we could write the above expression as

$$\mu(p + \Delta p, T) = \mu(p, T) + V_m \Delta p = \mu(p, T) + \frac{2\gamma V_m}{r} \quad (14.3.5)$$

which is Equation (14.3.3). Therefore the increase in chemical potential of a small system by a term $(2\gamma V_m/r)$ is a consequence of an increase in the pressure due to surface tension.

14.4 Size-Dependent Properties

Using the chemical potential (14.3.3), several size-dependent properties can be derived. We shall consider solubility and melting point. As noted above, small systems have a higher chemical potential due to the fact that they are under a higher pressure. This causes a change in their solubility and melting point.

14.4.1 Solubility

We consider a solid solute Y in equilibrium with its solution. The chemical potentials of Y in the solid and solution phases are equal. At equilibrium, the concentration of the solution is the saturation concentration called the **solubility**; we shall denote it by $[Y]_{eq}$. We shall denote the solid and solution phases with the subscripts ‘s’ and ‘l’ respectively.

As shown in Equation (8.3.17), in the molarity scale, the equilibrium chemical potential of the solute in the solution phase is $\mu_{Y,l} = \mu_Y^{c0} + RT \ln(\gamma_Y [Y]_{eq}/[Y]^0)$, in which γ_Y is the activity coefficient of Y (not to be mistaken for the interfacial energy γ) and $[Y]^0$ is the standard concentration equal to 1.0 M. For solute particles of radius r in equilibrium with the solution, $\mu_{Y,l} = \mu_{Y,s}$, which gives

$$\mu_{Y,l} = \mu_Y^{c0} + RT \ln \left(\frac{\gamma_Y [Y]_{eq}}{[Y]^0} \right) = \mu_{Y,s} = \mu_{Y,\infty} + \frac{2\gamma V_m}{r} \quad (14.4.1)$$

in which we have used Equation (14.3.3) for the chemical potential of the solid phase. The quantity $\mu_Y^{c0} - \mu_{Y,\infty} = \Delta G_{sol}$ is the molar Gibbs energy of solution (defined for large particles $r \rightarrow \infty$). Hence the above equation can be written as

$$RT \ln \left(\frac{\gamma_Y [Y]_{eq}}{[Y]^0} \right) = -\Delta G_{sol} + \frac{2\gamma V_m}{r}$$

i.e.

$$\left(\frac{\gamma_Y [Y]_{eq}}{[Y]^0} \right) = \exp \left(\frac{-\Delta G_{sol}}{RT} \right) \exp \left(\frac{2\gamma V_m}{rRT} \right) \quad (14.4.2)$$

If we denote the equilibrium concentration for solute particles of radius r by $[Y(r)]_{\text{eq}}$ and assume that the activity coefficient γ_Y does not vary much in the concentration range of interest, Equation (14.4.2) can be simplified to the following relation :

$$[Y(r)]_{\text{eq}} = [Y(\infty)]_{\text{eq}} \exp\left(\frac{2\gamma V_m}{rRT}\right) \quad (14.4.3a)$$

or, more generally,

$$a_Y(r)_{\text{eq}} = a_Y(\infty)_{\text{eq}} \exp\left(\frac{2\gamma V_m}{rRT}\right) \quad (14.4.3b)$$

in which a_Y is the activity of Y. These equations give solubility $[Y(r)]_{\text{eq}}$ as a function of the particle size. They tell us that the saturation concentration will be higher for smaller particles; that is smaller particles have higher solubility. It is generally called the **Gibbs–Thompson** equation but some authors also call it the **Ostwald–Freundlich** equation. The solubility of AgCl, AgBr and AgI particles whose size is in the range 2–20 nm can be satisfactorily explained using the Gibbs–Thompson equation (Figure 14.4).

The higher solubility of smaller particles has an interesting consequence. As shown in Figure 14.5, consider a supersaturated solution containing solute particles of different size or radii. Supersaturation means that the chemical potential of the solute in the solution phase is higher, $\mu_l > \mu_s$. Therefore the solute will begin to precipitate out and deposit on the solid particles. As the chemical potential in the solution phase decreases due to solute deposition on the solid phase, there will come a point at which the solution is in equilibrium with the smaller particles, $\mu_l \approx \mu_s(r_{\text{small}})$, but its chemical potential is still higher than that of the larger particles, $\mu_l > \mu_s(r_{\text{large}})$. Hence solute from the solution begins to deposit on the larger particles, causing a reduction of concentration in the vicinity of the larger particles. A concentration gradient is thus established, with higher concentration near smaller particles and lower concentration near larger particles. The solute then begins to flow from the vicinity of the smaller particles towards the larger particles. A consequent drop in concentration in the vicinity of the smaller particles causes them to dissolve while the larger particles continue to grow. As the smaller particles dissolve, their solubility increases, causing them to dissolve even faster and they ultimately disappear. Such growth of larger particles at the expense of smaller ones is called **Ostwald ripening**. It is a very slow process but it can be observed.

14.4.2 Melting Point

The higher chemical potential of small particles also has the effect of reducing their melting point. Let us consider a solid particle of radius r in equilibrium with the melt. Let T_m be the melting point for the bulk substance; it is the temperature at which large particles are in equilibrium with the melt. For small particles of radius r , due to their higher chemical potential, let us assume that the melting point is $T_m + \Delta T$. The chemical potential of a pure substance, $\mu(p, T)$, is a function of p and T . Using Equation (14.3.3) for the chemical potential of the solid particle, we see that the solid–melt equilibrium for large particles at T_m implies

$$\mu_{s\infty}(p, T_m) = \mu_l(p, T_m) \quad (14.4.4)$$

and the same for small particles at $T_m + \Delta T$ implies

$$\mu_s(p, T_m + \Delta T) = \mu_{s\infty}(p, T_m + \Delta T) + \frac{2\gamma V_m}{r} = \mu_l(p, T_m + \Delta T) \quad (14.4.5)$$

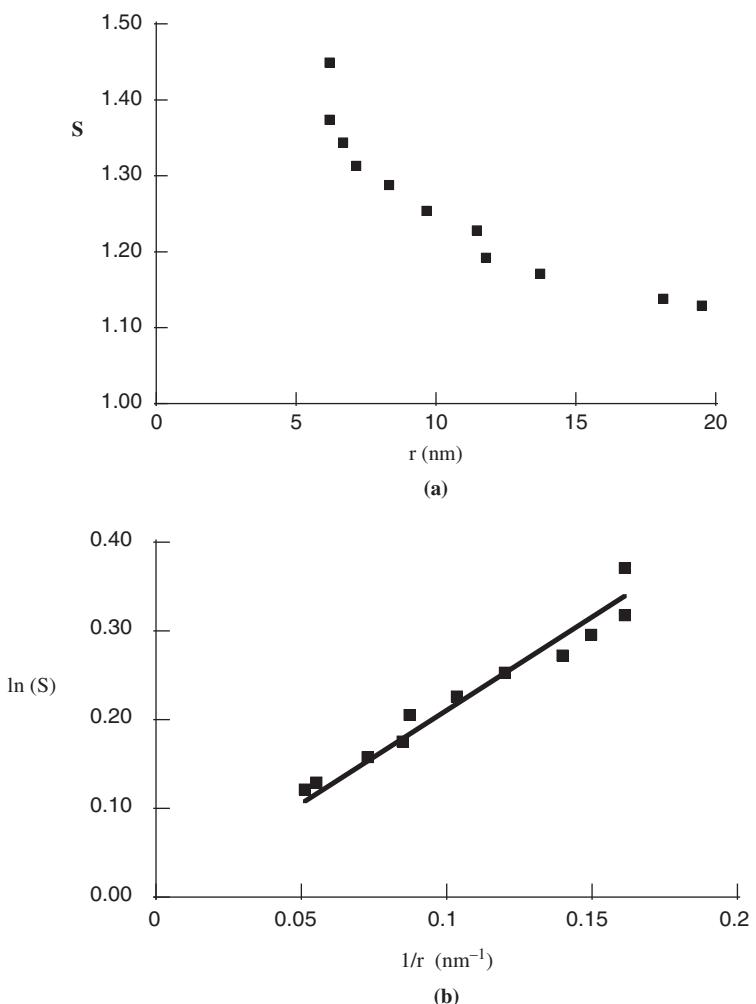


Figure 14.4 (a) Experimental data relating the solubility ratio $S = [Y(r)]_{\text{eq}}/[Y(\infty)]_{\text{eq}}$ to the particle size r for AgCl at 298 K. (b) Plot of $\ln(S)$ versus $1/r$ is a straight line in agreement with Equation (14.4.3a) (Data source: Sugimoto, T., Shiba, F., J. Phys. Chem. B, **103** (1999), 3607).

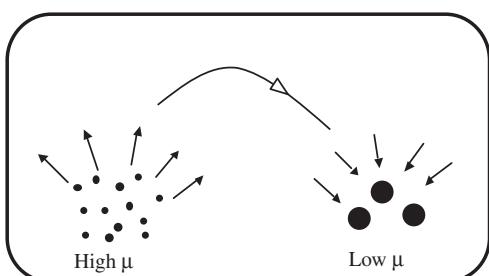


Figure 14.5 Ostwald ripening. Small particles have a higher chemical potential than larger particles. As a consequence, in a saturated solution, small particles dissolve while larger particles grow. The difference in chemical potential results in the effective transport of the solute.

In this equation we can use the relation

$$\mu(p, T_m + \Delta T) = \mu(p, T_m) + \int_{T_m}^{T_m + \Delta T} \left(\frac{\partial \mu}{\partial T} \right)_p dT$$

and write it as

$$\mu_{\infty}(p, T_m) + \int_{T_m}^{T_m + \Delta T} \left(\frac{\partial \mu_{\infty}}{\partial T} \right)_p dT + \frac{2\gamma V_m}{r} = \mu_l(p, T_m) + \int_{T_m}^{T_m + \Delta T} \left(\frac{\partial \mu_l}{\partial T} \right)_p dT$$

Using Equation (14.4.4) and noting that $(\partial \mu / \partial T)_p = -S_m$, the molar entropy, we can simplify this equation to

$$\int_{T_m}^{T_m + \Delta T} (S_{ml} - S_{ms}) dT + \frac{2\gamma V_m}{r} = 0$$

The difference in molar entropies between the liquid and the solid state $(S_{ml} - S_{ms}) \simeq \Delta H_{fus}/T$. The enthalpy of fusion ΔH_{fus} does not change much with T and may be assumed to be constant. With this approximation, the integral can be evaluated and we obtain

$$\Delta H_{fus} \ln \left(1 + \frac{\Delta T}{T_m} \right) + \frac{2\gamma V_m}{r} = 0$$

Since $\Delta T/T_m \ll 1$, we can approximate $\ln(1 + \Delta T/T_m) \simeq \Delta T/T_m$. If we write the melting point of particles of radius as $T_m(r) = T_m(\infty) + \Delta T$, in which we have used $T_m(\infty)$ in place of T_m , the above equation can be rearranged to

$$T_m(r) = T_m(\infty) \left(1 - \frac{2\gamma V_m}{\Delta H_{fus} r} \right) \quad (14.4.6)$$

Sometimes this equation is written in the parametric form:

$$T_m(r) = T_m(\infty) \left(1 - \frac{\rho}{r} \right) \quad (14.4.7)$$

in which ρ is expressed in nm. For many inorganic materials, ρ is in the range 0.2–1.7 nm. Also for metals, the solid–melt interfacial energy can be estimated using the formula [5]

$$\gamma = \frac{0.59RT_m}{aN_A}$$

in which T_m is the melting point and a is the area occupied by a single atom on the surface (approximately equal to the square of the diameter).

14.5 Nucleation

The transition from a vapor to a liquid phase occurs when the corresponding affinity is positive, i.e. liquid will condense from a vapor when the chemical potential of the liquid is lower than that of the vapor and similarly for the transition from a liquid to a solid phase. The condensation of vapor into liquid must take place through clustering of molecules that eventually grow into liquid drops. However, as we have seen, the

chemical potential of a small system increases with decreasing radius. Hence, the affinity is higher for larger clusters and, indeed, can be negative for very small clusters. We can see this clearly by writing the affinity for the transformation from a vapor to a liquid cluster of radius r , which we write as C_r :

$$\text{Transformation: } 1 \rightarrow C_r \quad (14.5.1)$$

$$\text{Affinity: } A = \mu_g - (\mu_{l\infty} + 2\gamma V_m/r) = \Delta\mu - 2\gamma V_m/r$$

in which the subscripts g and l stand for vapor and liquid respectively. Activities for nucleation of a solute from a solution or a solid from a melt will also have the same form as Equation (14.5.1). In each case, $\Delta\mu$ is the difference between the chemical potentials of the two phases. For crystallization from solution, $\Delta\mu$ is the difference between the solution and the solid solute; in the case of solidification of a melt, it is the difference between the chemical potentials of the melt and the solid. To reflect the generality of expression (14.5.1), we can consider a phase transition from the initial phase α that nucleates to phase β and write the affinity for a phase transformation as

$$A = \mu_\alpha - (\mu_{\beta\infty} + 2\gamma V_m/r) = \Delta\mu - 2\gamma V_m/r \quad (14.5.2)$$

We assume that initially $\Delta\mu \equiv \mu_\alpha - \mu_{\beta\infty} > 0$, that is phase α is a supersaturated vapor or a supersaturated solution or a supercooled melt.

Equation (14.5.2) implies that the affinity A is positive only when r is larger than a critical value, r^* , i.e. $A > 0$ only when $r > r^*$ (Figure 14.6). It is easy to see that

$$r^* = \frac{2\gamma V_m}{\mu_\alpha - \mu_{\beta\infty}} = \frac{2\gamma V_m}{\Delta\mu} \quad (14.5.3)$$

where r^* is called the **critical radius**. Due to random molecular motion, the molecules in α phase form clusters of β phase of various sizes. However, most clusters of radius $r < r^*$ will evaporate or dissolve and return to the α phase. Only when a cluster's radius reaches a value $r \geq r^*$ would a β phase have 'nucleated'; since the affinity (14.5.2) is positive for such nuclei, they will grow. It is through the growth of nuclei into liquid drops or solid particles that phase α converts to phase β . The formation of nuclei of radius $r \geq r^*$ takes place through random energy fluctuations. It is the process of **nucleation**, the gateway for the transition from phase α to phase β . As is clear from Equation (14.5.3), the critical radius r^* decreases with increasing $\Delta\mu$; that is the critical radius decreases as the supersaturation increases.

The above understanding of affinity for the formation of clusters and the corresponding changes in the Gibbs energy enables one to formulate a theory of nucleation rate. The theory we present here is the **classical theory of nucleation**. In small systems, which could be subsystems of larger systems, random fluctuations in Gibbs energy occur. Since Gibbs energy reaches its minimum value at equilibrium, fluctuations in systems

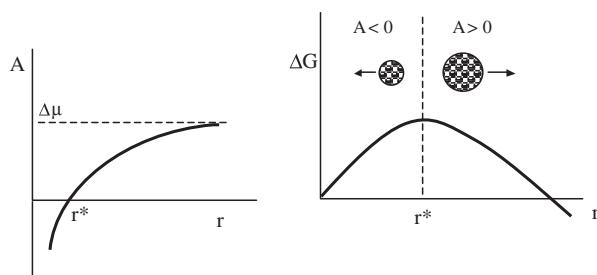


Figure 14.6 Affinity and the corresponding Gibbs energy change for nucleation. The critical nucleation radius is r^* . Clusters with radius $r < r^*$ will shrink while clusters with radius $r > r^*$ will grow.

in equilibrium can only increase its Gibbs energy. The clustering of molecules in the α phase to form small clusters of β phase takes place through fluctuations because the Gibbs energy change for such transformation is positive. If the Gibbs energy of the random fluctuations is large enough, a critical nucleus of radius r^* will form and begin to grow, thus initiating a phase transition. We therefore need to know the laws that govern fluctuations to understand the dynamics of nucleation. To this end, we can use the elegant thermodynamics theory of fluctuations discussed in Section 14.2. Following this theory, we can combine Equations (14.2.2), for the probability of fluctuations expressed in terms of the change in entropy ΔS , and Equation (14.1.2), for the change in Gibbs energy associated with a change in entropy, to obtain the probability $P(\Delta G)$ of a fluctuation in Gibbs energy of magnitude ΔG :

$$P(\Delta G) = Z^{-1} e^{-\Delta G/k_B T} \quad (14.5.4)$$

Here Z^{-1} is the normalization factor such that $\int_0^\infty P(\Delta G)d(\Delta G) = 1$ and k_B is the Boltzmann constant. Let $\Delta G(r^*)$ be the increase in Gibbs energy needed to form the critical nucleus. We can obtain the probability for the formation of a critical nucleus by substituting $\Delta G(r^*)$ into Equation (14.5.4). The rate of nucleation is clearly proportional to $P[\Delta G(r^*)]$. Hence the rate of nucleation, J (the number of nuclei formed per unit volume per unit time), can be written as

$$J = J_0 \exp[-\Delta G(r^*)/k_B T] \quad (14.5.5)$$

in which J_0 is the pre-exponential factor; it depends on the particular process being considered. The Gibbs energy of a nucleus of radius r^* of the β phase, containing N moles of substance, is $G_\beta(r^*) = \mu_{\beta\infty}N + \gamma 4\pi(r^*)^2$. The corresponding Gibbs energy in the α phase is $G_\alpha = \mu_\alpha N$. The change in Gibbs energy for this transformation from the α phase to the β phase, $\Delta G(r^*) = (G_\beta(r^*) - G_\alpha)$. This can be written as

$$\Delta G(r^*) = -\frac{4\pi(r^*)^3}{3V_m} \Delta\mu + \gamma 4\pi(r^*)^2 \quad (14.5.6)$$

Substitution of the expression (14.5.3) for the critical radius r^* into Equation (14.5.6) gives

$$\Delta G(r^*) = \frac{16\pi}{3} \frac{\gamma^3 V_m^2}{\Delta\mu^2} \quad (14.5.7)$$

Thus, the nucleation rate (14.5.5) can be written as

$$J = J_0 \exp \left[-\frac{16\pi}{3k_B T} \frac{\gamma^3 V_m^2}{\Delta\mu^2} \right] \quad (14.5.8)$$

This expression shows how the nucleation rate depends on the interfacial energy γ and the supersaturation expressed through $\Delta\mu$. Experimentally measured nucleation parameters for silver salts are shown in Table 14.1. The pre-exponential factor J_0 depends on the details of the kinetics of nucleation and it is

Table 14.1 Experimentally measured interfacial energies of AgCl, AgBr and AgI particles in water and their molar and molecular volumes V_m .

Compound	γ at 10 °C (mJ m ⁻²)	γ at 40 °C (mJ m ⁻²)	V_m (mL mol ⁻¹)	Molecular volume (mL)
AgCl	104	100	25.9	4.27×10^{-23}
AgBr	112	102	29.0	4.81×10^{-23}
AgI	128	112	41.4	6.88×10^{-23}

Source: Sugimoto, T., Shiba, F., *J. Phys. Chem. B*, **103** (1999), 3607.

generally difficult to estimate its value. Reported values of J_0 are in the range 10^{25} – 10^{30} for salts that are sparingly soluble. Equilibrium between the α phase and the β phase implies $\mu_{\beta\infty} = \mu_{\alpha}^0 + RT \ln a_{\alpha,\text{eq}}$. Since the chemical potential of the α phase, $\mu_{\alpha} = \mu_{\alpha}^0 + RT \ln a_{\alpha}$, it follows that

$$\Delta\mu = \mu_{\alpha} - \mu_{\beta\infty} = RT \ln(a_{\alpha}/a_{\text{eq}}) \quad (14.5.9)$$

Here the equilibrium activity a_{eq} is the activity at saturation in the case of vapors and solution and, for solidification of a melt, it is the activity of the liquid phase (melt) at the melting point. If the vapor α is considered an ideal gas, then $\Delta\mu = RT \ln(p_{\alpha}/p_{\text{sat}})$, in which p_{sat} is the saturated vapor pressure. Similarly, for an ideal solution of solute Y, $\Delta\mu = RT \ln([Y]/[Y]_S)$, in which $[Y]_S$ is the saturation concentration. For solidification from a melt, the dependence of the chemical potential on T must be considered. It can be shown that (Exercise 14.9) $\Delta\mu = \Delta H_{\text{fus}}(1 - T/T_m)$.

In the above theory, the nucleation rate (number of nuclei formed per unit volume per unit time) is independent of position; it is the same everywhere in the system. It is therefore called **homogeneous nucleation**. According to this theory, in a supersaturated vapor or solution, we should observe nucleation in all parts of the system with some uniformity – albeit with expected statistical fluctuations. However, most of the time we do not find this to be the case. Instead, we find that nucleation occurs on small impurity particles or on the walls of the container, indicating that nucleation occurs at higher rates at particular sites. Such nucleation is called **heterogeneous nucleation**. It happens because, on impurity particles or the walls, the interfacial energy γ is lower. The expression (14.5.8) is fundamentally correct but the value of γ (or more generally the nucleation Gibbs energy G^*) depends on the site where the nucleation takes place. At these sites (called **nucleation sites**) the rate of nucleation is higher. This is the reason why when crystals are grown from a solution, nucleation does not occur homogeneously throughout the system, but occurs heterogeneously at certain sites.

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Example

Example 14.1 Consider an ideal gas at $T = 298$ K and $p = 1.0$ atm. Calculate the molar amount N_1 of gas in a spherical volume of radius $1.0\ \mu\text{m}$ (the average value) and the magnitude of fluctuations in concentration (N_1/V_1).

Solution $N_1 = pV/RT = 101\ \text{kPa} \times (4\pi/3)(1.0 \times 10^{-6})^3\ \text{m}^3 / (8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}) = 1.7 \times 10^{-16}\ \text{mol}$.

The average concentrations $(N_1/V_1)_{\text{avg}} = 40.76\ \text{mol m}^{-3}$.

The magnitude of the fluctuations $\delta\tilde{N} = \sqrt{N_1 N_A} = 1.02 \times 10^4$.

Fluctuation in concentrations = $\sqrt{N_1 N_A}/N_A V_1\ \text{mol m}^{-3} = 4.02 \times 10^{-3}\ \text{mol m}^{-3}$.

The magnitude of $(\delta\tilde{N}/V_1)/(N_1 N_A/V_1) = 1/\sqrt{N_1 N_A} \simeq 10 \times 10^{-4}$.

Exercises

- 14.1** By considering the change $\delta^2 F$, obtain the condition for stability with respect to thermal fluctuations when N_k and V are constant.

- 14.2** Obtain the expression

$$\Delta_i S = -\frac{C_V(\delta T)^2}{2T^2} - \frac{1}{T\kappa_T} \frac{(\delta V)^2}{2V} - \sum_i \frac{R(\delta N_i)^2}{2N_i}$$

for an ideal system, where $\mu_k = \mu_{k0}(T) + RT \ln x_k$.

- 14.3** (a) Evaluate the normalization constant Z for Equation (14.2.6).
 (b) Obtain the probability $P(\delta T)$ for the fluctuations of the one variable δT .
 (c) Obtain average values for the square of the fluctuations by evaluating $\int_{-\infty}^{\infty} (\delta T)^2 P(\delta T) d(\delta T)$.

- 14.4** Obtain Equation (14.2.17) from Equation (14.2.11).

- 14.5** Consider an ideal gas at a temperature T and $p = 1$ atm. Assume this ideal gas has two components A and B in equilibrium with respect to interconversion, $A \rightleftharpoons B$. In a small volume δV , calculate the number of molecules that should convert from A to B to change the entropy by k_B in the considered volume. Equation (14.2.24) then gives the expected fluctuations.

- 14.6** Using the expression $G = \mu_\infty N + \gamma \Sigma$ show that $(\partial G / \partial N)_{p,T} = \mu = \mu_\infty + (2\gamma V_m/r)$.

- 14.7** Using the parameters in Table 14.1, determine the size of AgBr particles whose saturation concentration $[Y(r)]_{eq} = 1.3 [Y(\infty)]$. At $T = 40$ °C, estimate the number of AgBr molecules in these particles.

- 14.8** N moles of the phase α form a β phase cluster of radius r^* . For this process, assume that $G_\alpha = \mu_\alpha N$ and $G_\beta = \mu_{\beta\infty} N + \gamma 4\pi(r^*)^2$ and show that

$$G_\beta - G_\alpha = \Delta G(r^*) = \frac{16\pi}{3} \frac{\gamma^3 V_m^2}{\Delta\mu^2}$$

in which $\Delta\mu = \mu_\alpha - \mu_{\beta\infty}$.

- 14.9** For solidification from a melt, from the liquid phase α to the solid phase β , the chemical potential as a function of temperature must be analyzed. Assume $T = T_m - \Delta T$ in which $(\Delta T/T) \ll 1$ and show that $\Delta\mu = \mu_\alpha - \mu_\beta \approx \Delta H_{fus}(1 - T/T_m)$.

Part IV

Linear Nonequilibrium Thermodynamics

15

Nonequilibrium Thermodynamics: The Foundations

15.1 Local Equilibrium

As emphasized earlier, we live in a world that is not in thermodynamic equilibrium. The 2.8 K cosmic microwave background thermal radiation that fills the universe is not in thermal equilibrium with the matter in the galaxies. On a smaller scale, the Earth, its atmosphere, biosphere and the oceans are all in a nonequilibrium state due to the constant influx of energy from the Sun. In the laboratory, most of the time we encounter phenomena exhibited by systems not in thermodynamic equilibrium, while equilibrium systems are the exception.

Yet, thermodynamics that describes equilibrium states is of great importance and extremely useful. This is because almost all systems are *locally* in thermodynamic equilibrium. For almost every macroscopic system we can meaningfully assign a temperature and other thermodynamic variables to every ‘elemental volume’ ΔV . In most situations we may assume that *equilibrium thermodynamic relations are valid for the thermodynamic variables assigned to an elemental volume*. This is the concept of **local equilibrium**. In the following paragraphs we shall make this concept of local equilibrium precise. When this is done, we have a theory in which all intensive thermodynamic variables, T, p and μ , become functions of position \mathbf{x} and time t :

$$T = T(\mathbf{x}, t), \quad p = p(\mathbf{x}, t), \quad \mu = \mu(\mathbf{x}, t)$$

The extensive variables are replaced by densities s, u and n_k :

$$\begin{aligned} s(\mathbf{x}, t) &= \text{entropy per unit volume} \\ u(\mathbf{x}, t) &= \text{energy per unit volume} \\ n_k(\mathbf{x}, t) &= \text{moles per unit volume of reactant } k \end{aligned} \tag{15.1.1}$$

(In some formulations the extensive quantities are replaced by entropy, energy and volume per unit mass.) The Gibbs relation $dU = T dS - p dV + \sum_k \mu_k dN_k$ is assumed to be valid for small volume elements. With $U = uV$ and $S = sV$ it follows that relations such as

$$\left(\frac{\partial u}{\partial s} \right)_{n_k} = T, \quad T ds = du - \sum_k \mu_k dn_k \tag{15.1.2}$$

for the densities are valid (Exercise 15.1) at every position \mathbf{x} and time t . In these equations the volume does not appear because s , u and n_k are densities. The entire system is viewed as a collection of systems characterized by different values of T , μ , etc., which are interacting with each other.

Let us look at the physical conditions that make local equilibrium a valid assumption. First we must look at the concept of temperature. From statistical mechanics it can be seen that when the system is in equilibrium, the velocity distribution is Maxwellian, with a well-defined temperature. As discussed in Chapter 1, according to the **Maxwell distribution of velocities**, the probability $P(\mathbf{v})$ that a molecule has a velocity \mathbf{v} is given by

$$P(\mathbf{v}) d^3\mathbf{v} = \left(\frac{\beta}{\pi} \right)^{3/2} e^{-\beta v^2} d^3\mathbf{v} \quad (15.1.3)$$

$$\beta = \frac{m}{2k_B T} \quad (15.1.4)$$

In this expression, the temperature is identified through relation (15.1.4), in which m is the mass of the molecule and k_B is the Boltzmann constant. In practice, only under very extreme conditions do we find significant deviations from the Maxwell distribution. Any initial distribution of velocities quickly becomes Maxwellian due to molecular collisions. Computer simulations of molecular dynamics have revealed that the Maxwell distribution is reached in less than 10 times the average time between collisions, which in a gas at a pressure of 1 atm is about 10^{-8} s [1]. Consequently, physical processes that perturb the system significantly from the Maxwell distribution have to be very rapid. A detailed statistical mechanical analysis of the assumption of local equilibrium can be found in Reference [2].

Chemical reactions are of particular interest to us. In almost all reactions only a very small fraction of molecular collisions produce a chemical reaction. Collisions between molecules that produce a chemical reaction are called **reactive collisions**. For a gas at a pressure of 1 atm the collision frequency is about 10^{31} collisions per liter per second. If nearly every collision produced a chemical reaction, the resulting rate would be of the order of 10^8 mol L⁻¹ s⁻¹! Reaction rates that approach such a large value are extremely rare. Most of the reaction rates we encounter indicate that reactive collision rates are several orders of magnitude smaller than overall collision rates. Between reactive collisions the system quickly relaxes to equilibrium, redistributing the change in energy due to the chemical reaction. In other words, any perturbation of the Maxwell distribution due to a chemical reaction quickly relaxes back to the Maxwellian with a slightly different local temperature. Hence, on the timescale of chemical reactions, temperature is locally well defined. (Small corrections to the rate laws due to small deviations from the Maxwell distribution in highly exothermic reactions can be theoretically obtained [3–6]. These results have been found to agree well with the results of molecular dynamics simulations done on modern computers [7].)

Next, let us look at the sense in which thermodynamic variables, such as entropy and energy, may be considered functions of position. As we have seen in Chapters 12 and 14, every thermodynamic quantity undergoes fluctuations. For a small elemental volume ΔV we can meaningfully associate a value for a thermodynamic quantity Y only when the size of the fluctuations, e.g. the root mean square (rms) value, δY is very small compared to Y . Clearly, if ΔV is too small, this condition will not be satisfied. From Equation (14.2.6) it follows that if \tilde{N} is the number of particles in the considered volume, then the rms value of the fluctuations $\delta \tilde{N}_{\text{rms}} = \tilde{N}^{1/2}$. As an example, let us consider an ideal gas for which $N = \tilde{N}/N_A = (p/RT)\Delta V$. For a given ΔV it is easy to compute the relative value of the fluctuation $\delta \tilde{N}_{\text{rms}}/\tilde{N} = 1/\tilde{N}^{1/2}$. To understand how small ΔV can be, we consider a gas at a pressure $p = 1$ atm and $T = 298$ K, and compute the fluctuations in the number of particles \tilde{N} in a volume $\Delta V = (1 \mu\text{m})^3 = 10^{-15}$ L. We find that $\delta \tilde{N}_{\text{rms}}/\tilde{N} \approx 4 \times 10^{-7}$. For liquids and solids the same value of $\delta \tilde{N}_{\text{rms}}/\tilde{N}$ will correspond to an even smaller volume. Hence it is meaningful to assign a molar density to a volume with a characteristic size of a micrometer. The same is generally true for other thermodynamic variables. If we are to assign a molar density to a volume, ΔV , then the molar density in this volume should be nearly uniform. This means that the variation of molar density with position on

the scale of a micrometer should be very nearly zero, a condition satisfied by most macroscopic systems. Similarly the fluctuations in T at the scale of μm is very small. This shows that a theory based on local equilibrium is applicable to a wide range of macroscopic systems.

15.1.1 Extended Thermodynamics

In the above approach, an implicit assumption is that the thermodynamic quantities do not depend on the gradients in the system; i.e. it is postulated that entropy s is a function of the temperature T and the molar density n_k , but not their gradients. However, flows represent a level of organization. This implies that the local entropy in a nonequilibrium system may be expected to be smaller than the equilibrium entropy. In the recently developed formalism of **extended thermodynamics**, gradients are included in the basic formalism and there appears a small correction to the local entropy due to the flows. We shall not be discussing this more advanced formalism. For a detailed exposition of extended thermodynamics, we refer the reader to some recent books [8–11]. Extended thermodynamics finds application in systems where there are large gradients, such as in shock waves. For almost all systems that we encounter, thermodynamics based on local equilibrium has excellent validity.

15.2 Local Entropy Production

As we noted in the previous section, the Second Law of thermodynamics must be a local law. If we divide a system into r parts, then not only is

$$d_i S = d_i S^1 + d_i S^2 + \dots + d_i S^r \geq 0 \quad (15.2.1)$$

in which $d_i S^k$ is the entropy production in the k th part, but also

$$d_i S^k \geq 0 \quad (15.2.2)$$

for every k . Clearly, this statement that the entropy production due to irreversible processes is positive in every part is stronger than the classical statement of the Second Law that the entropy of an isolated system can only increase or remain unchanged. The modern formulation of the Second Law, as stated by (15.2.2), does not require the system to be isolated. *It is valid for all systems, regardless of the boundary conditions.*

There is a general point to note about the local nature of the First Law and the Second Law. To be compatible with the principle of relativity, that is to be valid regardless of the observer's state of motion, these laws *must* be local. Nonlocal laws of energy conservation or of entropy production are inadmissible because the notion of simultaneity is relative. Consider two parts of a system spatially separated by a nonzero distance. If changes in energy δu_1 and δu_2 occur in these two parts *simultaneously* in one frame of reference so that $\delta u_1 + \delta u_2 = 0$, the energy is conserved. However, in another frame of reference that is in motion with respect to the first, the two changes in energy *will not occur simultaneously*. One change, say δu_1 , will occur before the other. Thus, during the time interval between one change of u and the other, the law of conservation of energy will be violated. Similarly, the entropy changes in a system, δS_1 and δS_2 at two spatially separated parts of a system must be independently positive. It is inadmissible to have the simultaneous decrease of one and increase of the other so that their sum is positive.

The local increase of entropy in continuous systems can be defined by using the entropy density $s(\mathbf{x}, t)$. As was the case for the total entropy, $ds = d_i s + d_e s$, with $d_i s \geq 0$. We define local entropy production as

$$\sigma(\mathbf{x}, t) \equiv \frac{d_i s}{dt} \geq 0$$

(15.2.3)

$$\frac{d_i S}{dt} = \int_V \sigma(\mathbf{x}, t) dV \quad (15.2.4)$$

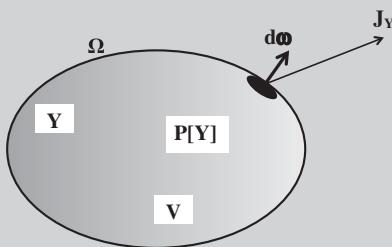
Nonequilibrium thermodynamics is founded on the explicit expression for σ in terms of the irreversible processes that we can identify and study experimentally. Before we begin deriving this expression, however, we shall write the explicit local forms of balance equations for energy and concentrations.

15.3 Balance Equation for Concentration

The balance equation for the molar density, $n_k(\mathbf{x})$, can easily be obtained using the general balance equation described in Box 15.1. For notational simplicity we shall not always explicitly show n_k as a function of \mathbf{x} . The changes in n_k are due to the transport of particles, through processes such as diffusion and convection, $d_e n_k$, and due to chemical reactions, $d_i n_k$; the total change $dn_k = d_e n_k + d_i n_k$. Denoting by $\mathbf{v}_k(\mathbf{x}, t)$ the velocity of the k th component at location \mathbf{x} at time t , the balance equation can be written as

$$\frac{\partial n_k}{\partial t} = \frac{\partial_e n_k}{\partial t} + \frac{\partial_i n_k}{\partial t} = -\nabla \cdot (n_k \mathbf{v}_k) + P[n_k] \quad (15.3.1)$$

Box 15.1 Differential form of the balance equation



Consider a quantity Y whose density is denoted by y . The change in the amount of Y in a volume V is the sum of the net flow of Y into the volume V and the production of Y within that volume. If \mathbf{J}_Y is the current density (flow through the unit area that is perpendicular to \mathbf{J}_Y per unit time), then the *change in Y due to the flow* = $\int_{\Omega} \mathbf{J}_Y \cdot d\omega$ in which $d\omega$ is the vector representing an area element, as illustrated. The magnitude of $d\omega$ equals the area of the element; its direction is perpendicular to the area pointing outwards. If $P[Y]$ is the amount of Y produced per unit volume per unit time, we have the *change in Y due to production* = $\int_V P[Y]dV$. Then the balance equation for the change in Y in the considered volume can be written as

$$\int_V \left(\frac{\partial y}{\partial t} \right) dV = \int_V P[Y]dV - \int_{\Omega} \mathbf{J}_Y \cdot d\omega$$

The negative sign in the second term is because $d\omega$ points outwards.

According to the Gauss theorem, for any vector field \mathbf{J} :

$$\int_{\Omega} \mathbf{J} \cdot d\omega = \int_V (\nabla \cdot \mathbf{J})dV$$

Applying this theorem to the surface integral of \mathbf{J}_Y in the balance equation, we see that

$$\int_V \left(\frac{\partial y}{\partial t} \right) dV = \int_V P[Y] dV - \int_V (\nabla \cdot \mathbf{J}_Y) dV$$

Since this relation should be valid for any volume, we can equate the integrands. This gives us the differential form of the balance equation for Y:

$$\left(\frac{\partial y}{\partial t} \right) + (\nabla \cdot \mathbf{J}_Y) = P[Y]$$

in which $P[n_k]$ is the production of the component k per unit volume, per unit time, due to chemical reactions, which could be positive or negative. As we have seen in Chapter 9, if v_k is the stoichiometric coefficient of the reactant k in a particular reaction (v_k is negative for reactants and positive products), the moles of k produced per unit time per unit volume is given by $v_k(1/V)(d\xi/dt)$ in which ξ is the extent of reaction. If there are several reactions, we can identify them by a subscript j . The velocity of the j th reaction is

$$v_j = \frac{1}{V} \frac{d\xi_j}{dt} \quad (15.3.2)$$

The velocities of reaction v_j are specified by empirical laws, as discussed in Chapter 9. The production of component k can now be expressed in terms of the reaction velocities v_j and the corresponding stoichiometric coefficients v_{kj} :

$$P[n_k] \equiv \sum_j v_{kj} v_j \quad (15.3.3)$$

The balance equation for n_k can now be written as

$$\frac{\partial n_k}{\partial t} = \frac{\partial_e n_k}{\partial t} + \frac{\partial_i n_k}{\partial t} = -\nabla \cdot n_k \mathbf{v}_k + \sum_j v_{kj} v_j \quad (15.3.4)$$

Convective flow is the motion of the center of mass whereas the flow with respect to the center of mass accounts for transport, such as diffusion, that is apart from convection. The center of mass velocity \mathbf{v} is given by

$$\mathbf{v} \equiv \frac{\sum_k M_k n_k \mathbf{v}_k}{\sum_k M_k n_k} \quad (15.3.5)$$

in which M_k is the molar mass of component k . The nonconvective flow or **diffusion flow** \mathbf{J}_k of component k is then defined as¹

$$\mathbf{J}_k = n_k (\mathbf{v}_k - \mathbf{v}) \quad (15.3.6)$$

The term $(\mathbf{v}_k - \mathbf{v})$ is the velocity of component k relative to the center of mass, called the barycentric velocity. The convectional and diffusional parts of the flow can be made explicit by using Equations (15.3.6) in (15.3.4):

$$\frac{\partial n_k}{\partial t} = -\nabla \cdot \mathbf{J}_k - \nabla \cdot (n_k \mathbf{v}) + \sum_j v_{kj} v_j \quad (15.3.7)$$

¹In the thermodynamics of superfluids it is more convenient to keep the motions of the components separate. Also, diffusion flow with respect to mean volume velocity, defined by replacing M_k in Equation (15.3.5) with specific volume, is also used.

By virtue of their definitions, the nonconvective flows \mathbf{J}_k must obey the relation

$$\sum_k M_k \mathbf{J}_k = 0 \quad (15.3.8)$$

i.e. these flows should not result in center of mass motion. Thus the \mathbf{J}_k are not all independent, a point that we shall return to in Chapter 16 while considering coupling between different flows. Also, based on the definition of $d_e n_k$ and $d_i n_k$, we can make the identification

$$\frac{\partial_e n_k}{\partial t} = -\nabla \cdot \mathbf{J}_k - \nabla \cdot (n_k \mathbf{v}) \quad \text{and} \quad \frac{\partial_i n_k}{\partial t} = \sum_j v_{kj} v_j \quad (15.3.9)$$

In the absence of convection, the flow is entirely \mathbf{J}_k . We then have

$$\frac{\partial n_k}{\partial t} = -\nabla \cdot \mathbf{J}_k + \sum_j v_{kj} v_j \quad (15.3.10)$$

In the presence of an external field, such as a static electric field, \mathbf{J}_k may have a part that depends on the field. When no field is present, \mathbf{J}_k is entirely due to diffusion. In Chapters 18 and 19 we shall study such *diffusion–reaction systems* under far-from-equilibrium conditions in some detail.

15.4 Energy Conservation in Open Systems

In Chapter 2 we saw the foundations of the concept of energy and its conservation. We have also noted how this conservation law must be local. We can express the local form of the law in a differential form. The total energy density e is a sum of the kinetic and the internal energies:

$$e = \frac{1}{2} \sum_k (M_k n_k) \mathbf{v}_k^2 + u \quad (15.4.1)$$

in which $(M_k n_k)$ is the mass per unit volume and \mathbf{v}_k is the velocity of component k . Equation (15.4.1) may be considered as the definition of the internal energy u , i.e. energy not associated with bulk motion. Using the center of mass velocity \mathbf{v} defined by Equation (15.3.5), Equation (15.4.1) can be written as

$$e = \frac{\rho}{2} \mathbf{v}^2 + \frac{1}{2} \sum_k (M_k n_k) (\mathbf{v}_k - \mathbf{v})^2 + u \quad (15.4.2)$$

in which the density $\rho = \sum_k M_k n_k$. The term $\frac{1}{2} \sum_k (M_k n_k) (\mathbf{v}_k - \mathbf{v})^2$ is sometimes referred to as the **kinetic energy of diffusion** [12]. Thus the total energy density is the sum of the kinetic energy associated with convection and diffusion, and the internal energy. In some formalisms, the sum of the last two terms is defined as the internal energy [12], in which case the internal energy includes the kinetic energy of diffusion.

When an external field is present, the energy of interaction $\sum_k \tau_k n_k \psi$, in which τ_k is the ‘coupling constant’ per mole and ψ is the potential, should also be considered. This energy can be introduced either as an additional term in Equation (15.4.1) or assumed to be included in the definition of u [12]. Following our formalism in Chapters 2 and 10, we shall assume that the term $\sum_k \tau_k n_k \psi$ is included in the definition of the internal energy u .

Since energy is conserved, there is no source term in the balance equation. Therefore the formal differential form for the conservation of energy is

$$\frac{\partial e}{\partial t} + \nabla \cdot \mathbf{J}_e = 0 \quad (15.4.3)$$

in which \mathbf{J}_e is the energy current density. In order to make this expression more explicit in terms of the processes in the system, we begin by looking at the change in u . Being a function of T and n_k , the change in the energy density $u(T, n_k)$ is

$$\begin{aligned} du &= \left(\frac{\partial u}{\partial T} \right)_{n_k} dT + \sum_k \left(\frac{\partial u}{\partial n_k} \right)_T dn_k \\ &= c_V dT + \sum_k u_k dn_k \end{aligned} \quad (15.4.4)$$

in which $u_k \equiv (\partial u / \partial n_k)_T$ is the partial molar energy of the k th component and c_V is the constant-volume heat capacity per unit volume. For the time variation of the internal energy density we can write

$$\frac{\partial u}{\partial t} = c_V \frac{\partial T}{\partial t} + \sum_k u_k \frac{\partial n_k}{\partial t} \quad (15.4.5)$$

Using the n_k balance equation (15.3.10), we can rewrite this equation as

$$\frac{\partial u}{\partial t} = c_V \frac{\partial T}{\partial t} + \sum_{kj} u_k v_{kj} v_j - \sum_k u_k \nabla \cdot \mathbf{J}_k \quad (15.4.6)$$

The quantity $\sum_k u_k v_{kj} = \sum_k (\partial u / \partial n_k)_T v_{kj}$ is the change in the internal energy per unit volume, at constant T , due to the j th chemical reaction. It is the heat of reaction of the j th reaction at constant volume and temperature; we shall denote it by $(r_{V,T})_j$. For exothermic reactions $(r_{V,T})_j$ is negative. Furthermore, to relate Equation (15.4.6) to the conservation equation (15.4.3), we can make use of the identity $u_k \nabla \cdot \mathbf{J}_k = \nabla \cdot (u_k \mathbf{J}_k) - \mathbf{J}_k \cdot (\nabla u_k)$ and rewrite Equation (15.4.6) as

$$\frac{\partial u}{\partial t} = c_V \frac{\partial T}{\partial t} + \sum_j (r_{V,T})_j v_j + \sum_k \mathbf{J}_k \cdot (\nabla u_k) - \sum_k \nabla \cdot (u_k \mathbf{J}_k) \quad (15.4.7)$$

Using Equations (15.4.2) and (15.4.7) the energy conservation equation (15.4.3) can be more explicitly written as

$$\begin{aligned} \frac{\partial e}{\partial t} &= c_V \frac{\partial T}{\partial t} + \sum_j (r_{V,T})_j v_j + \sum_k \mathbf{J}_k \cdot (\nabla u_k) - \sum_k \nabla \cdot (u_k \mathbf{J}_k) + \frac{\partial}{\partial t} (\text{KE}) \\ &= -\nabla \cdot \mathbf{J}_e \end{aligned} \quad (15.4.8)$$

in which (KE) is the kinetic energy associated with convection and diffusion:

$$(\text{KE}) \equiv \left(\frac{\rho}{2} \mathbf{v}^2 + \frac{1}{2} \sum_k M_k n_k (\mathbf{v}_k - \mathbf{v})^2 \right) \quad (15.4.9)$$

The energy flow \mathbf{J}_e can now be identified by defining a **heat flow** \mathbf{J}_q :

$$-\nabla \cdot \mathbf{J}_q \equiv c_V \frac{\partial T}{\partial t} + \sum_j (r_{V,T})_j v_j + \sum_k \mathbf{J}_k \cdot (\nabla u_k) + \frac{\partial}{\partial t} (\text{KE})$$

(15.4.10)

Finally, substituting Equation (15.4.10) into Equation (15.4.8), we can identify the energy flow as

$$\mathbf{J}_e = \mathbf{J}_q + \sum_k u_k \mathbf{J}_k \quad (15.4.11)$$

The definition of heat flow (15.4.10) leads to a physically appropriate interpretation of the processes that change the internal energy and the temperature. Using Equation (15.4.7) in Equation (15.4.10) we obtain

$$-\nabla \cdot \mathbf{J}_q = \frac{\partial u}{\partial t} + \nabla \cdot \left(\sum_k u_k \mathbf{J}_k \right) + \frac{\partial}{\partial t} (\text{KE})$$

which can be rewritten as

$$\boxed{\frac{\partial u}{\partial t} + \nabla \cdot \mathbf{J}_u = -\frac{\partial}{\partial t} (\text{KE})} \quad (15.4.12)$$

where

$$\boxed{\mathbf{J}_u = \mathbf{J}_q + \sum_k u_k \mathbf{J}_k} \quad (15.4.13)$$

This is the balance equation for the internal energy. It shows that the internal energy as defined above may be associated with a flow $\mathbf{J}_u = (\sum_k u_k \mathbf{J}_k + \mathbf{J}_q)$ and a source term on the right-hand side of Equation (15.4.12), which is the rate at which the kinetic energy is dissipated. Equation (15.4.12) shows that the changes in u are a result of heat flow \mathbf{J}_q and matter flow $u_k \mathbf{J}_k$, and is due to dissipation of kinetic energy of the bulk motion. The dissipation of kinetic energy can be related to viscous forces in the fluid. (Note that though \mathbf{J}_e and \mathbf{J}_u are the same, the total energy e is conserved but u is not because dissipation of kinetic energy generates heat and acts as a source of u . Since \mathbf{J}_e is a barycentric current defined with respect to the center of mass, it does not contain a term due to the motion of the entire system.)

The definition of heat flow (15.4.10) also gives an equation for the change in temperature

$$c_V \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{J}_q = P_{\text{heat}} \quad (15.4.14)$$

$$P_{\text{heat}} = - \sum_j (r_{V,T})_j v_j - \sum_k \mathbf{J}_k \cdot (\nabla u_k) - \frac{\partial}{\partial t} (\text{KE}) \quad (15.4.15)$$

Equation (15.4.14) is an extension of the Fourier equation for heat transport with the addition of a heat source P_{heat} . It is useful to note that the term $\nabla u_k = \sum_i (\partial u_k / \partial n_i) \nabla n_i + (\partial u_k / \partial T) \nabla T$. For ideal systems, in the absence of temperature gradients, since the partial molar energy u_k is independent of n_k , this term will vanish; it is the heat generated or absorbed due to molecular interaction when the molar density, n_k , of a nonideal system changes. In the following chapters, we shall not consider systems with convection. In addition, we will only consider situations in which the kinetic energy of diffusion remains small, so the term $\partial(\text{KE})/\partial t \approx 0$.

Definition (15.4.10) of \mathbf{J}_q is one of the many equivalent ways of defining the heat flow. Depending on the particular physical conditions and the experimental quantities that are measured, different definitions of \mathbf{J}_q are used. A more extensive discussion of this aspect may be found in the literature [12]. The various definitions of \mathbf{J}_q , of course, give the same physical results.

When an external field is present, as noted earlier (Chapter 10), the energy of interaction $\sum_k \tau_k n_k \psi$, in which τ_k is the ‘coupling constant’ per mole and ψ is the potential, should also be included in u so that

$$u(T, n_k) = u^0(T, n_k) + \sum_k n_k \tau_k \psi \quad (15.4.16)$$

where $u^0(T, n_k)$ is the energy density in the absence of the field. For an electric field $\tau_k = F z_k$, where F is the Faraday constant and z_k is the ion number; ψ is the electrical potential ϕ . For a gravitational field $\tau_k = M_k$,

the molar mass; ψ is the gravitational potential. For the time derivative of u , in place of Equation (15.4.5) we now have

$$\frac{\partial u}{\partial t} = c_V \frac{\partial T}{\partial t} + \sum_k (u_k^0 + \tau_k \psi) \frac{\partial n_k}{\partial t} \quad (15.4.17)$$

in which $u_k^0 = (\partial u^0 / \partial n_k)_T$. Equation (15.4.17) differs from Equation (15.4.5) only in that the term u_k is replaced by $(u_k^0 + \tau_k \psi)$. This means that the corresponding expressions for \mathbf{J}_q and \mathbf{J}_e can be obtained by simply replacing u_k with $(u_k^0 + \tau_k \psi)$. Thus we arrive at the conservation equation

$$\boxed{\frac{\partial e}{\partial t} + \nabla \cdot \mathbf{J}_e^\psi = 0} \quad (15.4.18)$$

in which

$$\boxed{\mathbf{J}_e^\psi = \mathbf{J}_q + \sum_k (u_k^0 + \tau_k \psi) \mathbf{J}_k} \quad (15.4.19)$$

In this case the heat current is defined by

$$-\nabla \cdot \mathbf{J}_q \equiv c_V \frac{\partial T}{\partial t} + \sum_j (r_{V,T})_j v_j + \sum_k \mathbf{J}_k \cdot (\nabla u_k) + \sum_k \tau_k \mathbf{J}_k \cdot \nabla \psi + \frac{\partial}{\partial t} (\text{KE}) \quad (15.4.20)$$

Comparing Equation (15.4.20) with Equation (15.4.10) we see the following. The term, $\nabla \psi$ is the negative of the field strength. In the case of an electric field, the last term becomes $-\mathbf{I} \cdot \mathbf{E}$ in which $\mathbf{E} = -\nabla \psi$ is the electric field and $\mathbf{I} = \sum_k \tau_k \mathbf{J}_k$ is the total current density; $\mathbf{I} \cdot \mathbf{E}$ is the ohmic heat produced by an electric current. For the balance equation of u , in place of Equation (15.4.12) we have

$$\boxed{\frac{\partial u}{\partial t} + \nabla \cdot \mathbf{J}_u = -\frac{\partial}{\partial t} (\text{KE}) + \mathbf{I} \cdot \mathbf{E}} \quad (15.4.21)$$

in which $\mathbf{J}_u = \sum_k u_k^0 \mathbf{J}_k + \mathbf{J}_q$. Similarly, Equation (15.4.14) is modified such that the source of heat will now contain an additional term due to the ohmic heat:

$$c_V \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{J}_q = P_{\text{heat}} \quad (15.4.22)$$

$$P_{\text{heat}} = -\sum_j (r_{V,T})_j v_j - \sum_k \mathbf{J}_k \cdot (\nabla u_k) - \frac{\partial}{\partial t} (\text{KE}) + \mathbf{I} \cdot \mathbf{E} \quad (15.4.23)$$

In this text we will only consider systems in mechanical equilibrium in which the kinetic energy of diffusion is small.

15.5 The Entropy Balance Equation

The balance equation for entropy can be derived using the conservation of energy and the balance equation for the concentrations. This gives us an explicit expression for entropy production σ – which can be related to irreversible processes such as heat conduction, diffusion and chemical reactions – and the entropy current \mathbf{J}_S . The formal entropy balance equation is

$$\boxed{\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_S = \sigma} \quad (15.5.1)$$

To obtain the explicit forms of \mathbf{J}_S and σ , we proceed as follows. For simplicity, we shall consider a system with no dissipation of kinetic energy due to convection or diffusion, and no external field. From the Gibbs relation $T \, ds = du - \sum \mu_k \, dn_k$ it follows that

$$\frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \sum_k \frac{\mu_k}{T} \frac{\partial n_k}{\partial t} \quad (15.5.2)$$

Now using the n_k balance equation (15.3.10) and the balance equation (15.4.12) for the internal energy with $\partial(\text{KE})/\partial t = 0$, expression (15.5.2) can be written as

$$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \mathbf{J}_u + \sum_k \frac{\mu_k}{T} \nabla \cdot \mathbf{J}_k - \sum_{k,j} \frac{\mu_k}{T} v_{kj} v_j \quad (15.5.3)$$

This equation can be simplified and written in the form (15.5.1) by making the following observations. First, the affinity of reaction j is

$$A_j = - \sum_k v_{jk} \mu_k \quad (15.5.4)$$

Second, if g is a scalar function and \mathbf{J} is a vector, then

$$\nabla \cdot (g\mathbf{J}) = \mathbf{J} \cdot (\nabla g) + g(\nabla \cdot \mathbf{J}) \quad (15.5.5)$$

Through an elementary calculation using Equations (15.5.4) and (15.5.5), we can rewrite Equation (15.5.3) to arrive at the following equation for the entropy balance:

$$\boxed{\frac{\partial s}{\partial t} + \nabla \cdot \left(\frac{\mathbf{J}_u}{T} - \sum_k \frac{\mu_k \mathbf{J}_k}{T} \right) = \mathbf{J}_u \cdot \nabla \frac{1}{T} - \sum_k \mathbf{J}_k \cdot \nabla \frac{\mu_k}{T} + \sum_j \frac{A_j v_j}{T}} \quad (15.5.6)$$

By comparing this equation with Equation (15.5.1), we can make the identifications

$$\boxed{\mathbf{J}_S = \left(\frac{\mathbf{J}_u}{T} - \sum_k \frac{\mu_k \mathbf{J}_k}{T} \right)} \quad (15.5.7)$$

and

$$\sigma = \mathbf{J}_u \cdot \nabla \frac{1}{T} - \sum_k \mathbf{J}_k \cdot \nabla \frac{\mu_k}{T} + \sum_j \frac{A_j v_j}{T} \geq 0 \quad (15.5.8)$$

where we have emphasized the Second Law, $\sigma \geq 0$.

As was done earlier, we identify the heat current \mathbf{J}_q through the relation $\mathbf{J}_u = \mathbf{J}_q + \sum_k u_k \mathbf{J}_k$. Then, using the relation $u_k = \mu_k + T s_k$ (Exercise 15.2), where $s_k = (\partial s / \partial n_k)_T$ is the partial molar entropy density of component k , the entropy current \mathbf{J}_S can be written as

$$\mathbf{J}_S = \left(\frac{\mathbf{J}_q}{T} + \sum_k \frac{u_k - \mu_k}{T} \mathbf{J}_k \right) = \left(\frac{\mathbf{J}_q}{T} + \sum_k s_k \mathbf{J}_k \right) \quad (15.5.9)$$

As was the case for the energy current, the expression for the entropy current consists of two parts, one due to heat flow and the other due to matter flow.

If an external field with potential ψ is included, from the Gibbs equation $T \, ds = du - \sum_k \mu_k dn_k - \sum_k \tau_k \psi dn_k$ it follows that

$$T \frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \sum_k (\mu_k + \tau_k \psi) \frac{\partial n_k}{\partial t} \quad (15.5.10a)$$

and

$$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \mathbf{J}_u + \sum_k \frac{\mu_k + \tau_k \psi}{T} \nabla \cdot \mathbf{J}_k - \sum_{k,j} \frac{\mu_k + \tau_k \psi}{T} v_{kj} v_j \quad (15.5.10b)$$

Comparing Equation (15.5.2) with Equations (15.5.10), we see that the only difference is that the chemical potential μ_k is replaced by the electrochemical potential $(\mu_k + \tau_k \psi)$. Correspondingly, the entropy current (15.5.7) and the entropy production (15.5.8) now become

$$\mathbf{J}_S = \left(\frac{\mathbf{J}_u}{T} - \sum_k \frac{\tau_k \psi + \mu_k}{T} \mathbf{J}_k \right) \quad (15.5.11)$$

$$\sigma = \mathbf{J}_u \cdot \nabla \frac{1}{T} - \sum_k \mathbf{J}_k \cdot \nabla \left(\frac{\mu_k}{T} \right) + \frac{\mathbf{I} \cdot (-\nabla \psi)}{T} + \sum_j \frac{\tilde{A}_j v_j}{T}$$

(15.5.12)

in which $\mathbf{J}_u = \mathbf{J}_q + \sum_k u_k^0 \mathbf{J}_k$, where u_k^0 is the partial molar energy in the absence of the field, $I = \sum_k \tau_k \mathbf{J}_k$ and \tilde{A} the electrochemical affinity. For a static electric field \mathbf{E} , we have $-\nabla \psi = \mathbf{E}$ and $\mathbf{I} = \sum_k \mathbf{I}_k$ is the total current density.

Expression (15.5.12) for the entropy production is fundamental to nonequilibrium thermodynamics. It shows that entropy production σ has the bilinear form

$$\sigma = \sum_{\alpha} F_{\alpha} \mathbf{J}_{\alpha}$$

(15.5.13)

of forces F_{α} and currents or flows J_{α} . It is through this expression that we identify the thermodynamic forces and the flows they drive. For example, the force $\nabla(1/T)$ drives the flow \mathbf{J}_u ; the chemical affinities A_j drive the chemical reactions with velocities v_j . These forces and the corresponding flows are identified in Table 15.1. A transformation that leaves σ invariant and alternative forms of writing σ are discussed in Appendix 15.1.

Table 15.1 Table of thermodynamic forces and flows.

	Force F_{α}	Flow (current) J_{α}
Heat and matter flow	$\nabla \frac{1}{T}$	Internal energy flow \mathbf{J}_u
Diffusion	$-\nabla \frac{\mu_k}{T}$	Diffusion current \mathbf{J}_k
Electrical conduction	$\frac{-\nabla \psi}{T} = \frac{\mathbf{E}}{T}$	Ion current densities \mathbf{I}_k
Chemical reactions	$\frac{A_j}{T}$	Velocity of reaction $v_j = \frac{1}{V} \frac{d\xi_j}{dt}$

Appendix 15.1 Entropy Production

A15.1.1 Transformation that Leaves σ Invariant

The entropy production remains invariant under certain transformations. One theorem [13] states that: *under mechanical equilibrium, σ is invariant under the transformation*

$$\mathbf{J}_k \rightarrow \mathbf{J}'_k = \mathbf{J}_k + \mathbf{V}n_k \quad (\text{A15.1.1})$$

in which the \mathbf{J}_k are the matter currents, n_k is the concentration of component k and \mathbf{V} is an arbitrary velocity. This statement implies that a uniform ‘drift velocity’ imposed on all the components of the system leaves the entropy production unchanged.

To prove this theorem, we first obtain a relation that the chemical potentials must satisfy in a system at mechanical equilibrium. If $n_k \mathbf{f}_k$ is the force acting on component k , then for mechanical equilibrium we have

$$\sum_k n_k \mathbf{f}_k - \nabla p = 0 \quad (\text{A15.1.2})$$

This condition can be written in terms of the chemical potential using the Gibbs–Duhem equation:

$$s dT - dp + \sum_k n_k d\mu_k = 0 \quad (\text{A15.1.3})$$

Since

$$dp = (\nabla p) \cdot d\mathbf{r} \quad \text{and} \quad d\mu_k = (\nabla \mu_k) \cdot d\mathbf{r} \quad (\text{A15.1.4})$$

under isothermal conditions ($dT = 0$), substituting Equation (A15.1.4) into Equation (A15.1.3) we obtain the relation

$$\nabla p = \sum_k n_k \nabla \mu_k \quad (\text{A15.1.5})$$

Using this expression, condition (A15.1.2) for mechanical equilibrium can now be written in terms of the chemical potential as

$$\sum_k (n_k \mathbf{f}_k - n_k \nabla \mu_k) = 0 \quad (\text{A15.1.6})$$

With this result, the invariance of entropy production σ under the transformation (A15.1.1) can be shown as follows. In the presence of an external force \mathbf{f}_k per mole, acting on the component k , under isothermal conditions and no chemical reactions, the entropy production per unit volume (15.5.12) can be written by identifying $\mathbf{f}_k = -\tau_k \nabla \psi$. This takes the simple form

$$\sigma = \sum_k \frac{\mathbf{J}_k}{T} \cdot (\mathbf{f}_k - \nabla \mu_k) \quad (\text{A15.1.7})$$

The transformation (A15.1.1) implies that $\mathbf{J}_k = \mathbf{J}'_k - \mathbf{V}n_k$. If we substitute this expression into (A15.1.7), the entropy production becomes

$$\sigma = \sum_k \frac{\mathbf{J}'_k}{T} \cdot (\mathbf{f}_k - \nabla \mu_k) - \mathbf{V} \cdot \sum_k (n_k \mathbf{f}_k - n_k \nabla \mu_k) \quad (\text{A15.1.8})$$

Due to the condition for mechanical equilibrium (A15.1.6), the second summation on the right-hand side is zero. Thus we have the invariance theorem, according to which

$$\sigma = \sum_k \frac{\mathbf{J}_k}{T} \cdot (\mathbf{f}_k - \nabla \mu_k) = \sum_k \frac{\mathbf{J}'_k}{T} \cdot (\mathbf{f}_k - \nabla \mu_k) \quad (\text{A15.1.9})$$

This theorem remains valid when chemical reactions and temperature gradients are included.

A15.1.2 Alternative Forms for Entropy Production

Different definitions of the heat current \mathbf{J}_q give somewhat different expressions for σ . We have defined the heat current \mathbf{J}_q through the relation $\mathbf{J}_u = \mathbf{J}_q + \sum_k u_k \mathbf{J}_k$. However, some authors define \mathbf{J}_u as the heat current; then the flow associated with $\nabla(1/T)$ will be the heat current [12].²

Another form of σ arises when the force associated with the matter flow \mathbf{J}_k is written as $-\nabla \mu_k$ instead of $-\nabla(\mu_k/T)$. By separating the gradient of μ_k from the gradient of $(1/T)$, it is straightforward to show that Equation (15.5.12) can be rewritten as

$$\sigma = \mathbf{J}'_u \cdot \nabla \frac{1}{T} - \sum_k \frac{\mathbf{J}_k \cdot \nabla \mu_k}{T} + \sum_k \frac{\mathbf{I}_k \cdot (-\nabla \mu)}{T} + \sum_j \frac{\tilde{A}_j v_j}{T} \quad (\text{A15.1.10})$$

in which

$$\mathbf{J}'_u = \mathbf{J}_u - \sum_k \mu_k \mathbf{J}_k = \mathbf{J}_q + \sum_k (u_k^0 - \mu_k) \mathbf{J}_k = \mathbf{J}_q + \sum_k T s_k \mathbf{J}_k$$

where we have used the relation $u_k^0 \equiv (\partial u^0 / \partial n_k)_T = \mu_k + T s_k$ (Exercise 15.2).

It is useful to write the expression for the entropy production, (5.5.12), in terms of $(\nabla \mu_k)_T$, the gradient of μ at constant T . This can be done by noting that

$$\frac{\partial \mu_k}{\partial x} = \left(\frac{\partial \mu_k}{\partial T} \right)_{n_k} \frac{\partial T}{\partial x} + \sum_k \left(\frac{\partial \mu_k}{\partial n_k} \right)_T \frac{\partial n_k}{\partial x}$$

Since this is also true for the y and the z derivatives, it follows that

$$\nabla \mu_k = \frac{\partial \mu_k}{\partial T} \nabla T + (\nabla \mu_k)_T \quad (\text{A15.1.11})$$

where $(\nabla \mu_k)_T = \sum_j (\partial \mu_k / \partial n_j)_T \nabla n_j$. As a consequence of Equation (A15.1.11), we have

$$\begin{aligned} \nabla \frac{\mu_k}{T} &= \left[\mu_k - T \left(\frac{\partial \mu_k}{\partial T} \right) \right] \nabla \frac{1}{T} + \frac{(\nabla \mu)_T}{T} \\ &= u_k^0 \nabla \frac{1}{T} + \frac{(\nabla \mu)_T}{T} \end{aligned} \quad (\text{A15.1.12})$$

where once again we have used the relation $u_k^0 \equiv (\partial u^0 / \partial n_k)_T = \mu_k + T s_k = \mu_k - T(\partial \mu / \partial T)_{n_k}$. Substitution of Equation (A15.1.12) into Equation (15.5.12) gives

$$\sigma = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \sum_k \frac{\mathbf{J}_k \cdot (\nabla \mu_k)_T}{T} + \sum_k \frac{\mathbf{I}_k \cdot (-\nabla \psi)}{T} + \sum_j \frac{\tilde{A}_j v_j}{T} \quad (\text{A15.1.13})$$

²We can establish the relation between the heat currents in this text and those used in the classic text of de Groot and Mazur [12]: $\mathbf{J}_u = \mathbf{J}_q^{\text{DM}}$ and $\mathbf{J}_q = \mathbf{J}_q^{\text{IDM}}$, in which the superscript DM indicates the quantity used by de Groot and Mazur.

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Exercises

15.1 Assume that the Gibbs relation $dU = T dS - p dV + \sum_k \mu_k dN_k$ is valid for a small volume element V . Show the validity of the relation $T ds = du - \sum_k \mu_k dn_k$ in which $s = (S/V)$, $u = (U/V)$ and $n_k = (N_k/V)$.

15.2 (a) Using the Helmholtz energy density f and an appropriate Maxwell relation, show that

$$u_k \equiv \left(\frac{\partial u}{\partial n_k} \right)_T = \mu_k + Ts_k = \mu_k - T \left(\frac{\partial \mu_k}{\partial T} \right)_{n_k}$$

in which

$$s_k = \left(\frac{\partial s}{\partial n_k} \right)_T$$

(b) We have seen that in the presence of a field $u = u^0 + \sum_k \tau_k n_k \psi$. Show that $f_k = (\mu_k + \tau_k \psi)$ and

$$u_k^0 \equiv \left(\frac{\partial u^0}{\partial n_k} \right)_T = \mu_k + Ts_k = \mu_k - T \left(\frac{\partial \mu_k}{\partial T} \right)_{n_k}$$

15.3 Using the law of conservation of energy (15.4.3) and the concentration balance equation (15.3.10), show that the current as defined by Equation (15.4.11) satisfies the energy conservation equation (15.4.8).

15.4 From Equations (15.4.16) and (15.4.17) obtain Equations (15.4.18) and (15.4.19).

15.5 Obtain Equations (A15.1.10a) and (A15.1.10b) from Equation (15.5.12).

16

Nonequilibrium Thermodynamics: The Linear Regime

16.1 Linear Phenomenological Laws

When a system is close to equilibrium, a general theory based on linear relations between forces and flows could be formulated. In the previous chapter we have seen that the entropy production per unit volume, σ , can be written as

$$\sigma = \sum_k F_k J_k \quad (16.1.1)$$

in which F_k are forces, such as the gradient of $(1/T)$, and J_k are flows, such as the heat flow. The forces drive the flows; a nonvanishing gradient of $(1/T)$ causes the flow of heat. At equilibrium, all the forces and the corresponding flows vanish, i.e. the flows J_k depend on forces F_k such that they vanish when $F_k = 0$. Though the flows are driven by the forces, they are not entirely determined by them; the flows can depend on other factors such as the presence of catalysts. For a fixed value of the affinity, the corresponding flow, the rate of a chemical reaction, can be altered by the presence of a catalyst.

For a small deviation in the forces from their equilibrium value of zero, the flows can be expected to be linear functions of the forces. (In other words, the flows are assumed to be analytic functions of the forces, as is the case with most physical variables.) Accordingly, the following relation between the flows and the forces is assumed:

$$J_k = \sum_j L_{kj} F_j \quad (16.1.2)$$

Here the coefficients L_{kj} are constants called **phenomenological coefficients**. Note how Equation (16.1.2) implies that not only can a force, such as the gradient of $(1/T)$, drive the flow of heat but it can also drive other flows, such as a flow of matter or an electrical current. The thermoelectric effect is one such cross-effect, in which a thermal gradient drives not only a heat flow but also an electrical current and vice versa (Figure 16.1). Another example is cross-diffusion, in which a gradient in the concentration of one compound can drive

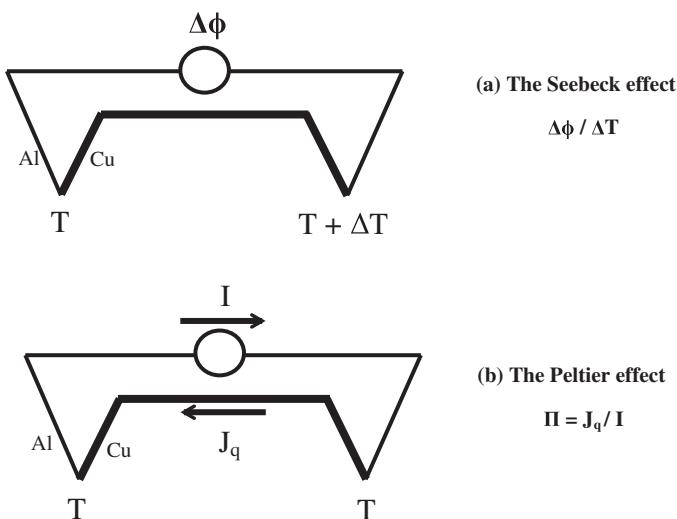


Figure 16.1 The thermoelectric effect is a ‘cross-effect’ relating thermodynamic forces and flows. (a) In the Seebeck effect, two dissimilar metal wires are joined and the junctions are maintained at different temperatures. As a result an EMF is generated. The EMF generated is generally of the order of 10^{-5} V K^{-1} of temperature difference and it may vary from sample to sample. (b) In the Peltier effect, the two junctions are maintained at the same temperature and an electric current is passed through the system. The electric current drives a heat flow J_q from one junction to the other. The Peltier heat current is generally of the order of 10^{-5} J s^{-1} per amp [1].

a diffusion current of another. Such cross-effects were known long before thermodynamics of irreversible processes was formulated. Each cross-effect was studied on an individual basis, but without a unifying formalism. For example, the thermoelectric phenomenon was investigated in the 1850s and William Thomson (Lord Kelvin) [2] gave theoretical explanations for the observed Seebeck and Peltier effects (Figure 16.1). (Kelvin’s reasoning was later found to be incorrect.) Similarly, other cross-effects were observed and studied in the nineteenth century. Neglecting the cross-effects, some of the well-established phenomenological laws are as follows:

$$\text{Fourier's law of heat conduction: } \mathbf{J}_q = -\kappa \nabla T(x) \quad (16.1.3)$$

$$\text{Fick's law of diffusion: } \mathbf{J}_k = -D_k \nabla n_k(x) \quad (16.1.4)$$

$$\text{Ohm's law of electrical conduction: } I = \frac{V}{R} \quad (16.1.5a)$$

$$\text{Alternative form of Ohm's law: } \mathbf{I} = \frac{\mathbf{E}}{\rho} \quad (16.1.5b)$$

In these equations, κ is the heat conductivity, D_k is the diffusion coefficient of compound k and n_k is the concentration of compound k . Ohm’s law is usually stated as (16.1.5a) in which I is the electrical current, R is the resistance and V is the voltage. It can also be stated in terms of the electric current density \mathbf{I} , the electric field \mathbf{E} and the resistivity ρ (resistance per unit length per unit area of cross-section). Other quantities in the above equations are as defined in Table 15.1.

As a specific example of the general relation (16.1.2), let us consider the thermoelectric phenomenon mentioned above (Figure 16.1). The equations that describe thermoelectric cross-coupling are¹

$$\mathbf{J}_q = L_{qq} \nabla \left(\frac{1}{T} \right) + L_{qe} \frac{\mathbf{E}}{T} \quad (16.1.6)$$

$$\mathbf{I}_e = L_{ee} \frac{\mathbf{E}}{T} + L_{eq} \nabla \frac{1}{T} \quad (16.1.7)$$

in which L_{qq} , L_{qe} , etc., correspond to L_{kj} in Equation (16.1.2). Experimentally these coefficients can be measured for various conductors. We shall discuss this and other examples in detail in later sections of this chapter. Phenomenological laws and the cross-effects between the flows were independently studied and, until the formalism presented here was developed in the 1930s, there was no *unified* theory of all the cross-effects. Relating the entropy production to the phenomenological laws is the first step in developing a unified theory. For conditions under which the linear phenomenological laws (16.1.2) are valid, entropy production (16.1.1) takes the quadratic form

$$\boxed{\sigma = \sum_{jk} L_{jk} F_j F_k > 0} \quad (16.1.8)$$

In this expression, if F_k are vectors, the product $F_j F_k$ is a scalar product. The forces F_k can be positive or negative. A matrix L_{jk} that satisfies the condition (16.1.8) is said to be positive definite. The properties of **positive definite** matrices are well characterized. For example, a two-dimensional matrix L_{ij} is positive definite only when the following conditions are satisfied (Exercise 16.1):

$$L_{11} > 0, \quad L_{22} > 0, \quad (L_{12} + L_{21})^2 < 4L_{11}L_{22} \quad (16.1.9)$$

In general, the diagonal elements of a positive definite matrix must be positive. In addition, a necessary and sufficient condition for a matrix L_{ij} to be positive definite is that its determinant and all the determinants of lower dimension obtained by deleting one or more rows and columns must be positive. Thus, according to the Second Law, the ‘proper coefficients’ L_{kk} should be positive; the ‘cross coefficients’ L_{ik} ($i \neq k$) can be of either sign. Furthermore, as we shall see in the next section, the elements L_{jk} also obey the *Onsager reciprocal relations* $L_{jk} = L_{kj}$. The positivity of entropy production and the Onsager relations form the foundation for linear nonequilibrium thermodynamics.

16.2 Onsager Reciprocal Relations and the Symmetry Principle

That reciprocal relations, $L_{ij} = L_{ji}$, were associated with cross-effects, which was noticed by William Thomson (Lord Kelvin) and others even during the last century. The early explanations of the reciprocal relations were based on thermodynamic reasoning that was not on a firm footing. For this reason, William Thomson and others regarded the reciprocal relations only as conjectures. A well-founded theoretical explanation for these relations was developed by Lars Onsager (1903–1976) in 1931 [3]. Onsager’s theory is based on the *principle of detailed balance or microscopic reversibility* that is valid for systems at equilibrium.

¹Note that $\mathbf{J}_u = \mathbf{J}_q$ when $\sum u_k \mathbf{J}_k = 0$.



Lars Onsager (1903–1976).

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The principle of detailed balance or microscopic reversibility is formulated using the general thermodynamic theory of equilibrium fluctuations that we discussed in Section 14.2. A summary of the main results of this section is as follows.

- The entropy $\Delta_i S$ associated with fluctuations α_i can be written as

$$\Delta_i S = -\frac{1}{2} \sum_{k,j} g_{kj} \alpha_j \alpha_k = \frac{1}{2} \sum_k F_k \alpha_k \quad (16.2.1)$$

in which

$$F_k = \frac{\partial \Delta_i S}{\partial \alpha_k} = - \sum_j g_{kj} \alpha_j \quad (16.2.2)$$

is the conjugate thermodynamic force for the thermodynamic flow $d\alpha_k/dt$.

- According to the Einstein formula (14.2.2), the entropy associated with the fluctuations gives the following probability distribution for the fluctuations:

$$P(\alpha_1, \alpha_2, \dots, \alpha_m) = Z^{-1} \exp(\Delta_i S/k_B) = Z^{-1} \exp\left[-\frac{1}{2k_B} \sum_{i,j} g_{ij} \alpha_i \alpha_j\right] \quad (16.2.3)$$

in which k_B is the Boltzmann constant and Z is the normalization constant.

- As was shown in Section 14.2, using the probability distribution (16.2.3), the following expressions for correlations between F_i and α_j can be obtained:

$$\langle F_i \alpha_j \rangle = -k_B \delta_{ij} \quad (16.2.4)$$

$$\langle \alpha_i \alpha_j \rangle = k_B (g^{-1})_{ij} \quad (16.2.5)$$

in which $(g^{-1})_{ij}$ is the inverse of the matrix g_{ij} .

These are the basic results of the theory of fluctuations needed to derive the reciprocal relations $L_{ik} = L_{ki}$.

16.2.1 The Onsager Reciprocal Relations

Onsager's theory begins with the assumption that, where linear phenomenological laws are valid, a deviation α_k decays according to the linear law

$$J_k = \frac{d\alpha_k}{dt} = \sum_j L_{kj} F_j \quad (16.2.6a)$$

which, by virtue of Equation (16.2.2), can also be written as

$$J_k = \frac{d\alpha_k}{dt} = - \sum_{j,i} L_{kj} g_{ji} \alpha_i = \sum_i M_{ki} \alpha_i \quad (16.2.6b)$$

in which the matrix M_{ki} is the product of the matrices L_{kj} and g_{ji} . The equivalence of Equations (16.2.6a) and (16.2.6b) shows that phenomenological equations for the flows that are usually written in the form (16.2.6b) can be transformed into (16.2.6a) in which the flows are linear functions of the forces F_k .

As we shall see, according to the principle of detailed balance, the effect of α_i on the flow $(d\alpha_k/dt)$ is the same as the effect of α_k on the flow $(d\alpha_i/dt)$. This condition can be expressed in terms of the correlation $\langle \alpha_i d\alpha_k/dt \rangle$ between α_i and $(d\alpha_k/dt)$ as

$$\left\langle \alpha_i \frac{d\alpha_k}{dt} \right\rangle = \left\langle \alpha_k \frac{d\alpha_i}{dt} \right\rangle \quad (16.2.7)$$

In a way, this correlation isolates that part of the flow $(d\alpha_k/dt)$ that depends on the variable α_i . Once the validity of Equation (16.2.7) is accepted, the reciprocal relations directly follow from Equation (16.2.6a). Multiplying (16.2.6a) by α_i and taking the average, we obtain

$$\left\langle \alpha_i \frac{d\alpha_k}{dt} \right\rangle = \sum_j L_{kj} \langle \alpha_i F_j \rangle = -k_B \sum_j L_{kj} \delta_{ji} = -k_B L_{ki} \quad (16.2.8)$$

where we have used $\langle F_j \alpha_i \rangle = -k_B \delta_{ji}$. Similarly,

$$\left\langle \alpha_k \frac{d\alpha_i}{dt} \right\rangle = \sum_j L_{ij} \langle \alpha_k F_j \rangle = -k_B \sum_j L_{ij} \delta_{jk} = -k_B L_{ik} \quad (16.2.9)$$

If the equality (16.2.7) is valid, we immediately obtain the **Onsager reciprocal relations**

$$\boxed{L_{ki} = L_{ik}}^2 \quad (16.2.10)$$

We are then naturally led to ask why Equation (16.2.7) is valid. Onsager argued that this equality is valid because of **microscopic reversibility**, which, according to Onsager, is:

... the assertion that transitions between two (classes of) configurations A and B should take place equally often in the directions $A \rightarrow B$ and $B \rightarrow A$ in a given time τ [3, p. 418].

This statement is the same as the **principle of detailed balance** that was discussed in Chapter 9. According to this principle, if α_i has a value $\alpha_i(t)$ at time t , and if at time $t + \tau$ a correlated variable α_k has a value $\alpha_k(t + \tau)$, then the time-reversed transition should occur equally often. This means that

$$\boxed{\langle \alpha_i(t) \alpha_k(t + \tau) \rangle = \langle \alpha_k(t) \alpha_i(t + \tau) \rangle} \quad (16.2.11)$$

Note that Equation (16.2.11) remains unchanged if τ is replaced by $-\tau$.

From this equality, relation (16.2.7) can be obtained by noting that

$$\frac{d\alpha_k}{dt} \approx \frac{\alpha_k(t + \tau) - \alpha_k(t)}{\tau}$$

so that

$$\left\langle \alpha_i \frac{d\alpha_k}{dt} \right\rangle = \left\langle \alpha_i(t) \left\{ \frac{\alpha_k(t + \tau) - \alpha_k(t)}{\tau} \right\} \right\rangle = \frac{1}{\tau} \langle \alpha_i(t) \alpha_k(t + \tau) - \alpha_i(t) \alpha_k(t) \rangle \quad (16.2.12)$$

$$\left\langle \alpha_k \frac{d\alpha_i}{dt} \right\rangle = \left\langle \alpha_k(t) \left\{ \frac{\alpha_i(t + \tau) - \alpha_i(t)}{\tau} \right\} \right\rangle = \frac{1}{\tau} \langle \alpha_k(t) \alpha_i(t + \tau) - \alpha_k(t) \alpha_i(t) \rangle \quad (16.2.13)$$

If we now use the relation $\langle \alpha_i(t) \alpha_k(t + \tau) \rangle = \langle \alpha_k(t) \alpha_i(t + \tau) \rangle$ and use the fact that $\langle \alpha_i(t) \alpha_k(t) \rangle = \langle \alpha_k(t) \alpha_i(t) \rangle$ in Equations (16.2.12) and (16.2.13), equality (16.2.7) follows.

Thus we see that the principle of detailed balance or microscopic reversibility, expressed as $\langle \alpha_i(t) \alpha_k(t + \tau) \rangle = \langle \alpha_k(t) \alpha_i(t + \tau) \rangle$, leads to the reciprocal relations $L_{ij} = L_{ji}$.

16.2.2 The Symmetry Principle

Though forces and flows are coupled in general, the possible coupling is restricted by a general symmetry principle. This principle, which states that *macroscopic causes always have fewer or equal symmetries than the effects they produce*, was originally stated by Pierre Curie [4] but not in the context of thermodynamics. Prigogine [5] introduced the principle into nonequilibrium thermodynamics because it enables us to eliminate the possibility of coupling between certain forces and flows on the basis of symmetry. We shall refer to this principle as the **symmetry principle**; in some texts it is also called the **Curie principle**. For example, a scalar thermodynamic force such as chemical affinity, which has the high symmetry of isotropy, cannot drive a heat

²In the presence of a magnetic field \mathbf{B} , L_{ij} may be functions of \mathbf{B} . In this case the reciprocal relations take the form $L_{ki}(\mathbf{B}) = L_{ik}(-\mathbf{B})$.

current, which has lower symmetry because of its directionality. As an explicit example, let us consider a system in which there is heat transport and chemical reaction. The entropy production is (with $\mathbf{J}_u = \mathbf{J}_q$)

$$\sigma = \mathbf{J}_q \cdot \nabla \frac{1}{T} + \frac{A}{T} v \quad (16.2.14)$$

The general linear phenomenological laws that follow from this are

$$\mathbf{J}_q = L_{qq} \nabla \frac{1}{T} + L_{qc} \frac{A}{T} \quad (16.2.15)$$

$$v = L_{cc} \frac{A}{T} + L_{cq} \nabla \frac{1}{T} \quad (16.2.16)$$

According to the symmetry principle, the scalar process of chemical reaction, due to its higher symmetry of isotropy and homogeneity, cannot generate a heat current that has a direction – and hence is anisotropic. Another way of stating this principle is that *a scalar cause cannot produce a vectorial effect*. Therefore $L_{qc} = 0$. As a consequence of the reciprocal relations, we have $L_{qc} = L_{cq} = 0$. In general, irreversible processes of different tensorial character (scalars, vectors and higher-order tensors) do not couple to each other.

Because of the symmetry principle, the entropy production due to scalar, vectorial and tensorial processes should each be positive. In the above case, we must have

$$\mathbf{J}_q \cdot \nabla \frac{1}{T} \geq 0, \quad \frac{A}{T} v \geq 0 \quad (16.2.17)$$

(Also, the entropy production due to chemical reactions in each phase should be separately positive.) Thus, the symmetry principle provides constraints for the coupling of, and the entropy production due to, irreversible processes.

In the following sections we shall present several cross-effects in detail to illustrate the experimental implications of Onsager's reciprocal relations.

16.3 Thermoelectric Phenomena

As a first illustration of the theory presented in the last two sections, let us consider thermoelectric effects that involve the flow of heat \mathbf{J}_q and electric current \mathbf{I}_e in conducting wires (the subscript e indicates that the flow corresponds to the flow of electrons). The entropy production rate per unit volume due to these two irreversible processes and the linear phenomenological laws associated with it are

$$\sigma = \mathbf{J}_q \cdot \nabla \left(\frac{1}{T} \right) + \frac{\mathbf{I}_e \cdot \mathbf{E}}{T} \quad (16.3.1)$$

$$\boxed{\mathbf{J}_q = L_{qq} \nabla \left(\frac{1}{T} \right) + L_{qe} \frac{\mathbf{E}}{T}} \quad (16.3.2)$$

$$\boxed{\mathbf{I}_e = L_{ee} \frac{\mathbf{E}}{T} + L_{eq} \nabla \frac{1}{T}} \quad (16.3.3)$$

where \mathbf{E} is the electric field. For a one-dimensional system, such as a conducting wire, the vectorial aspect of \mathbf{J}_q and \mathbf{I}_e is unimportant and both may be treated as scalars. To relate the coefficients L_{qq} and L_{ee} with

the heat conductivity κ and resistance R , we can write Equations (16.3.2) and (16.3.3) in a one-dimensional system as

$$J_q = -\frac{1}{T^2} L_{qq} \frac{\partial}{\partial x} T + L_{qe} \frac{E}{T} \quad (16.3.4)$$

$$I_e = L_{ee} \frac{E}{T} - \frac{1}{T^2} L_{eq} \frac{\partial}{\partial x} T \quad (16.3.5)$$

Fourier's law (16.1.3) of heat conduction is valid when the electric field $E = 0$. Comparing the heat conduction term $J_q = -(1/T^2)L_{qq}\partial T/\partial x$ to Fourier's law (16.1.3) leads to the identification

$$\kappa = \frac{L_{qq}}{T^2} \quad (16.3.6)$$

We can now specify more precisely what is meant by the **near-equilibrium linear regime**. It means that L_{qq} , L_{ee} , etc., may be treated as constants. Since $T(x)$ is a function of position, such an assumption is strictly not valid. It is valid only in the approximation that the change in T from one end of the system to another is small compared to the average T , i.e. if the average temperature is T_{avg} , then $|T(x) - T_{avg}| / T_{avg} \ll 1$ for all x . Hence we may approximate $T^2 \approx T_{avg}^2$ and use κT_{avg}^2 in place of κT^2 .

To find the relation between L_{ee} and the resistance R , we note that $V = -\Delta \phi = \int_0^l E \, dx$ in which l is the length of the system. The current I_e is independent of x . At constant temperature ($\partial T/\partial x = 0$), the current is entirely due to the electrical potential difference. Integrating Equation (16.3.5) over the length of the system, we obtain

$$\int_0^l I_e \, dx = \frac{L_{ee}}{T} \int_0^l E \, dx \quad \text{or} \quad I_e l = \frac{L_{ee}}{T} V \quad (16.3.7)$$

Comparing this equation with Ohm's law (16.1.5a), we make the identification

$$L_{ee} = \frac{T}{R/l} = \frac{T}{r} \quad (16.3.8)$$

in which r is the *resistance per unit length*. As noted in Equation (16.1.5b), Ohm's law can also be stated in general as

$$\mathbf{I} = \frac{\mathbf{E}}{\rho} \quad (16.3.9)$$

in which ρ is the *specific resistance*, \mathbf{I} is the current density and \mathbf{E} is the electric field. Comparing Equation (16.3.3) with Equation (16.3.9) we have the general relation

$$L_{ee} = \frac{T}{\rho} \quad (16.3.10)$$

When we consider a one-dimensional system, ρ is replaced by r , resistance per unit length.

16.3.1 The Seebeck Effect

The cross-coefficients L_{qe} and L_{eq} can also be related to experimentally measured quantities. In the Seebeck effect (Box 16.1), a temperature difference between two junctions of dissimilar metals produces an EMF. This EMF is measured at zero current. For this system, Equations (16.3.4) and (16.3.5) may be used. Setting $I_e = 0$ in Equation (16.3.5) we obtain

$$0 = L_{ee} ET - L_{eq} \frac{\partial}{\partial x} T \quad (16.3.11)$$

This equation may now be integrated to obtain a relation between the temperature difference ΔT and the EMF generated due to this temperature difference, $\Delta\phi = - \int E dx$. In doing this integration, we shall assume that the total variation ΔT is small and make the approximation $\int TE dx \approx T \int E dx = -T \Delta\phi$. This gives us the relation

$$L_{eq} = -L_{ee} T \left(\frac{\Delta\phi}{\Delta T} \right)_{I=0} \quad (16.3.12)$$

The ratio $-(\Delta\phi/\Delta T)_{I=0}$, called the **thermoelectric power**, is experimentally measured. Some typical values of thermoelectric power are shown in Table 16.1; its sign may be positive or negative. Using Equation (16.3.12), the coefficient L_{eq} can be related to the measured quantities.

Box 16.1 Onsager reciprocal relations in thermoelectric phenomena

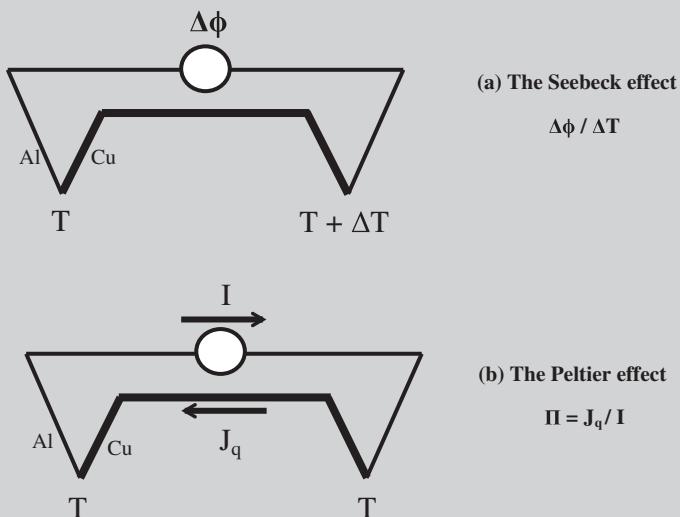


Table 16.1 Some experimental data confirming Onsager reciprocal relations.*

Thermocouple	T (°C)	Π/T ($\mu\text{V K}^{-1}$)	$-\Delta\phi/\Delta T$ ($\mu\text{V K}^{-1}$)	L_{qe}/L_{eq}
Cu-Al	15.8	2.4	3.1	0.77
Cu-Ni	0	18.6	20.0	0.930
Cu-Ni	14	20.2	20.7	0.976
Cu-Fe	0	-10.16	-10.15	1.000
Cu-Bi	20	-71	-66	1.08
Fe-Ni	16	33.1	31.2	1.06
Fe-Hg	18.4	16.72	16.66	1.004

*More extensive data can be found in Reference [1].

16.3.2 The Peltier Effect

In the Peltier effect, the two junctions are maintained at a constant temperature while a current I is passed through the system (Box 16.1). This causes a flow of heat from one junction to another. The two junctions are maintained at the same temperature by removing heat from the junction receiving heat and thus maintaining a steady heat flow J_q . Under these conditions, the ratio called the **Peltier heat**

$$\Pi = \left(\frac{J_q}{I_e} \right) \quad (16.3.13)$$

can be measured. Some typical values of (Π/T) are shown in Table 16.1. The phenomenological coefficient L_{qe} can be related to the Peltier heat as follows. Since there is no temperature difference between the two junctions, $\partial T/\partial x = 0$, and Equations (16.3.4) and (16.3.5) become

$$J_q = L_{qe} \frac{E}{T} \quad (16.3.14)$$

$$I_e = L_{ee} \frac{E}{T} \quad (16.3.15)$$

Dividing one equation by the other and using Equations (16.3.8) and (16.3.13), we obtain

$$L_{qe} = \Pi L_{ee} = \Pi \frac{T}{R/l} = \Pi \frac{T}{r} \quad (16.3.16)$$

In this manner, the phenomenological coefficients L_{qe} and L_{eq} can be related to the experimental parameters of the cross-effects.

Having identified all the linear phenomenological coefficients in terms of the experimentally measured quantities, we can now turn to the reciprocal relations, according to which one must find

$$L_{qe} = L_{eq} \quad (16.3.17)$$

Upon using Equation (16.3.12) for L_{eq} and Equation (16.3.16) for L_{qe} , we find

$$- L_{ee} T \left(\frac{\Delta\varphi}{\Delta T} \right) = \Pi L_{ee} \quad \text{or} \quad \boxed{- \left(\frac{\Delta\varphi}{\Delta T} \right) = \frac{\Pi}{T}} \quad (16.3.18)$$

Experimental data verifying this prediction for pairs of conductors are shown in Table 16.1.

16.4 Diffusion

In this section we will apply the theory of linear nonequilibrium thermodynamics to the process of diffusion. When several species are simultaneously diffusing, it is found that the flow of one species influences the flow of another; i.e. there are cross-effects between diffusing species. The entropy production per unit volume associated with simultaneous diffusion of several species is

$$\sigma = - \sum_k \mathbf{J}_k \cdot \nabla \left(\frac{\mu_k}{T} \right) \quad (16.4.1)$$

in which \mathbf{J}_k is the matter current and μ_k is the chemical potential of species k . Under isothermal conditions, the associated linear laws are

$$\mathbf{J}_i = - \sum_k \frac{L_{ik}}{T} \nabla \mu_k \quad (16.4.2)$$

Table 16.2 Some Fick's law diffusion coefficients showing cross-effects in a molten silicate solution.*

$T(K)$	$D_{11} (\text{m}^2 \text{s}^{-1})$	$D_{12} (\text{m}^2 \text{s}^{-1})$	$D_{21} (\text{m}^2 \text{s}^{-1})$	$D_{22} (\text{m}^2 \text{s}^{-1})$
1723	$(6.8 \pm 0.3) \times 10^{-11}$	$(-2.0 \pm 0.5) \times 10^{-11}$	$(-3.3 \pm 0.5) \times 10^{-11}$	$(4.1 \pm 0.7) \times 10^{-11}$
1773	$(1.0 \pm 0.1) \times 10^{-10}$	$(-2.8 \pm 0.8) \times 10^{-11}$	$(-4.2 \pm 0.8) \times 10^{-11}$	$(7.3 \pm 0.4) \times 10^{-11}$
1823	$(1.8 \pm 0.2) \times 10^{-10}$	$(-4.6 \pm 0.6) \times 10^{-11}$	$(-6.4 \pm 0.5) \times 10^{-11}$	$(1.5 \pm 0.1) \times 10^{-10}$

*The composition of the silicate is 40% CaO, 20% Al₂O₃ and 40% SiO by weight [6, 7].

Our first task is to relate the linear coefficients L_{ik} to the experimentally measured diffusion coefficients D_{ij} . For simultaneous diffusion of several species (under isothermal conditions), a 'generalized Fick's law' may be written as

$$\mathbf{J}_i = - \sum_k D_{ik} \nabla n_k(\mathbf{x}) \quad (16.4.3)$$

in which $n_k(\mathbf{x})$ is the concentration of the component k at position \mathbf{x} . As an example, diffusion coefficients D_{ij} in a molten silicate solution of CaO–Al₂O₃–SiO₂ at various temperatures [6, 7] are shown in Table 16.2. (Diffusion coefficients for some gases and liquids are given in Chapter 10.) Let us consider a system with two components. The Gibbs–Duhem relation tells us that the chemical potentials, and hence the forces $-\nabla(\mu_k/T)$, are not all independent. For a two-component system when T and p are constant, we have

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (16.4.4)$$

Since $d\mu_k = d\mathbf{r} \cdot \nabla \mu_k$ for an arbitrary $d\mathbf{r}$, Equation (16.4.4) leads to the following relation between the gradients of the chemical potentials:

$$n_1 \nabla \mu_1 + n_2 \nabla \mu_2 = 0 \quad (16.4.5)$$

This shows that the thermodynamic forces are not all independent. Nor are all the flows \mathbf{J}_k independent. In most physical situations, the relation between the flows is more conveniently expressed as the condition for 'no volume flow'[1]. For a two-component system, this is expressed as

$$\mathbf{J}_1 v_1 + \mathbf{J}_2 v_2 = 0 \quad (16.4.6)$$

in which the v_k are partial molar volumes. For notational simplicity we use v_k for the partial molar volume instead of $V_{m,k}$. This equation is the statement that the diffusion flows do not result in any change in volume (Figure 16.2).

As a consequence of Equation (16.4.5), the entropy production due to diffusion under isothermal conditions can be written (Exercise 16.4) as³

$$\sigma = -\frac{1}{T} \left(\mathbf{J}_1 - \frac{n_1}{n_2} \mathbf{J}_2 \right) \cdot \nabla \mu_1 \quad (16.4.7)$$

Now, using condition (16.4.6) for no volume flow, the expression for entropy production can be written as

$$\sigma = -\frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) \mathbf{J}_1 \cdot \nabla \mu_1 \quad (16.4.8)$$

³As shown in Appendix 15.1, even if there is a constant volume flow, σ remains unchanged.

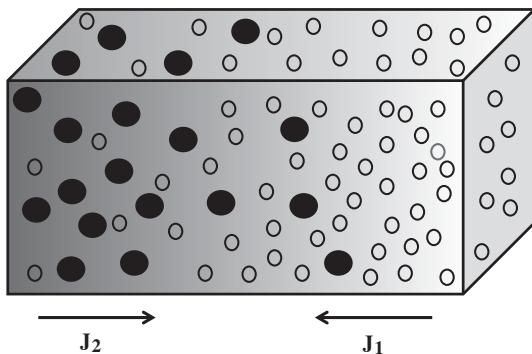


Figure 16.2 Diffusion in a two-component system. In most physical situations the flow of the components due to diffusion does not produce a change in volume.

The linear phenomenological law that relates the flux \mathbf{J}_1 to the conjugate force in Equation (16.4.8) is

$$\mathbf{J}_1 = -L_{11} \frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) \nabla \mu_1 \quad (16.4.9)$$

We can relate this equation to Fick's law, usually written as $\mathbf{J}_1 = -D_1 \nabla n_1$, by noting that $\nabla \mu_1 = (\partial \mu_1 / \partial n_1) \nabla n_1$. We then have

$$\mathbf{J}_1 = -L_{11} \frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) \left(\frac{\partial \mu_1}{\partial n_1} \right) \nabla n_1 = -D_1 \nabla n_1 \quad (16.4.10)$$

From this it follows that the relation between the phenomenological coefficient L_{11} and the diffusion coefficient is

$$L_{11} = \frac{D_1 T}{\left(1 + \frac{v_1 n_1}{v_2 n_2} \right) \left(\frac{\partial \mu_1}{\partial n_1} \right)} \quad (16.4.11)$$

For diffusion of a solute in a solution, n_2 is the concentration of the solution and n_1 the concentration of the solute. For *dilute ideal solutions* recall that $\mu_1 = \mu_0(p, T) + RT \ln x_1$, in which $x_1 = n_1/(n_1 + n_2) \approx n_1/n_2$, and also that $n_1 \ll n_2$. These conditions simplify the relation between L_{11} and D_1 to

$$L_{11} = \frac{D_1 n_1}{R} \quad (16.4.12)$$

This is the relation we saw in Chapter 10 between the usual diffusion coefficient and the corresponding phenomenological coefficient.

To verify Onsager's reciprocal relations we need at least three components. For three-component isothermal diffusion, the entropy production per unit volume is

$$\sigma = -\frac{\mathbf{J}_1}{T} \cdot \nabla \mu_1 - \frac{\mathbf{J}_2}{T} \cdot \nabla \mu_2 - \frac{\mathbf{J}_3}{T} \cdot \nabla \mu_3 \quad (16.4.13)$$

For a three-component system, the corresponding Gibbs–Duhem equation and the condition for no volume flow are as follows (Equations (16.4.5) and (16.4.6)):

$$n_1 \nabla \mu_1 + n_2 \nabla \mu_2 + n_3 \nabla \mu_3 = 0 \quad (16.4.14)$$

$$\mathbf{J}_1 v_1 + \mathbf{J}_2 v_2 + \mathbf{J}_3 v_3 = 0 \quad (16.4.15)$$

Let us assume that \mathbf{J}_3 and μ_3 are the variables for the solvent while \mathbf{J}_1 , μ_1 and \mathbf{J}_2 , μ_2 are the variables of two solutes whose diffusion cross-effects are of interest. Using Equations (16.4.14) and (16.4.15), \mathbf{J}_3 and μ_3 can be eliminated from the expression for the entropy production. The entropy production can then be written in terms of only the variables \mathbf{J}_1 , μ_1 and \mathbf{J}_2 , μ_2 of the two solutes (Exercise 16.5):

$$\sigma = \mathbf{F}_1 \cdot \mathbf{J}_1 + \mathbf{F}_2 \cdot \mathbf{J}_2 \quad (16.4.16)$$

in which the thermodynamic forces \mathbf{F}_1 and \mathbf{F}_2 are

$$\mathbf{F}_1 = -\frac{1}{T} \left[\nabla \mu_1 + \frac{n_1 v_1}{n_3 v_3} \nabla \mu_1 + \frac{n_2 v_1}{n_3 v_3} \nabla \mu_2 \right] \quad (16.4.17)$$

and

$$\mathbf{F}_2 = -\frac{1}{T} \left[\nabla \mu_2 + \frac{n_2 v_2}{n_3 v_3} \nabla \mu_2 + \frac{n_1 v_2}{n_3 v_3} \nabla \mu_1 \right] \quad (16.4.18)$$

The associated phenomenological laws then take the form

$$\mathbf{J}_1 = L_{11} \mathbf{F}_1 + L_{12} \mathbf{F}_2 \quad (16.4.19)$$

$$\mathbf{J}_2 = L_{21} \mathbf{F}_1 + L_{22} \mathbf{F}_2 \quad (16.4.20)$$

To verify the reciprocal relations, we must now relate L_{ik} and the experimentally measured diffusion coefficients D_{ik} of the generalized Fick's law:

$$\mathbf{J}_1 = -D_{11} \nabla n_1 - D_{12} \nabla n_2 \quad (16.4.21)$$

$$\mathbf{J}_2 = -D_{21} \nabla n_1 - D_{22} \nabla n_2 \quad (16.4.22)$$

If $\mathbf{J}_2 = 0$, note how these equations imply that a constant flow, $\mathbf{J}_1 = \text{constant}$, due to a concentration gradient in n_1 , will produce a concentration gradient in n_2 . Let us assume that the flow and concentration gradients are along only one direction, say x , so that all the gradients correspond to derivatives with respect to x . (Extending the following calculation to three dimensions is straightforward.) We can write the forces F_k in terms of the gradients of the two diffusing components because the chemical potentials μ_k are functions of n_k . Thus

$$\frac{\partial \mu_1}{\partial x} = \frac{\partial \mu_1}{\partial n_1} \frac{\partial n_1}{\partial x} + \frac{\partial \mu_1}{\partial n_2} \frac{\partial n_2}{\partial x} \quad (16.4.23)$$

A similar relation can be written for the gradient of μ_2 . Using these relations in Equations (16.4.17) and (16.4.18) and substituting them in Equations (16.4.19) and (16.4.20), the flows \mathbf{J}_k can be written in terms

of the gradients of n_k . After some calculation (Exercise 16.6) the following relations between the diffusion coefficients and the linear Onsager coefficients can be obtained:

$$L_{11} = T \frac{dD_{11} - bD_{12}}{ad - bc}, \quad L_{12} = T \frac{aD_{12} - cD_{11}}{ad - bc} \quad (16.4.24)$$

$$L_{21} = T \frac{dD_{21} - bD_{22}}{ad - bc}, \quad L_{22} = T \frac{aD_{22} - cD_{21}}{ad - bc} \quad (16.4.25)$$

in which

$$a = \left(1 + \frac{n_1 v_1}{n_3 v_3}\right) \left(\frac{\partial \mu_1}{\partial n_1}\right) + \frac{n_2 v_1}{n_3 v_3} \left(\frac{\partial \mu_2}{\partial n_1}\right), \quad b = \left(1 + \frac{n_2 v_2}{n_3 v_3}\right) \left(\frac{\partial \mu_2}{\partial n_1}\right) + \frac{n_1 v_2}{n_3 v_3} \left(\frac{\partial \mu_1}{\partial n_1}\right) \quad (16.4.26)$$

$$c = \left(1 + \frac{n_1 v_1}{n_3 v_3}\right) \left(\frac{\partial \mu_1}{\partial n_2}\right) + \frac{n_2 v_1}{n_3 v_3} \left(\frac{\partial \mu_2}{\partial n_2}\right), \quad d = \left(1 + \frac{n_2 v_2}{n_3 v_3}\right) \left(\frac{\partial \mu_2}{\partial n_2}\right) + \frac{n_1 v_2}{n_3 v_3} \left(\frac{\partial \mu_1}{\partial n_2}\right) \quad (16.4.27)$$

(Note that the only difference between Equations (16.4.26) and (16.4.27) is that the derivative $\partial/\partial n_1$ is replaced by $\partial/\partial n_2$.) These relations can be written more compactly in matrix notation (Exercise 16.7). From these relations it is easy to see that the implication of the reciprocal relations $L_{12} = L_{21}$ is

$$aD_{12} + bD_{22} = cD_{11} + dD_{21} \quad (16.4.28)$$

Experimental data for several three-component systems is summarized in Tables 16.3 and 16.4. Often the relations between the chemical potential and the concentration are not known precisely and accurate measurement of diffusion coefficients is rather difficult. Nevertheless, we see that within experimental error the reciprocal relations seem to hold very well.

Table 16.3 Experimental data on cross-diffusion in molten silicates and verification of Onsager's reciprocal relations [1, 6, 7].

System	D_{11} ($\text{m}^2 \text{s}^{-1}$)	D_{12} ($\text{m}^2 \text{s}^{-1}$)	D_{21} ($\text{m}^2 \text{s}^{-1}$)	D_{22} ($\text{m}^2 \text{s}^{-1}$)	L_{12}/L_{21}	T (K)
CaO–Al ₂ O ₃ –SiO ₂	6.8×10^{-11}	-2.0×10^{-11}	-3.3×10^{-11}	4.1×10^{-11}	1.46 ± 0.44	1723
CaO–Al ₂ O ₃ –SiO ₂	1.0×10^{-10}	-2.8×10^{-11}	-4.2×10^{-11}	7.3×10^{-11}	1.46 ± 0.44	1773
CaO–Al ₂ O ₃ –SiO ₂	1.8×10^{-10}	-4.6×10^{-11}	-6.4×10^{-11}	1.5×10^{-10}	1.29 ± 0.36	1823

Table 16.4 Experimental diffusion coefficients for the toluene–chlorobenzene–bromobenzene system at $T = 30^\circ\text{C}$ and verification of Onsager's reciprocal relations [8].

X_1^*	X_2^*	$D_{11}/10^{-9}$ ($\text{m}^2 \text{s}^{-1}$)	$D_{12}/10^{-9}$ ($\text{m}^2 \text{s}^{-1}$)	$D_{21}/10^{-9}$ ($\text{m}^2 \text{s}^{-1}$)	$D_{22}/10^{-9}$ ($\text{m}^2 \text{s}^{-1}$)	L_{12}/L_{21}
0.25	0.50	1.848	-0.063	-0.052	1.797	1.052
0.26	0.03	1.570	-0.077	-0.012	1.606	0.980
0.70	0.15	2.132	0.051	-0.071	2.062	0.942
0.15	0.70	1.853	0.049	-0.068	1.841	0.915

* X_1 = mole fraction of toluene; X_2 = mole fraction of chlorobenzene.

16.5 Chemical Reactions

In this section we shall look at the meaning of linear phenomenological laws in the context of chemical reactions. In a formalism in which the principle of detailed balance or microscopic reversibility is incorporated through the condition that forward rates of every elementary step balance the corresponding reverse rate, the Onsager reciprocity is implicit. No additional relations can be derived for the reaction rates if it is assumed that at equilibrium each elementary step is balanced by its reverse. Therefore, the main task in this section will be to relate the Onsager coefficients L_{ij} and the experimentally measured reaction rates. In our formalism the Onsager reciprocal relations will be automatically valid.

The entropy production due to chemical reactions is

$$\sigma = \sum_k \frac{A_k}{T} \frac{1}{V} \left(\frac{d\xi_k}{dt} \right) = \sum_k \frac{A_k}{T} v_k \quad (16.5.1)$$

in which we have written v_k for the velocity of the k th reaction. In this case the thermodynamic forces are $F_k = (A_k/T)$ and the flows $J_k = v_k$. In Chapter 9 we have seen that *for a chemical reaction that can be identified as an elementary step*, the velocity v and the affinity A can be related to the forward and reverse reactions through the following relations:

$$v_k = R_{kf} - R_{kr} \quad (16.5.2)$$

$$A_k = RT \ln \left(\frac{R_{kf}}{R_{kr}} \right) \quad (16.5.3)$$

in which R_{kf} and R_{kr} are forward and reverse rates of the k th reaction and R is the gas constant. Using Equation (16.5.3) in Equation (16.5.2), we can write the velocity v_k as

$$v_k = R_{kf} \left(1 - e^{-A_k/RT} \right) \quad (16.5.4)$$

a useful expression for discussing the linear phenomenological laws near thermodynamic equilibrium. It is important to keep in mind that Equation (16.5.4) is valid only for an elementary step. Note that Equation (16.5.3) incorporates the principle of detailed balance or microscopic reversibility according to which the forward and reverse reactions of every elementary step balance each other at equilibrium (which leads to the Onsager reciprocal relations). Also, the limit $A_k \rightarrow \infty$ implies that the velocity is entirely due to the forward reaction.

Equation (16.5.4) *does not* give the reaction velocity v_k as a function of the affinity A_k , because the term R_{kf} has to be specified. There is no general thermodynamic expression relating velocities and affinities. Reaction velocities depend on many nonthermodynamic factors such as the presence of catalysts. (A catalyst does not have any effect on the state of equilibrium; also, because a catalyst changes the forward and reverse rate by the same factor, it does not alter the affinity either.) Close to thermodynamic equilibrium, however, there is a general linear relation between the two quantities. In this context, the general postulate of the linear phenomenological laws takes the form

$$v_k = \sum_j L_{kj} \frac{A_j}{T} \quad (16.5.5)$$

The coefficients L_{kj} can be related to the experimental quantities such as reaction rates, as shown below.

16.5.1 Single Reaction

For simplicity, let us consider a single reaction that is an elementary step. Then Equation (16.5.4) becomes

$$v = R_f(1 - e^{-A/RT}) \quad (16.5.6)$$

At equilibrium $A = 0$. Let us denote the equilibrium value of the forward reaction rate by $R_{f,\text{eq}}$. Away from equilibrium, A has a nonzero value. By ‘close to equilibrium’ we mean that

$$\left| \frac{A}{RT} \right| \ll 1 \quad (16.5.7)$$

When A is small compared to RT and $R_f = R_{f,\text{eq}} + \Delta R_f$, we can expand Equation (16.5.6) to obtain a linear relation between v and A :

$$v = R_{f,\text{eq}} \frac{A}{RT} + \dots \quad (16.5.8)$$

to the leading order by ignoring smaller terms such as products of ΔR_f and A . Comparing Equation (16.5.8) with the phenomenological law $v = LA/T$, we make the identification

$$L = \frac{R_{f,\text{eq}}}{R} = \frac{R_{r,\text{eq}}}{R} \quad (16.5.9)$$

where the last equality follows from the fact that the forward and reverse reaction rates of every elementary step are equal at equilibrium.

16.5.2 Many Reactions

When the system consists of many reacting species and reactions, not all the reactions are independent. Take, for example, the following reactions:



The third reaction is the sum of the first two reactions. Therefore not all three are independent reactions. Thermodynamically this means that the affinity of the third reaction can be written as the sum of the first two. We have seen in Chapter 4 that the affinity of a sum of reactions is the sum of the affinities. Since the phenomenological relations are written in terms of independent thermodynamic forces, only the independent affinities are to be used. Also, *without loss of generality we may consider affinities of elementary steps only because all reactions can be reduced to elementary steps*.

If all the chemical reactions in the system are independent, then, close to equilibrium, each velocity v_k is dependent on only the corresponding affinity and the equilibrium reaction rate, as in Equation (16.5.8). There are no cross-coupling terms. In the general formalism, cross-terms for chemical reactions appear when the total number of reactions is not the same as the number of independent reactions. In this case, some of the affinities can be expressed as linear functions of others. Let us look at an example. For simplicity but without loss of generality, we consider a simple set of unimolecular reactions, all of which are elementary. We denote their corresponding rates R_{kf} and R_{kr} , affinities A_k and velocities v_k as shown:



where the subscripts f and r stand for forward and reverse reaction rates, respectively. Only two out of the three reactions are independent, because the third can be expressed as the sum of the other two. Consequently, we have the relation

$$A_1 + A_2 = A_3 \quad (16.5.14)$$

The entropy production per unit volume due to these reactions is

$$\sigma = v_1 \frac{A_1}{T} + v_2 \frac{A_2}{T} + v_3 \frac{A_3}{T} \quad (16.5.15)$$

Using the relation between the affinities (16.5.14), this expression can be written in terms of two independent affinities A_1 and A_2 :

$$\begin{aligned} \sigma &= (v_1 + v_3) \frac{A_1}{T} + (v_2 + v_3) \frac{A_2}{T} \\ &= v'_1 \frac{A_1}{T} + v'_2 \frac{A_2}{T} > 0 \end{aligned} \quad (16.5.16)$$

where $v'_1 = v_1 + v_3$ and $v'_2 = v_2 + v_3$. In terms of these independent velocities and affinities, the linear phenomenological laws may be written as [9]

$$v'_1 = L_{11} \frac{A_1}{T} + L_{12} \frac{A_2}{T} \quad (16.5.17)$$

$$v'_2 = L_{21} \frac{A_1}{T} + L_{22} \frac{A_2}{T} \quad (16.5.18)$$

The relation between the phenomenological coefficients L_{ik} and the experimentally measured reaction rates can be obtained by using the general relation (16.5.4) between the velocities v_k and the affinities A_k . For example, close to equilibrium, i.e. when $|A_k/RT| \ll 1$, we can write v'_1 as

$$\begin{aligned} v'_1 &= v_1 + v_3 = R_{1f}(1 - e^{-A_1/RT}) + R_{3f}(1 - e^{-A_3/RT}) \\ &\approx R_{1f,eq} \frac{A_1}{RT} + R_{3f,eq} \frac{A_3}{RT} = \left(\frac{R_{1f,eq} + R_{3f,eq}}{R} \right) \frac{A_1}{T} + \frac{R_{3f,eq}}{R} \frac{A_2}{T} \end{aligned} \quad (16.5.19)$$

using the fact that near equilibrium we have $R_{kf} \approx R_{kf,eq}$, the forward reaction rate at equilibrium. Comparing Equation (16.5.19) with Equation (16.5.17), we see that

$$L_{11} = \left(\frac{R_{1f,eq} + R_{3f,eq}}{R} \right) \quad \text{and} \quad L_{12} = \frac{R_{3f,eq}}{R} \quad (16.5.20)$$

Similarly, it is straightforward to show that

$$L_{22} = \left(\frac{R_{2f,eq} + R_{3f,eq}}{R} \right) \quad \text{and} \quad L_{21} = \frac{R_{3f,eq}}{R} \quad (16.5.21)$$

Thus one can relate the phenomenological coefficients L_{ik} to the reaction rates at equilibrium. We see that $L_{12} = L_{21}$. Since the principle of detailed balance or microscopic reversibility is incorporated into the formalism through $R_{3f} = R_{3r} = R_{3f,eq}$, the Onsager reciprocal relations are automatically valid.

16.5.3 Alternative Forms for σ

From the above considerations it is clear that the entropy production can be written in terms of A_2 and A_3 instead of A_1 and A_2 . There is no unique way of writing the entropy production. In whatever way the

independent affinities and velocities are chosen, the corresponding linear phenomenological coefficients can be obtained. The entropy production σ can be written in terms of different sets of independent reaction velocities and affinities:

$$\sigma = \sum_k v_k \frac{A_k}{T} = \sum_k v'_k \frac{A'_k}{T} > 0 \quad (16.5.22)$$

Equations (16.5.15) and (16.5.16) are examples. The number of independent reactions, and therefore the affinities, is constrained by the number of reacting species. In homogeneous closed systems in which the change in the concentrations of all the reacting species is only due to chemical reactions, we may choose the extents of reaction ξ_k to define the state of a system instead of the concentrations n_k . The chemical potentials μ_k are then functions of ξ_k , p and T . However, since an extent of reaction relates the change in at least two reacting species, in a system consisting of r reacting species there are at most $(r - 1)$ independent extents of reaction ξ_k . Thus all of r chemical potentials can be expressed as $\mu_k(\xi_1, \xi_2, \xi_3, \dots, \xi_{r-1}, p, T)$. From this it is clear that, at any given pressure p and temperature T , there are only $(r - 1)$ independent chemical potentials. Since the affinities A_k are linear functions of the chemical potentials, *in a system with r reacting species, there can be at most $(r - 1)$ independent affinities.* (Sometimes this fact is derived using the ‘conservation of mass’ in chemical reactions. Although this may be valid in ordinary chemical reactions, since mass is not conserved in nuclear reactions, the argument is not general. In fact, mass is incidental to chemical reactions whose main consequence is the change in the number of molecules of the various reacting species.)

16.5.4 Linearity in Coupled Reactions

We have seen that the linear phenomenological laws are valid for chemical reactions with affinity A if the condition $|A/RT| \ll 1$ is satisfied. However, if the overall chemical reaction



consists of m intermediates, W_1, W_2, \dots, W_m , one may still be justified in using the linearity even if $|A/RT| \ll 1$ is not valid. To see how this might happen, let us suppose that the overall reaction (16.5.23) goes through the following series of reactions:



The entropy production for this set of $(m + 1)$ reactions is

$$T\sigma = A_1 v_1 + A_2 v_2 + \cdots + A_{m+1} v_{m+1} \quad (16.5.25)$$

If the intermediate components W_k interconvert rapidly, then the reaction velocity of each of these reactions is essentially determined by the rate of the slowest reaction, which is called the **rate-determining step**. Let us assume that the last step $W_m \rightleftharpoons Y$ is the slow rate-determining step. The rate equations for this system are

$$\begin{aligned} \frac{d[X]}{dt} &= -v_1 \\ \frac{d[W_1]}{dt} &= v_1 - v_2 \\ \frac{d[W_2]}{dt} &= v_2 - v_3 \\ &\vdots \\ \frac{d[Y]}{dt} &= v_{m+1} \end{aligned} \quad (16.5.26)$$

Because of the rapid interconversion, we may assume that a steady state is established for $[W_k]$ so that $d[W_k]/dt \approx 0$. (Such an assumption is used, for example, in obtaining the Michaelis–Menten rate law for enzyme kinetics.) This implies

$$v_1 = v_2 = \dots = v_{m+1} = v \quad (16.5.27)$$

Then the entropy production for the system becomes

$$T\sigma = (A_1 + A_2 + \dots + A_{m+1}) v = Av \quad (16.5.28)$$

in which the overall affinity

$$A = A_1 + A_2 + \dots + A_{m+1} \quad (16.5.29)$$

Now if $|A_k/RT| \ll 1$ for each of the $(m + 1)$ reactions, we are still in the region where the linear laws are valid, so from Equation (16.5.8) we have

$$v_1 = R_{1f,eq} \frac{A_1}{RT}, \quad v_2 = R_{2f,eq} \frac{A_2}{RT}, \dots, v_{m+1} = R_{(m+1)f,eq} \frac{A_{m+1}}{RT} \quad (16.5.30)$$

in which $R_{if,eq}$ is the forward equilibrium reaction rate of reaction (1) in the scheme (16.5.24), etc.

In the above case, even if

$$|A| = \left| \sum_{k=1}^{m+1} A_k \right| > RT$$

the linear phenomenological laws will be valid. A simple calculation (Exercise 16.9) using Equations (16.5.27), (16.5.28) and (16.5.30) shows that

$$v = \frac{R_{\text{eff}}}{RT} A \quad (16.5.31)$$

in which the ‘effective reaction rate’ R_{eff} is given by

$$\frac{1}{R_{\text{eff}}} = \frac{1}{R_{1f,eq}} + \frac{1}{R_{2f,eq}} + \frac{1}{R_{3f,eq}} + \dots + \frac{1}{R_{(m+1)f,eq}} \quad (16.5.32)$$

Since the overall reaction is not an elementary step but a result of many elementary steps, the relation $v = R_{\text{eff}}(1 - e^{-A/RT})$ is not valid.

Though we considered a coupled set of unimolecular reactions (16.5.24) to obtain Equation (16.5.31), the result is more generally valid. Thus, *the linear phenomenological law is valid for an overall chemical reaction if $|A/RT| \ll 1$ for every elementary step in the reaction, and if concentrations of all the reaction intermediates may be assumed to be in a steady state.*

16.6 Heat Conduction in Anisotropic Solids

In an anisotropic solid, the flow of heat \mathbf{J}_q may not be in the direction of the temperature gradient; a temperature gradient in one direction can cause the heat to flow in a different direction. The entropy production rate is

$$\sigma = \sum_{i=1}^3 \mathbf{J}_{qi} \cdot \frac{\partial}{\partial x_i} \left(\frac{1}{T} \right) \quad (16.6.1)$$

in which x_i are the Cartesian coordinates. The phenomenological laws for this system are

$$\mathbf{J}_{qi} = \sum_k L_{ik} \frac{\partial}{\partial x_k} \left(\frac{1}{T} \right) = \sum_k \left(\frac{-L_{ik}}{T^2} \right) \frac{\partial T}{\partial x_k} \quad (16.6.2)$$

For anisotropic solids the heat conductivity κ is a tensor of the second rank. The empirical Fourier law of heat conduction is then written as

$$\mathbf{J}_{qi} = - \sum_k \kappa_{ik} \frac{\partial T}{\partial x_k} \quad (16.6.3)$$

Comparison of Equations (16.6.2) and (16.6.3) leads to

$$L_{ik} = T^2 \kappa_{ik} \quad (16.6.4)$$

Reciprocal relations $L_{ik} = L_{ki}$ then imply that

$$\kappa_{ik} = \kappa_{ki} \quad (16.6.5)$$

i.e. the heat conductivity is a symmetric tensor. However, for many solids, if the symmetry of the crystal structure itself implies that $\kappa_{ik} = \kappa_{ki}$, experimental verification of this equality would not confirm the reciprocal relations. On the other hand, solids with trigonal (C_3 , C_{3i}), tetragonal (C_4 , S_4 , C_{4h}) and hexagonal (C_6 , C_{3h} , C_{6h}) crystal symmetries imply that

$$\kappa_{12} = -\kappa_{21} \quad (16.6.6)$$

If the reciprocal relations are valid, then

$$\kappa_{12} = \kappa_{21} = 0 \quad (16.6.7)$$

Equation (16.6.6) implies that a temperature gradient in the x direction causes heat to flow in the positive y direction but a gradient in the y direction will cause heat to flow in the negative x direction. Onsager's reciprocal relations imply that this is not possible. One method of experimental verification of this relation is due to Voigt and Curie (Figure 16.3). Another method may be found in an article by Miller [1]. For crystals of apatite (calcium phosphate) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) it was found that $(\kappa_{12}/\kappa_{11}) < 0.0005$ [1], in accord with the reciprocal relations.

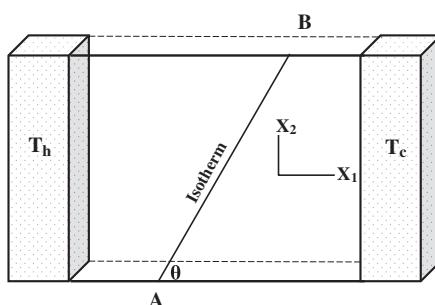


Figure 16.3 The method of Curie and Voigt to verify the reciprocal relations for anisotropic heat conduction. An anisotropic solid whose crystal symmetry implies $\kappa_{12} = -\kappa_{21}$ is placed in contact with two heat reservoirs of temperature T_h and T_c . If the reciprocal relations are valid then $\kappa_{12} = \kappa_{21} = 0$. If this is true, the isotherms should be perpendicular to the direction x_1 , i.e. θ should be 90° .

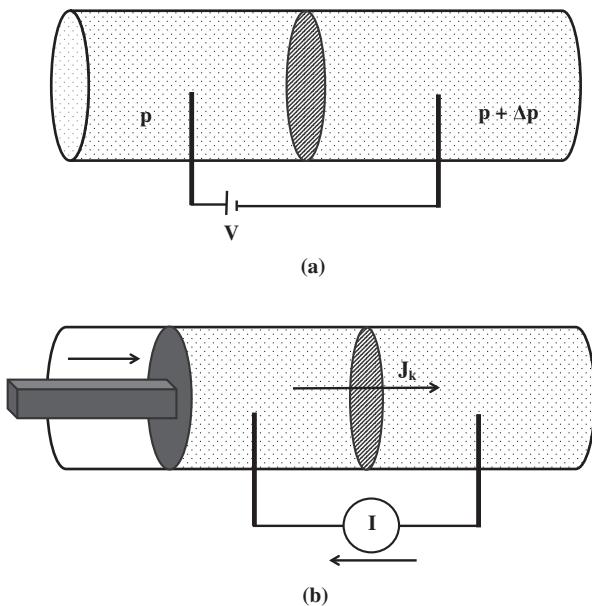


Figure 16.4 Electrokinetic phenomena. Two chambers containing electrolytes are separated by a porous wall or capillary. (a) An applied potential V generates a pressure difference Δp , called the electro-osmotic pressure. (b) If the fluid is made to flow from one chamber to another through an applied pressure gradient, it generates an electrical current I , called the streaming current.

16.7 Electrokinetic Phenomena and the Saxon Relations

Electrokinetic phenomena are due to the coupling between the electrical current and matter flow. Consider two chambers, 1 and 2, containing electrolytes and separated by a porous wall. If a voltage V is applied between the two chambers (Figure 16.4), a current will flow until a pressure difference Δp is established at the steady state. This pressure difference is called the *electro-osmotic pressure*. Conversely, if a fluid flow J from one chamber to another is achieved by a piston, an electric current I , called the *streaming current*, flows through the electrodes. As before, the thermodynamic description of these effects begins with the expression for the entropy production under the conditions specified above. In this case we essentially have a discontinuous system in which there are no gradients but differences in chemical potentials between the two chambers. For discontinuous systems the entropy production per unit volume σ is replaced by the total entropy production d_iS/dt . Furthermore, the entropy produced by the flow from chamber 1 to chamber 2 may be formally thought of as a chemical reaction for which the difference in the electrochemical potential becomes the affinity. Thus we have

$$\frac{d_iS}{dt} = \sum_k \frac{\tilde{A}_k}{T} \frac{d\xi_k}{dt} \quad (16.7.1)$$

in which

$$\tilde{A}_k = (\mu_k^1 + z_k F \varphi^1) - (\mu_k^2 + z_k F \varphi^2) \quad (16.7.2)$$

$$d\xi_k = -dn_k^1 = dn_k^2 \quad (16.7.3)$$

In these equations, the superscripts refer to the two chambers, where z_k is the ion number of the component k , F is the Faraday constant and ϕ is the electrical potential. For a relatively small difference in the pressure between the two chambers, since $(\partial \mu_k / \partial p) = v_k$, the partial molar volume, we may write

$$(\mu_k^1 - \mu_k^2) = v_k \Delta p \quad (16.7.4)$$

Equation (16.7.1) may now be written as

$$\frac{d_i S}{dt} = \frac{1}{T} \sum_k \left(-v_k \frac{dn_k^1}{dt} \right) \Delta p + \frac{1}{T} \sum_k (-I_k) \Delta \phi \quad (16.7.5)$$

in which $\Delta \phi = \phi^1 - \phi^2$ and $I_k = z_k F d n_k^1 / dt$, the electric current due to the flow of component k . Combining all the matter flow terms and the ion flow terms, Equation (16.7.5) can now be written in the compact form

$$\frac{d_i S}{dt} = \frac{J \Delta p}{T} + \frac{I \Delta \phi}{T} \quad (16.7.6)$$

where

$$J = - \sum_k v_k \frac{dn_k^1}{dt} \text{ is the 'volume flow'} \quad (16.7.7)$$

$$I = - \sum_k I_k \text{ is the electric current} \quad (16.7.8)$$

The phenomenological equations that follow from Equation (16.7.6) are

$$I = L_{11} \frac{\Delta \phi}{T} + L_{12} \frac{\Delta p}{T} \quad (16.7.9)$$

$$J = L_{21} \frac{\Delta \phi}{T} + L_{22} \frac{\Delta p}{T} \quad (16.7.10)$$

The reciprocal relations are

$$L_{12} = L_{21} \quad (16.7.11)$$

Experimentally, the following quantities can be measured:

- The streaming potential

$$\left(\frac{\Delta \phi}{\Delta p} \right)_{I=0} = - \frac{L_{12}}{L_{11}} \quad (16.7.12)$$

- Electro-osmosis

$$\left(\frac{J}{I} \right)_{\Delta p=0} = \frac{L_{21}}{L_{11}} \quad (16.7.13)$$

- Electro-osmotic pressure

$$\left(\frac{\Delta p}{\Delta \phi} \right)_{J=0} = - \frac{L_{21}}{L_{22}} \quad (16.7.14)$$

- Streaming current

$$\left(\frac{I}{J} \right)_{\Delta \phi=0} = \frac{L_{12}}{L_{22}} \quad (16.7.15)$$

As a consequence of the reciprocal relations $L_{12} = L_{21}$, we see from Equations (16.7.12) to (16.7.15) that

$$\left(\frac{\Delta\phi}{\Delta p} \right)_{I=0} = - \left(\frac{J}{I} \right)_{\Delta p=0} \quad (16.7.16)$$

$$\left(\frac{\Delta p}{\Delta\phi} \right)_{J=0} = - \left(\frac{I}{J} \right)_{\Delta\phi=0} \quad (16.7.17)$$

These two relations, called the **Saxen relations**, were obtained originally by kinetic considerations for particular systems, but by virtue of the formalism of nonequilibrium thermodynamics we see their general validity.

16.8 Thermal Diffusion

The interaction between heat and matter flows produces two effects, the **Soret effect** and the **Dufour effect**. In the Soret effect, heat flow drives a flow of matter. In the Dufour effect, concentration gradients drive a heat flow. The reciprocal relations in this context can be obtained by writing the entropy production due to diffusion and heat flow:

$$\begin{aligned} \sigma &= \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^w \mathbf{J}_k \cdot \nabla \left(\frac{\mu_k}{T} \right) \\ &= \left(\mathbf{J}_u - \sum_{k=1}^w \mathbf{J}_k \mu_k \right) \cdot \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^w \mathbf{J}_k \cdot \frac{1}{T} \nabla \mu_k \end{aligned} \quad (16.8.1)$$

This expression, however, does not quite separate the thermal and concentration gradients as we would like, because the term $\nabla \mu_k$ contains the gradient of T (due to the fact that μ_k is a function of T , n_k and p). The explicit form of $\nabla \mu_k$ can be written using the relation

$$d\mu_k = (d\mu_k)_{p,T} + \left(\frac{\partial \mu_k}{\partial T} \right)_{n_k,p} dT + \left(\frac{\partial \mu_k}{\partial p} \right)_{n_k,T} dp \quad (16.8.2)$$

in which

$$(d\mu_k)_{p,T} = \left(\frac{\partial \mu_k}{\partial n} \right)_{p,T} dn_k$$

is a variation due to concentration only.

In the following, g and h are Gibbs energy and enthalpy densities corresponding to G and H respectively. In the above, the term

$$\left(\frac{\partial \mu_k}{\partial T} \right)_{n_k,p} = \frac{\partial}{\partial T} \left(\frac{\partial g}{\partial n_k} \right)_{p,T} = \left(\frac{\partial}{\partial n_k} \left(\frac{\partial g}{\partial T} \right) \right)_{p,T} = - \left(\frac{\partial s}{\partial n_k} \right)_{p,T}$$

Thus we see that Equation (16.8.2) can be written as

$$d\mu_k = (d\mu_k)_{p,T} - s_k dT + \left(\frac{\partial \mu_k}{\partial p} \right)_{n_k,T} dp \quad (16.8.3)$$

in which the partial molar entropy $s_k = (\partial s / \partial n_k)_{p,T}$ (Section 5.5). In this section we will consider systems in mechanical equilibrium for which $dp = 0$. Since the variation of any quantity Y with position can be written as $dY = (\nabla Y) \bullet dr$, it follows that using Equation (16.8.3) we can write

$$\begin{aligned}\nabla \mu_k &= (\nabla \mu_k)_{p,T} - s_k \nabla T \\ &= (\nabla \mu_k)_{p,T} + s_k T^2 \nabla \frac{1}{T}\end{aligned}\quad (16.8.4)$$

Here we have used the fact that $dp = 0$ because the system is assumed to be in mechanical equilibrium. Substituting Equation (16.8.4) into Equation (16.8.1) we obtain

$$\sigma = \left(\mathbf{J}_u - \sum_{k=1}^w \mathbf{J}_k (\mu_k + Ts_k) \right) \bullet \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^w \mathbf{J}_k \bullet \frac{1}{T} (\nabla \mu_k)_{p,T} \quad (16.8.5)$$

Now, using the relation $g = h - Ts$, it is easily seen that $\mu_k + Ts_k = h_k$, where $h_k = (\partial h / \partial n_k)_{p,T}$ is the partial molar enthalpy. With this identification, a heat current that takes into account matter current can be defined as

$$\mathbf{J}_q \equiv \mathbf{J}_u - \sum_{k=1}^w h_k \mathbf{J}_k \quad (16.8.6)$$

In a closed system under constant pressure, the change in enthalpy due to a change in composition is equal to the heat exchanged with the exterior. In an open system of a fixed volume, the heat exchanged is the difference between the change in energy and the change in enthalpy due to the matter flow. The vector \mathbf{J}_q defined in Equation (16.8.6) is called the **reduced heat flow**. In terms of \mathbf{J}_q the entropy production may be written as

$$\sigma = \mathbf{J}_q \bullet \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^w \mathbf{J}_k \bullet \frac{(\nabla \mu_k)_{T,p}}{T} \quad (16.8.7)$$

For simplicity, we shall consider a two-component system so that $w = 2$. As we noted in Section 16.4 on diffusion, because of the Gibbs–Duhem relation at constant p and T , the chemical potentials are not independent. From Equation (16.4.5) we have the following relation:

$$n_1 (\nabla \mu_1)_{p,T} + n_2 (\nabla \mu_2)_{p,T} = 0 \quad (16.8.8)$$

In addition, for no volume flow, we have, from Equation (16.4.6), the condition

$$\mathbf{J}_1 v_1 + \mathbf{J}_2 v_2 = 0 \quad (16.8.9)$$

As when obtaining Equation (16.4.8), relations (16.8.8) and (16.8.9) can be used in Equation (16.8.7) to give

$$\sigma = \mathbf{J}_q \bullet \nabla \left(\frac{1}{T} \right) - \frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) \mathbf{J}_1 \bullet (\nabla \mu_1)_{p,T} \quad (16.8.10)$$

Thus, in place of two matter flows, \mathbf{J}_1 and \mathbf{J}_2 , we have only independent matter flow \mathbf{J}_1 . We can now write the phenomenological laws for the flows of heat and matter:

$$\mathbf{J}_q = L_{qq} \nabla \left(\frac{1}{T} \right) - L_{q1} \frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) (\nabla \mu_1)_{p,T} \quad (16.8.11)$$

$$\mathbf{J}_1 = L_{1q} \nabla \left(\frac{1}{T} \right) - L_{11} \frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) (\nabla \mu_1)_{p,T} \quad (16.8.12)$$

To relate the terms in this expression to the Fourier law of heat conduction and Fick's law of diffusion, we write the gradients as $\nabla\mu_1 = (\partial\mu_1/\partial n_1)\nabla n_1$ and $\nabla(1/T) = -(1/T^2)\nabla T$, so the two flows become

$$\mathbf{J}_q = -\frac{L_{qq}}{T^2}\nabla T - L_{q1}\frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2}\right) \frac{\partial\mu_1}{\partial n_1} \nabla n_1 \quad (16.8.13)$$

$$\mathbf{J}_1 = -\frac{L_{1q}}{T^2}\nabla T - L_{11}\frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2}\right) \frac{\partial\mu_1}{\partial n_1} \nabla n_1 \quad (16.8.14)$$

We can now identify the diffusion coefficient and the heat conductivity:

$$D_1 = L_{11}\frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2}\right) \frac{\partial\mu_1}{\partial n_1}, \quad \kappa = \frac{L_{qq}}{T^2} \quad (16.8.15)$$

and we have the reciprocal relations

$$L_{q1} = L_{1q} \quad (16.8.16)$$

The cross-flow $-(L_{1q}/T^2)\nabla T$ is usually written as $-n_1 D_T \nabla T$, in which D_T is the **coefficient of thermal diffusion**, so that the flow of matter is proportional to n_1 . The ratio of the thermal diffusion coefficient to the ordinary diffusion coefficient is the **Soret coefficient**:

$$s_T = \frac{D_T}{D_1} = \frac{L_{1q}}{D_1 T^2 n_1} \quad (16.8.17)$$

In a closed system with a temperature gradient (Figure 16.5) a concentration gradient is set up due to the heat flow. The stationary state concentration gradient can be obtained by setting $\mathbf{J}_1 = 0$:

$$\mathbf{J}_1 = -\frac{L_{1q}}{T^2}\nabla T - D_1 \nabla n_1 = 0 \quad (16.8.18)$$

Since $L_{1q}/T^2 = n_1 D_T$, the ratio of the two gradients is

$$\frac{\nabla n_1}{\nabla T} = -\frac{n_1 D_T}{D_1} = -n_1 s_T \quad (16.8.19)$$

The Soret coefficient has the dimensions of T^{-1} . It is generally small, in the range 10^{-2} to 10^{-3} K^{-1} for electrolytes, nonelectrolytes and gases [10], but it might become larger in polymer solutions. Thermal diffusion has been utilized to separate isotopes [11].

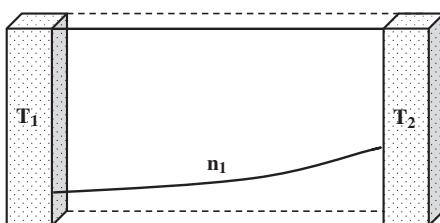


Figure 16.5 Thermal diffusion: a temperature gradient and the consequent flow of heat causes a concentration gradient.

The heat current carried by a flow of matter is identified by the **Dufour coefficient** D_d . Since the heat carried by the matter flow is proportional to the concentration n_1 , the Dufour coefficient is defined by

$$n_1 D_d = L_{q1} \frac{1}{T} \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) \frac{\partial \mu_1}{\partial n_1} \quad (16.8.20)$$

Since $L_{1q}/T^2 = n_1 D_T$, the Onsager reciprocal relations $L_{1q} = L_{q1}$ predict the relation

$$\frac{D_d}{D_T} = T \left(1 + \frac{v_1 n_1}{v_2 n_2} \right) \frac{\partial \mu_1}{\partial n_1} \quad (16.8.21)$$

for the ratio of the Dufour and thermal diffusion coefficients. This prediction has been confirmed experimentally.

Thus nonequilibrium thermodynamics gives a unified theory of irreversible processes. Onsager reciprocal relations are general, valid for all systems in which linear phenomenological laws apply.

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Exercises

- 16.1** For a positive definite 2×2 matrix, show that Equation (16.1.9) must be valid.
- 16.2** Give examples of the equality (16.2.11) hypothesized by Onsager. Give examples of situations in which it is not valid.
- 16.3** Estimate the cross-diffusion current of one component due to a gradient of another from the data given in Table 16.2 for reasonable gradients.
- 16.4** Obtain Equation (16.4.7) from Equations (16.4.1) and (16.4.5) and generalize it to many components.
- 16.5** For diffusion in a three-component system, show that the entropy production is

$$\sigma = \mathbf{F}_1 \cdot \mathbf{J}_1 + \mathbf{F}_2 \cdot \mathbf{J}_2$$

in which the thermodynamic forces \mathbf{F}_1 and \mathbf{F}_2 are

$$\mathbf{F}_1 = -\frac{1}{T} \left[\nabla \mu_1 + \frac{n_1 v_1}{n_3 v_3} \nabla \mu_1 + \frac{n_2 v_1}{n_3 v_3} \nabla \mu_2 \right]$$

and

$$\mathbf{F}_2 = -\frac{1}{T} \left[\nabla \mu_2 + \frac{n_2 v_2}{n_3 v_3} \nabla \mu_2 + \frac{n_1 v_2}{n_3 v_3} \nabla \mu_1 \right]$$

- 16.6** For diffusion in a three-component system, show that the phenomenological coefficients are given by Equations (16.4.24) to (16.4.27). (You can obtain this using *Mathematica* or *Maple*.)
- 16.7** For diffusion in a three-component system, write Equations (16.4.17) to (16.4.27) in matrix notation.
- 16.8** For the chemical reaction $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$, specify the conditions in which the linear phenomenological laws may be used.
- 16.9** Using Equations (16.5.27), (16.5.28) and (16.5.30) show that a linear phenomenological relation $v = (R_{\text{eff}}/RT)A$ (Equation (16.5.31)) can be obtained in which the “effective reaction rate” R_{eff} is given by

$$\frac{1}{R_{\text{eff}}} = \frac{1}{R_{1f,\text{eq}}} + \frac{1}{R_{2f,\text{eq}}} + \frac{1}{R_{3f,\text{eq}}} + \cdots + \frac{1}{R_{(m+1)f,\text{eq}}}$$

17

Nonequilibrium Stationary States and Their Stability: Linear Regime

17.1 Stationary States under Nonequilibrium Conditions

A system can be maintained in a nonequilibrium state through a flow of energy and matter. In the previous chapter, we have seen some examples of nonequilibrium systems in the linear regime. In this section, we will study some of these systems in more detail to understand the nature of the nonequilibrium states. In general, a system that is not in thermodynamic equilibrium need not be in a stationary (time-independent) state. Indeed, as we shall see in Chapters 18 and 19, systems that are far from equilibrium, for which the linear phenomenological laws are not valid, can exhibit very complex behavior, such as concentration oscillations, propagating waves and even chaos. In the linear regime, however, all systems evolve to stationary states in which there is constant entropy production. Let us consider some simple examples to understand the entropy production and entropy flow in nonequilibrium stationary states in the linear regime.

17.1.1 Thermal Gradients

Let us consider a system of length L in contact with a hot thermal reservoir at a temperature T_h at one end and a cold thermal reservoir at temperature T_c at the other (Figure 17.1). In Section 3.5, and in more detail in Chapter 16, we discussed the entropy production due to heat flow but we did not consider entropy balance in detail. Here we assume that the conduction of heat is the only irreversible process. For this system, using Table 15.1 for the flows and forces, we see that the entropy production per unit volume is

$$\sigma = \mathbf{J}_q \cdot \nabla \frac{1}{T} \quad (17.1.1)$$

If we assume that the temperature gradient is only in the x direction, σ per unit length is given by

$$\sigma(x) = J_{qx} \frac{\partial}{\partial x} \frac{1}{T(x)} = -J_{qx} \frac{1}{T^2} \frac{\partial T(x)}{\partial x} \quad (17.1.2)$$

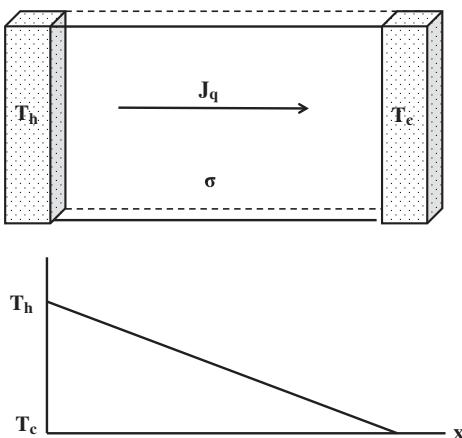


Figure 17.1 A simple thermal gradient maintained by a constant flow of heat. In the stationary state, the entropy current $J_{s,\text{out}} = d_i S/dt + J_{s,\text{in}}$. The stationary state can be obtained either as a solution of the Fourier equation for heat conduction or by using the theorem of minimum entropy production. Both lead to a temperature $T(x)$ that is a linear function of the position x .

The total entropy production

$$\frac{d_i S}{dt} = \int_0^L \sigma(x) dx = \int_0^L J_{qx} \left(\frac{\partial}{\partial x} \frac{1}{T} \right) dx \quad (17.1.3)$$

Such a system will reach a state with stationary temperature distribution and a uniform heat flow \mathbf{J}_q . (A stationary temperature $T(x)$ implies that the heat flow is uniform; otherwise there will be an accumulation or depletion of heat, resulting in a time-dependent temperature.) The evolution of the temperature distribution can be obtained explicitly by using the Fourier law of heat conduction:

$$C \frac{\partial T}{\partial t} = \nabla \cdot \mathbf{J}_q, \quad \mathbf{J}_q = -\kappa \nabla T \quad (17.1.4)$$

in which C is the heat capacity per unit volume and κ is the coefficient of heat conductivity. The first of these equations expresses the conservation of energy when the change in energy is entirely due to heat flow. (For Fourier, who supported the caloric theory, this equation expressed the conservation of caloric.) For a one-dimensional system, these two equations can be combined to obtain

$$C \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} \quad (17.1.5)$$

It is easy to see that the stationary state, $\partial T/\partial t = 0$, is one in which $T(x)$ is a linear function of x (Figure 17.1) and $\mathbf{J}_q = \text{constant}$. A stationary state also implies that all other thermodynamic quantities such as the total entropy S of the system are constant:

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} = 0 \quad (17.1.6)$$

The total entropy can be constant only when the entropy flowing out of the system is equal to the entropy entering the system plus the entropy produced in the system. This can be seen explicitly by evaluating the integral (17.1.3) (in which J_q is a constant):

$$\frac{d_i S}{dt} = \int_0^L J_q \left(\frac{\partial}{\partial x} \frac{1}{T} \right) dx = \left. \frac{J_q}{T} \right|_0^L = \frac{J_q}{T_c} - \frac{J_q}{T_h} > 0 \quad (17.1.7)$$

We can now identify (J_q/T_h) as the entropy flowing into the system, $J_{s,in}$, and (J_q/T_c) as the entropy flowing out of the system, $J_{s,out}$. The entropy exchanged with the exterior is $d_e S/dt = [(J_q/T_h) - (J_q/T_c)]$. Note that the positivity of the entropy production requires that J_q be positive. Thus we have the entropy balance

$$\frac{d_i S}{dt} + (J_{s,in} - J_{s,out}) = \frac{d_i S}{dt} + \frac{d_e S}{dt} = 0 \quad (17.1.8)$$

Since $d_i S/dt > 0$, the entropy exchanged with the exterior is $d_e S/dt = (J_{s,in} - J_{s,out}) < 0$. The nonequilibrium state is maintained through a net outflow of entropy into the outside world; the system discards the entropy produced by the irreversible processes.

17.1.2 Open Chemical Systems

In an open chemical system that exchanges matter and energy with the exterior, we can identify the energy and entropy flows associated with the exchange of matter and energy. Using the kinetic equations, we can obtain the stationary state. As an example, let us consider a chemical system undergoing a monomolecular reaction such as isomerization:



The associated entropy production per unit volume is

$$\sigma = \frac{A_1}{T} v_1 + \frac{A_2}{T} v_2 > 0 \quad (17.1.10)$$

in which A_k and v_k ($k = 1, 2$) are the affinities and velocities of the two reactions respectively. As we discussed in Section 9.5, if R_{kf} is the forward reaction rate and R_{kr} is the reverse reaction rate, then

$$v_k = R_{kf} - R_{kr} \quad \text{and} \quad A_k = RT \ln \left(\frac{R_{kf}}{R_{kr}} \right) \quad (17.1.11)$$

We shall assume that the system is well mixed to maintain homogeneous concentrations and temperature. As illustrated in Figure 17.2, this system is in contact with the reservoir with chemical potentials μ_A and μ_B , and the heat of reaction is compensated by a heat flow that keeps the system at a constant temperature.

In a stationary state, the total entropy of the system remains constant, i.e.

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} = 0 \quad \text{where} \quad \frac{d_i S}{dt} = \int_V \sigma dV > 0 \quad (17.1.12)$$

which means that the entropy exchange with the exterior must be negative:

$$\frac{d_e S}{dt} = -\frac{d_i S}{dt} < 0 \quad (17.1.13)$$

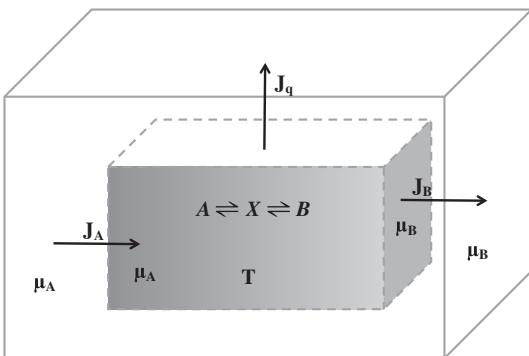


Figure 17.2 An open chemical system in which the chemical potentials μ_A and μ_B are maintained at a given nonequilibrium value by an inflow of component A and an outflow of component B. In this system the concentration of X is maintained at a nonequilibrium value. The system is also maintained at a constant temperature by removal of the heat of reaction.

We can obtain a more explicit expression for the entropy flow $d_e S/dt$ by integrating the entropy balance equation $\partial s/\partial t = -\nabla \cdot \mathbf{J}_s + \sigma$ over the volume of the system:

$$\frac{\partial}{\partial t} \int_V s dV = - \int_V \nabla \cdot \mathbf{J}_s dV + \int_V \sigma dV$$

We can now identify the first term on the right-handside of the above equation as $d_e S/dt$. In Section 15.5 (Equation (15.5.7)) we have seen that the entropy current \mathbf{J}_s is given by

$$\mathbf{J}_s = \frac{\mathbf{J}_u}{T} - \sum_k \frac{\mu_k \mathbf{J}_k}{T} \quad (17.1.14)$$

in which \mathbf{J}_u is the energy flow. Now using the Gauss divergence theorem we can write

$$\frac{d_e S}{dt} = - \oint \mathbf{J}_s \cdot d\mathbf{a} = - \frac{1}{T} \oint \mathbf{J}_u \cdot d\mathbf{a} + \frac{\mu_A}{T} \oint \mathbf{J}_A \cdot d\mathbf{a} + \frac{\mu_B}{T} \oint \mathbf{J}_B \cdot d\mathbf{a} \quad (17.1.15)$$

in which the integrals indicate integration over the surface enclosing the system.

From Equation (15.5.9) the entropy current can also be written as $\mathbf{J}_s = \mathbf{J}_q/T + \sum_k S_k \mathbf{J}_k$, in which the partial molar entropy is $S_k = (\partial s/\partial n_k)_T$ and \mathbf{J}_q is the heat flow. Using the expression for the entropy current, $d_e S/dt$ can be written as¹

$$\frac{d_e S}{dt} = - \frac{1}{T} \oint \mathbf{J}_q \cdot d\mathbf{a} + \oint S_A \mathbf{J}_A \cdot d\mathbf{a} + \oint S_B \mathbf{J}_B \cdot d\mathbf{a} < 0 \quad (17.1.16)$$

This means that heat and chemical species flowing out of the system must carry more entropy than the species entering the system. If the reaction is exothermic, there is a net heat flow out of the system. If the enthalpy of reaction is very small, then the entropy of the species flowing out of the system must be larger than the entropy of the species flowing into the system.

¹Note that the units of S_A and S_B are entropy mol⁻¹.

The stationary value of $[X]$ is easily obtained from the kinetic equations:

$$\begin{aligned}\frac{d[X]}{dt} &= v_1 - v_2 = (R_{1f} - R_{1r}) - (R_{2f} - R_{2r}) \\ &= k_{1f}[A] - k_{1r}[X] - k_{2f}[X] + k_{2r}[B]\end{aligned}\quad (17.1.17)$$

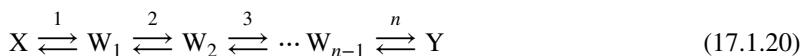
Though it is more common to write the kinetic equations (17.1.17) in terms of concentrations, writing them in terms of velocities is more general – for it does not presume a rate law – and more convenient for formulating the thermodynamics of chemical reactions. The stationary state solution, $d[X]/dt = 0$, for (17.1.17) is simply

$$v_1 = v_2 \quad (17.1.18)$$

or

$$[X] = \frac{k_{1f}[A] + k_{2r}[B]}{k_{1r} + k_{2f}} \quad (17.1.19)$$

If we have a series of coupled reactions:



with an inflow of M and an outflow of N , the above result for the steady state can be generalized to (Exercise 17.4)

$$v_1 = v_2 = \cdots = v_n \quad (17.1.21)$$

in which the v_k are velocities of the indicated reactions.

17.1.3 Entropy Production in Electrical Circuit Elements

The irreversible conversion of electrical energy into heat in electrical circuit elements, such as resistors, capacitors and inductances, also leads to entropy production. The thermodynamic formalism of circuit elements can be developed by considering the changes in the energies associated with them. Section 10.1 showed that in the presence of a field we have

$$dU = T dS - p dV + \sum_k \mu_k dN_k + \sum_k F z_k \phi_k dN_k \quad (17.1.22)$$

in which F is the Faraday constant and z_k the ion number; $F z_k dN_k$ represents the amount of charge transferred, dQ . If this charge is transferred from a potential ϕ_1 to a potential ϕ_2 by an irreversible process within a system, the entropy production is

$$\begin{aligned}\frac{d_i S}{dt} &= \frac{1}{T} \sum_k \mu_k \frac{dN_k}{dt} - \frac{(\phi_2 - \phi_1)}{T} \sum_k F z_k \frac{dN_k}{dt} \\ &= \frac{1}{T} \sum_k A_k v_k - \frac{(\phi_2 - \phi_1)}{T} \frac{dQ}{dt}\end{aligned}\quad (17.1.23)$$

The first term is the entropy production due to chemical reactions, which can be dropped when considering only electrical circuit elements. For a resistor and a capacitor, $(\phi_1 - \phi_2)$ in the second term may be identified as the voltage V across the element and dQ/dt as the electric current I . If R is the resistance, according to Ohm's law, the voltage across the resistor $V_R = (\phi_1 - \phi_2) = IR$. The entropy production is

$$\frac{d_i S}{dt} = \frac{V_R I}{T} = \frac{RI^2}{T} > 0 \quad (17.1.24)$$

In this expression RI^2 is the well-known ohmic heat produced per unit time by a current passing through a resistor. The entropy production is simply the rate of ohmic heat generation divided by the temperature.

For a capacitor with capacitance C , the voltage decreases by dV_C with the transfer of charge dQ is given by $dV_C = -dQ/C$. The entropy production is therefore

$$\begin{aligned}\frac{d_iS}{dt} &= \frac{V_C I}{T} = \frac{V_C}{T} \frac{dQ}{dt} = -\frac{C}{T} V_C \frac{dV_C}{dt} \\ &= -\frac{1}{T} \frac{d}{dt} \left(\frac{CV_C^2}{2} \right) = -\frac{1}{T} \frac{d}{dt} \left(\frac{Q^2}{2C} \right) > 0\end{aligned}\quad (17.1.25)$$

where the term $CV_C^2/2 = Q^2/2C$ is the electrostatic energy stored in a capacitor. The entropy production is the rate of loss of this energy divided by its temperature. An ideal capacitor, once charged, will keep its charge indefinitely. Within such an ideal capacitor there is no dissipation of energy or entropy production. However, all real capacitors will eventually lose their charge and reach equilibrium; Equation (17.1.25) corresponds to the entropy production due to this irreversible process. (The internal discharging of a capacitor is the reaction $e^- + M^+ \rightarrow M$, in which M are the atoms that carry the charge. Note also that the flow of charge into a capacitor by the application of an external voltage corresponds to d_eS .)

The entropy production due to an inductance can be written in a similar manner, by noting that the energy stored in an inductance L carrying current I is equal to $LI^2/2$ and the voltage across it is $V_L = -L dI/dt$ (Exercise 17.5). This energy is stored in the magnetic field. The entropy production associated with the dissipation of this energy is

$$\frac{d_iS}{dt} = -\frac{1}{T} \frac{d}{dt} \left(\frac{LI^2}{2} \right) = -\frac{LI}{T} \frac{dI}{dt} = \frac{V_L I}{T} > 0 \quad (17.1.26)$$

As in the case of an ideal capacitor, in an ideal inductance there is no loss of energy; a current once started will continue to exist indefinitely, as if in a perfect superconductor. In real inductances, however, the current decays with time. The entropy production for this irreversible process is given by Equation (17.1.26).

The entropy production in circuit elements (Equations (17.1.24) to (17.1.26)) is in the form of a product of a thermodynamic force and a flow. In each case we can write the following linear phenomenological law relating the flows and the forces:

$$I = L_R \frac{V_R}{T} \quad (17.1.27)$$

$$I = L_C \frac{V_C}{T} \quad (17.1.28)$$

$$I = L_L \frac{V_L}{T} \quad (17.1.29)$$

in which L_R , L_C and L_L are linear phenomenological coefficients. In the case of the resistor, we identify (L_R/T) with the resistance $(1/R)$, in accordance with Ohm's law. For the capacitor we may think of an internal resistance $R_C = (T/L_C)$ that represents the slow dissipation of the charge. Equation (17.1.28) may be represented by an equivalent circuit (Figure 17.3). By replacing I with dQ/dt in Equation (17.1.28) we obtain a differential equation for the decay of the charge in the capacitor. Similarly, for the inductance, we identify the internal resistance by $R_L = (T/L_L)$. Equation (17.1.29) represents the irreversible decay of current in an inductance. In all three cases the entropy production is equal to the product of the voltage and the current divided by the temperature.

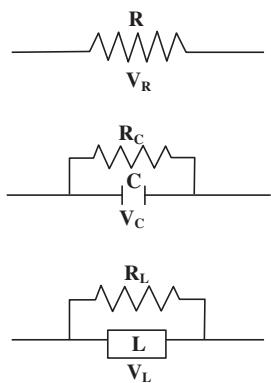


Figure 17.3 Elementary circuit elements, such as a resistor R , a capacitor C and an inductance L , also dissipate energy and produce entropy. In the thermodynamic formalism there are no ideal circuit elements with no dissipation of energy. Linear phenomenological laws give expressions for the rate of entropy production and dissipation of energy.

17.2 The Theorem of Minimum Entropy Production

In the previous section we have seen some examples of nonequilibrium stationary states in which one or more thermodynamic forces were maintained at a nonzero value. In the case of heat conduction, using Fourier's law of heat conduction (17.1.5), we found that the stationary state corresponded to a constant heat flow. In an open chemical system (17.1.9) in which the concentrations of A and B were maintained constant, using the kinetic equation (17.1.17) we found that in the stationary state the velocities of the two reactions were equal. This result could be extended to the case of many intermediates (17.1.20), in which case all the velocities of the reactions will be equal in the stationary state.

In terms of a general formalism, in the previous chapter we have seen how different flows J_k , $k = 1, 2, \dots, n$, are coupled to the thermodynamic forces F_k in the linear regime. A system may be maintained away from equilibrium by constraining some forces F_k , $k = 1, 2, \dots, s$, to be at a fixed nonzero value, while leaving the remaining forces F_k , $k = s + 1, \dots, n$, free. In such systems, one often finds that the flows corresponding to the constrained forces reach a constant, $J_k = \text{constant}$, $k = 1, 2, \dots, s$, whereas the unconstrained forces adjust so as to make their corresponding flows zero, $J_k = 0$, $k = s + 1, \dots, n$. An example is thermal diffusion in which the stationary state corresponds to zero matter flow and constant heat flow (Figure 16.5). In the linear regime, where the Onsager reciprocal relations are valid, all stationary states in which unconstrained thermodynamic flows vanish are characterized by the following general extremum principle [1, 2]:

In the linear regime, the total entropy production in a system subject to flow of energy and matter, $d_i S/dt = \int \sigma dV$, reaches a minimum value at the nonequilibrium stationary state.

Such a general criterion was sought by Lord Rayleigh, who suggested a 'principle of least dissipation of energy' [3]. Lars Onsager (1903–1976), in his well-known article on the reciprocal relations, comments on this principle and suggests that 'the rate of increase of entropy plays the role of a potential' [4]. The general formulation and the demonstration of the validity of this principle is due to Prigogine [1]. Let us look at the proof of this theorem and some examples that demonstrate its application.

For the case of coupled forces and flows, the principle of minimum entropy production can be demonstrated as follows. Consider a system with two forces and flows that are coupled. For notational convenience, we shall represent the total entropy production per unit time by P . Therefore,

$$P \equiv \frac{d_i S}{dt} = \int (F_1 J_1 + F_2 J_2) dV \quad (17.2.1)$$

Let us assume that the force F_1 is maintained at a fixed value by a suitable nonequilibrium constraint (contact with a reservoirs, for example). Using kinetic equations that relate the rate of change of state variables to the flows close to equilibrium, one generally finds that in the stationary state $J_1 = \text{constant}$ and $J_2 = 0$; i.e. for a fixed value of F_1 , F_2 adjusts so that J_2 is zero. We now show that this stationary state corresponds to the state in which the entropy production P is minimized.

The linear phenomenological laws give

$$J_1 = L_{11}F_1 + L_{12}F_2 \quad \text{and} \quad J_2 = L_{21}F_1 + L_{22}F_2 \quad (17.2.2)$$

Substituting Equations (17.2.2) into Equation (17.2.1) and using the Onsager reciprocal relations $L_{12} = L_{21}$, we obtain

$$P = \int (L_{11}F_1^2 + 2L_{12}F_1F_2 + L_{22}F_2^2) dV \quad (17.2.3)$$

From Equation (17.2.3) it follows that, for a fixed F_1 , P as a function of F_2 is minimized when

$$\frac{\partial P}{\partial F_2} = \int 2(L_{22}F_2 + L_{21}F_1)dV = 0 \quad (17.2.4)$$

Since this equation is valid for an arbitrary volume, the integrand must equal zero. By noting that $J_2 = L_{21}F_1 + L_{22}F_2$, we see at once that the entropy production is minimized when

$$J_2 = L_{21}F_1 + L_{22}F_2 = 0 \quad (17.2.5)$$

That is, $P \equiv d_i S/dt$ is minimized when the flow J_2 corresponding to the unconstrained force F_2 vanishes. This result can easily be generalized to an arbitrary number of forces and flows. The stationary state is the state of minimum entropy production in which the flows J_k , corresponding to the unconstrained forces, are zero. Although nonequilibrium stationary states are generally obtained through kinetic considerations, minimization of entropy production provides an alternative way.

We shall now present examples to illustrate the general applicability of the theorem of minimum entropy production.

17.2.1 Example 1: Stationary States in Chemical Systems

Consider the chemical system (17.1.9) discussed in the previous section (Figure 17.2):



As before, the flows of A and B keep the chemical potentials μ_A and μ_B fixed, which implies that the sum of the affinities has a fixed value, \bar{A} , not one of the two affinities:

$$A_1 + A_2 = (\mu_A - \mu_X) + (\mu_X - \mu_B) = \mu_A - \mu_B \equiv \bar{A} = \text{constant} \quad (17.2.7)$$

In the previous section, by using kinetics, we have already seen that the nonequilibrium stationary state is completely specified by Equation (17.1.18):

$$v_1 = v_2 \quad (17.2.8)$$

We shall now show how this condition may also be obtained using the principle of minimum entropy production. The entropy production per unit volume for this system (which we assume is homogeneous) is

$$\begin{aligned}\frac{1}{V} \frac{d_i S}{dt} &= \frac{P}{V} = \sigma = \frac{A_1}{T} v_1 + \frac{A_2}{T} v_2 \\ &= \frac{A_1}{T} v_1 + \frac{(\bar{A} - A_1)}{T} v_2\end{aligned}\quad (17.2.9)$$

in which V is the system volume and in which we have included the constraint \bar{A} , which is constant. The value of the chemical potential (or concentration) of X in the stationary state determines the value of A_1 , and hence the value of the entropy production (17.2.9). We will now minimize the entropy production and obtain (17.2.8). In the linear regime, since the two reactions are independent, we have

$$v_1 = L_{11} \frac{A_1}{T}, \quad v_2 = L_{22} \frac{A_2}{T} = L_{22} \frac{(\bar{A} - A_1)}{T} \quad (17.2.10)$$

in which we have used Equation (17.2.7). Substituting Equations (17.2.10) into Equation (17.2.9) we obtain σ as a function of A_1 :

$$\sigma(A_1) = L_{11} \frac{A_1^2}{T^2} + L_{22} \frac{(\bar{A} - A_1)^2}{T^2} \quad (17.2.11)$$

This function reaches its minimum value when

$$\frac{\partial \sigma(A_1)}{\partial A_1} = \frac{L_{11}}{T^2} 2A_1 - \frac{L_{22}}{T^2} 2(\bar{A} - A_1) = 0 \quad (17.2.12)$$

i.e.

$$\frac{L_{11} A_1}{T} - \frac{L_{11} A_2}{T} = v_1 - v_2 = 0 \quad (17.2.13)$$

In the linear regime, the entropy production is minimized at the nonequilibrium stationary state.

Alternatively, we may describe the system with the following set of affinities and velocities: $A'_1 = (A_1 + A_2)/2$, $A'_2 = (A_1 - A_2)/2$, $v'_1 = (v_1 + v_2)/2$, $v'_2 = (v_1 - v_2)/2$. The rate of entropy production in terms of these affinities and velocities is $\sigma = 2(A'_1 v'_1 + A'_2 v'_2)$. In this case, A'_1 is constrained and the flow corresponding to the affinity A'_2 will be zero at steady state: $v'_2 = (v_1 - v_2)/2 = 0$ (as was the case in the proof of the theorem presented above).

We have expressed σ as a function of A_1 . It is not necessary to express σ in terms of the affinities of the system, though it is convenient; σ can also be expressed in terms of the concentration [X]. The value of [X] that minimizes σ is the stationary state. We shall outline the main steps in this alternative demonstration of the principle, leaving some details as exercises.

In Section 9.5 we have seen that the entropy production per unit volume for the two reactions (17.2.6) can also be written as

$$\frac{1}{V} \frac{d_i S}{dt} = \sigma = R \{(R_{1f} - R_{1r}) \ln(R_{1f}/R_{1r}) + (R_{2f} - R_{2r}) \ln(R_{2f}/R_{2r})\} \quad (17.2.14)$$

in which R_{kf} and R_{kr} are the forward and reverse reaction rates of reaction k and R is the gas constant. Now if these forward and reverse reaction rates are written in terms of the concentrations, we have an expression

for σ in terms of the concentrations. Assuming reactions in (17.2.6) are elementary steps, the rates may be written as

$$R_{1f} = k_{1f}[A], \quad R_{1r} = k_{1r}[X], \quad R_{2f} = k_{2f}[X], \quad R_{2r} = k_{2r}[B] \quad (17.2.15)$$

At equilibrium, each reaction is balanced by its reverse. The equilibrium concentrations of $[A]_{eq}$, $[X]_{eq}$ and $[B]_{eq}$ are easily evaluated using the principle of detailed balance:

$$[X]_{eq} = \frac{k_{1f}}{k_{1r}}[A]_{eq} = \frac{k_{2r}}{k_{2f}}[B]_{eq} \quad (17.2.16)$$

We now define small deviations in concentrations from the equilibrium state:

$$\delta_A = [A] - [A]_{eq}, \quad \delta_X = [X] - [X]_{eq}, \quad \delta_B = [B] - [B]_{eq} \quad (17.2.17)$$

The deviations in $[A]$ and $[B]$ are due to the inflow of A and the outflow of B, so δ_A and δ_B are fixed by the flows. Only the concentration δ_X is determined by the chemical reactions. Using Equations (17.2.17) in Equation (17.2.14), the entropy production σ to the leading order in deviations (17.2.17) may be written (Exercise 17.8) as

$$\sigma(\delta_X) = R \left\{ \frac{(k_{1f}\delta_A - k_{1r}\delta_X)^2}{k_{1f}[A]_{eq}} + \frac{(k_{2f}\delta_X - k_{2r}\delta_B)^2}{k_{2f}[X]_{eq}} \right\} \quad (17.2.18)$$

By setting $\partial\sigma/\partial\delta_X = 0$, the value of δ_X that minimizes σ can easily be shown to be

$$\delta_X = \frac{k_{1f}\delta_A + k_{2r}\delta_B}{k_{1r} + k_{2f}} \quad (17.2.19)$$

(This is another way of expressing Equation (17.2.8)). That δ_X given by Equation (17.2.19) is identical to the stationary value can easily be verified. The kinetic equation for $[X]$ that follows from the two reactions (17.2.6) is

$$\frac{d[X]}{dt} = k_{1f}[A] - k_{1r}[X] - k_{2f}[X] + k_{2r}[B] \quad (17.2.20)$$

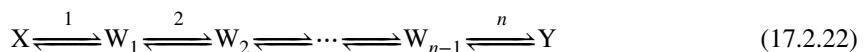
Substituting Equations (17.2.17) into Equation (17.2.20) gives the stationary state

$$\frac{d[X]}{dt} = k_{1f}\delta_A - k_{1r}\delta_X - k_{2r}\delta_X + k_{2r}\delta_B = 0 \quad (17.2.21)$$

The solution δ_X of this equation is identical to Equation (17.1.19). Thus the stationary value of δ_X is also the value for which the entropy production is minimized.

17.2.2 Example 2: A Sequence of Chemical Reactions

The principle of minimum entropy production can easily be demonstrated for more complex chemical systems. Example 1 can be generalized to an arbitrary number of intermediates:



The entropy production in this case is

$$\frac{1}{V} \frac{d_i S}{dt} = \sigma \frac{1}{T} (v_1 A_1 + v_2 A_2 + \cdots + v_n A_n) \quad (17.2.23)$$

We assume that the system is homogeneous, so we may assume the volume $V = 1$ without loss of generality. The affinity \bar{A} of the net reaction $X \rightleftharpoons{\bar{A}} Y$ is the sum of the affinities of the constituent reactions:

$$\bar{A} = \sum_{k=1}^n A_k \quad (17.2.24)$$

The inflow of X and outflow of Y keeps \bar{A} at a fixed nonzero value, keeping the system away from thermodynamic equilibrium. This nonequilibrium constraint can be made explicit by writing $A_n = (\bar{A} - \sum_{k=1}^{n-1} A_k)$ and substituting it in Equation (17.2.23). We then have σ as a function of $(n - 1)$ independent affinities A_k :

$$\sigma = \frac{1}{T} \left(v_1 A_1 + v_2 A_2 + \cdots + v_{n-1} A_{n-1} + v_n \left(\bar{A} - \sum_{k=1}^{n-1} A_k \right) \right) \quad (17.2.25)$$

Now, using the linear phenomenological laws, $v_k = L_{kk} (A_k/T)$, in this equation, we obtain

$$\sigma = \frac{1}{T^2} \left(L_{11} A_1^2 + L_{22} A_2^2 + \cdots + L_{(n-1)(n-1)} A_{n-1}^2 + L_{nn} \left(\bar{A} - \sum_{k=1}^{n-1} A_k \right)^2 \right) \quad (17.2.26)$$

An elementary calculation shows that the condition for minimum entropy production $\partial\sigma/\partial A_k = 0$ leads to $v_k = v_n$. Since this is valid for all k , we have the following generalization of Equation (17.2.8):

$$v_1 = v_2 = \cdots = v_{n-1} = v_n \quad (17.2.27)$$

Since the kinetic equations for (17.2.22) are

$$\frac{d[W_k]}{dt} = v_k - v_{k+1} \quad (17.2.28)$$

it is clear that the stationary states $d[W_k]/dt = 0$ are identical to the states that minimize entropy production.

17.2.3 Example 3: Coupled Chemical Reactions

As an example of a chemical reaction in which one of the affinities is unconstrained by the nonequilibrium conditions, let us consider the synthesis of HBr from H_2 and Br_2 . In this case we expect the velocity of the unconstrained reaction to equal zero at the stationary state. We assume that the affinity of the net reaction



is maintained at a fixed nonzero value by a suitable inflow of H_2 and Br_2 and removal of HBr. The intermediates of the reaction, H and Br, appear through the reactions



The affinity of the net reaction (17.2.29) is

$$A_2 + A_3 = \bar{A} \quad (17.2.33)$$

which we assume is kept at a nonzero value. The affinity A_1 of reaction (17.2.30) is not constrained. The entropy production per unit volume for this system is

$$\begin{aligned}\sigma &= \frac{1}{T} (v_1 A_1 + v_2 A_2 + v_3 A_3) \\ &= \frac{1}{T} (v_1 A_1 + v_2 A_2 + v_3 (\bar{A} - A_2))\end{aligned}\quad (17.2.34)$$

Again we shall assume a homogeneous system with $V = 1$, so that minimizing σ is equivalent to minimizing the total entropy production P . As was done above, using the phenomenological laws $v_k = L_{kk} (A_k/T)$ and setting $\partial\sigma/\partial A_k = 0$ for the two independent affinities A_1 and A_2 , we see that the entropy production is extremized when

$$v_1 = 0 \quad \text{and} \quad v_2 = v_3 \quad (17.2.35)$$

This must also be the stationary state. Turning to the kinetic equations for H and Br, we have

$$\frac{d[H]}{dt} = v_2 - v_3 \quad (17.2.36)$$

$$\frac{d[Br]}{dt} = 2v_1 - v_2 + v_3 \quad (17.2.37)$$

The stationary states of these equations are the same as Equations (17.2.35).

17.2.4 Example 4: Stationary States in Thermal Conduction

As an example of a continuous system, let us look at stationary states in heat conduction using the system we considered in Figure 17.1. For a one-dimensional system the entropy production is

$$P \equiv \frac{d_i S}{dt} = \int_0^L J_q \left(\frac{\partial}{\partial x} \frac{1}{T} \right) dx \quad (17.2.38)$$

Using the linear phenomenological law $J_q = L_{qq} \partial(1/T)/\partial x$, the above expression can be written as

$$P = \int_0^L L_{qq} \left(\frac{\partial}{\partial x} \frac{1}{T} \right)^2 dx \quad (17.2.39)$$

Among the possible functions $T(x)$, our goal is to identify the function that minimizes the entropy production P . This can be done using the following basic result from the calculus of variations. The integral

$$I = \int_0^L \Lambda(f(x), \dot{f}(x)) dx \quad (17.2.40)$$

in which the integrand $\Lambda(f(x), \dot{f}(x))$, a function of f and its derivative $\dot{f} \equiv \partial f / \partial x$ (for notational convenience we shall use \dot{f} in place of $\partial f / \partial x$), is extremized when the function $f(x)$ is a solution of the following well-known Euler–Lagrange equation in the calculus of variations:

$$\frac{d}{dx} \frac{\partial \Lambda}{\partial \dot{f}} - \frac{\partial \Lambda}{\partial f} = 0 \quad (17.2.41)$$

In applying this result to the entropy production (17.2.39), we identify f with $(1/T)$ so that $\Lambda = L_{qq} \dot{f}^2$. Also, as was discussed in Section 16.3 (Equation (16.3.6)), in this calculation we assume that $L_{qq} = \kappa T^2 \approx \kappa T_{\text{avg}}^2$ (in which κ is the thermal conductivity and T_{avg} is the average temperature) is approximately constant in

accordance with the linear approximation. Then writing Equation (17.2.41) for the entropy production, we obtain

$$\frac{d}{dx} L_{qq}\dot{f} = 0 \quad (17.2.42)$$

Because we identified f with $(1/T)$, this condition implies

$$L_{qq}\dot{f} = L_{qq}\frac{\partial}{\partial x}\frac{1}{T} = J_q = \text{constant} \quad (17.2.43)$$

Since $L_{qq} \approx \kappa T_{\text{avg}}^2$, this condition can also be written as

$$\frac{\partial T}{\partial x} = \text{constant} \quad (17.2.44)$$

Thus the function $T(x)$ that minimizes the entropy production P is linear in x ; i.e. the entropy production is minimized when the heat current reaches a uniform value along the length of the system. This result has a formal similarity with the velocities of a sequence of coupled reactions all being constant along the reaction chain (Example 2). As expected, the stationary state obtained in the previous section using the heat conduction equation (17.1.5) is identical to Equation (17.2.44).

A nice experimental demonstration of the evolution of an initial distribution of $T(x)$ to a stationary distribution, decreasing the rate of entropy production to its minimum value along the way, can be found in Reference [5].

17.2.5 Example 5: Stationary States in Electrical Circuit Elements

In the previous section we have seen that the entropy production for electrical circuit elements is given by $T \frac{d_i S}{dt} = VI$, in which V is the voltage across the circuit element and I the current passing through it. For each element k , the phenomenological laws imply that $I_k = L_{kk}(V_k/T)$. Let us consider n circuit elements connected in series, as shown in Figure 17.4 (C). We assume that the total voltage drop V across the whole circuit is maintained at a constant value (just as a constant temperature was maintained for thermal conduction):

$$V = \sum_{k=1}^n V_k \quad (17.2.45)$$

The total entropy production for such a system will then be

$$\begin{aligned} P &= \frac{d_i S}{dt} = \frac{1}{T}(V_1 I_1 + V_2 I_2 + \dots + V_n I_n) \\ &= \frac{1}{T^2} \left(L_{11} V_1^2 + L_{22} V_2^2 + \dots + L_{(n-1)(n-1)} V_{n-1}^2 + L_{nn} \left(V - \sum_{k=1}^{n-1} V_k \right)^2 \right) \end{aligned} \quad (17.2.46)$$

in which we have used Equation (17.2.45) to eliminate V_n . This equation is similar to Equation (17.2.26), obtained for a sequence of chemical reactions in which the V_k take the place of the affinities A_k . We may now minimize the entropy production with respect to the $(n-1)$ independent V_k by setting $\partial P / \partial V_k = 0$. The result, as in the case of chemical reactions, is that the flows I_k must be equal:

$$I_1 = I_2 = \dots = I_n \quad (17.2.47)$$

Thus, in a circuit element, the entropy production is minimized when the current is uniform along the circuit. (Feynman [6] indicates that he has observed this relation between entropy production and uniformity of electric current.) In the analysis of electrical circuits, the condition that the current should be uniform

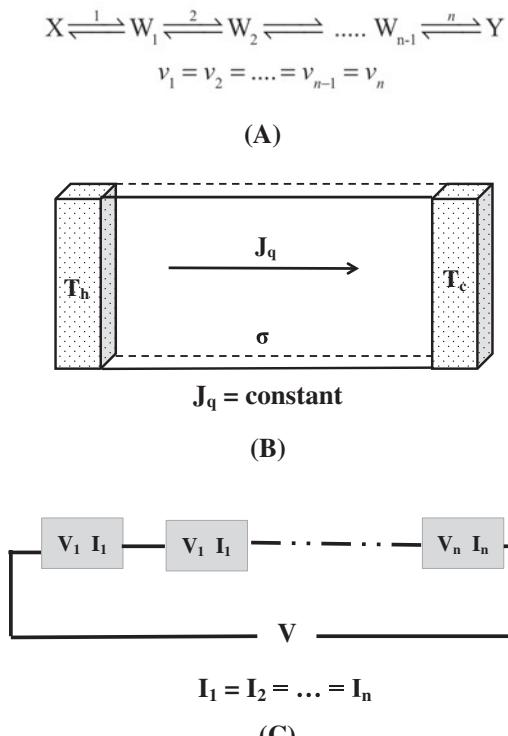


Figure 17.4 For a nonequilibrium system consisting of a series of coupled subsystems, the entropy production in the linear regime is minimized when all the flows are equal. It is also the stationary state.

is usually imposed on the system because we do not observe any charge accumulation in any part of the system. In electrical systems the relaxation to the stationary state of uniform I is extremely rapid, and hence nonuniform or discontinuous I are not observed.

Examples 2, 4 and 5 illustrate a common feature implied by the principle of minimum entropy production (Figure 17.4): in a series of coupled systems, entropy production is extremized when the flows are equal. In a chemical reaction it was the velocity v_k ; for heat conduction it was the heat flow J_q ; for an electric circuit it is the electric current I_k .

17.3 Time Variation of Entropy Production and the Stability of Stationary States

In the previous section we have seen that the stationary states in the linear regime are also states that extremize the internal entropy production. We shall now consider the stability of these states and also show that the entropy production is *minimized*. In Chapter 14 we saw that the fluctuations near the equilibrium state decrease the entropy and that the irreversible processes drive the system back to the equilibrium state of maximum entropy. As the system approaches the state of equilibrium, the entropy production approaches zero. The approach to equilibrium can be described not only as a steady increase in entropy to its maximum value but also as a steady *decrease in entropy production to zero*. It is this latter approach that naturally extends to the linear regime, close to equilibrium.

Let us look at the time variation of the entropy production due to chemical reactions in an open system in the linear regime. As before, we assume homogeneity and unit volume. The entropy production is

$$P \equiv \frac{d_i S}{dt} = \sum_k \frac{A_k}{T} \frac{d\xi_k}{dt} = \sum_k \frac{A_k}{T} v_k \quad (17.3.1)$$

In this equation, all the affinities A_k are functions of p , T and the extents of reaction ξ_k . In the linear regime, since $v_k = \sum_i L_{ki}(A_i/T)$, Equation (17.3.1) becomes

$$P = \sum_{ik} \frac{L_{ik}}{T^2} A_i A_k \quad (17.3.2)$$

The time derivative of P can now be explicitly written by noting that at constant p and T ,

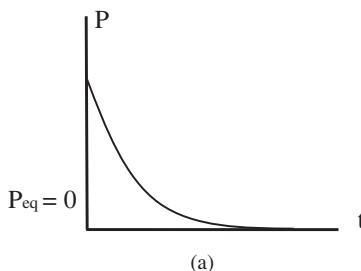
$$\frac{dA_k}{dt} = \sum_j \left(\frac{\partial A_k}{\partial \xi_j} \right)_{p,T} \frac{d\xi_j}{dt} \quad (17.3.3)$$

Thus we find

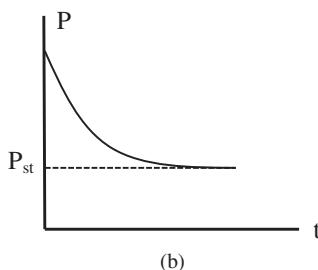
$$\frac{dP}{dt} = \frac{1}{T^2} \sum_{ijk} L_{ik} \left[A_k \left(\frac{\partial A_i}{\partial \xi_j} \right) \frac{d\xi_j}{dt} + A_i \left(\frac{\partial A_k}{\partial \xi_j} \right) \frac{d\xi_j}{dt} \right] \quad (17.3.4)$$

By using the Onsager reciprocal relations $L_{ik} = L_{ki}$ and identifying $d\xi_k/dt \equiv v_k = \sum_i L_{ki}(A_i/T)$, Equation (17.3.4) can be reduced to

$$\frac{dP}{dt} = \frac{2}{T} \sum_{ij} \left(\frac{\partial A_i}{\partial \xi_j} \right) v_i v_j \quad (17.3.5)$$



(a)



(b)

Figure 17.5 The time variation of the entropy production $P = d_i S/dt = \sum_k F_k J_k$ for equilibrium and near-equilibrium states. (a) For a fluctuation from the equilibrium state, the initial nonzero value of P decreases to its equilibrium value of zero. (b) In the linear regime, a fluctuation from a nonequilibrium steady state can only increase the value of P above the stationary value P_{st} ; irreversible processes drive P back to its minimum value P_{st} .

To see that Equation (17.3.5) is negative, we turn to the stability conditions in Chapter 14, in particular to the following condition (14.1.9b) for stability with respect to fluctuations $\delta\xi_i$ in the extents of reaction:

$$\Delta_i S = \frac{1}{2T} \sum_{ij} \left(\frac{\partial A_i}{\partial \xi_j} \right)_{eq} \delta \xi_i \delta \xi_j < 0 \quad (17.3.6)$$

Since $\delta\xi_k$ can be positive or negative, condition (17.3.6) for stability of the equilibrium state implies that the matrix $(\partial A_i / \partial \xi_j)_{eq}$ must be negative definite. In a neighborhood of the equilibrium state, $(\partial A_i / \partial \xi_j)$ would retain its negative definiteness. Then, in this neighborhood, expression (17.3.5) must also be negative definite. Hence in the neighborhood of equilibrium we have the inequalities

$$P > 0 \quad (17.3.7)$$

$$\frac{dP}{dt} = \frac{2}{T} \sum_{ij} \left(\frac{\partial A_i}{\partial \xi_j} \right) v_i v_j < 0 \quad (17.3.8)$$

close to the equilibrium state (Figure 17.5). At the stationary state, P has its minimum value. If a fluctuation drives P to a higher value, irreversible processes drive P back to its minimum stationary value. The result $dP/dt < 0$ for nonequilibrium states can be more generally proved [7]. The two conditions (17.3.7) and (17.3.8) constitute the ‘Lyapunov conditions’ for the stability of a state, a topic we will discuss in detail in the next chapter.

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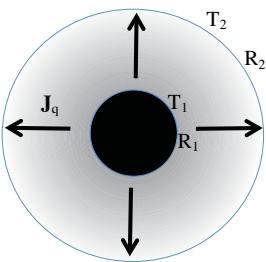
Exercises

- 17.1 (a)** Using the Fourier law $\mathbf{J}_q = -\kappa \nabla T$, obtain the time-dependent equation for heat conduction:

$$C \frac{\partial T}{\partial t} = \kappa \nabla^2 T$$

in which C is the heat capacity per unit volume.

- (b) For a one-dimensional system, show that the stationary state of the system leads to a linear temperature distribution.



- (c) In planets the core is hotter than the surface. Consider a sphere of radius R whose core of radius R_1 is at a higher temperature T_1 than the surface temperature T_2 . Obtain the stationary distribution of $T(r)$ and the heat flux \mathbf{J}_q as a function of the radial distance r , using the Fourier law of heat conduction. (The conductivity of the Earth cannot account for the heat flux measured at the surface of the Earth. The transport of heat is therefore thought to be due to convective processes within the Earth.)

- 17.2** (a) Using the relation $s_m = s_{mo} + C_{mV} \ln T$ for the molar entropy of a system, in which C_{mV} is the molar heat capacity, obtain an expression for the total entropy of the system shown in Figure 17.1. Let ρ be the density and M the molar mass. Assume that the distance between the hot and cold ends is L and that the area of cross-section is unity. Also assume that the density ρ does not change much with T so that it is nearly uniform.
 (b) Suppose the system were suddenly removed from being in contact with the reservoirs and then insulated so that no heat escaped.
 (i) What would the final temperature of the system be when it reaches equilibrium?
 (ii) What would be the final entropy of the system?
 (iii) What would be the increase in entropy compared to the initial nonequilibrium state?

- 17.3** Write a *Mathematica* code to simulate the reaction

$$\frac{d[X]}{dt} = k_{1f}[A] - k_{1r}[X] - k_{2f}[X] + k_{2r}[B]$$

Use it to study the relaxation of $[X]$ and the entropy production σ to its stationary value assuming that $[A]$ and $[B]$ are constant.

- 17.4** For a series of chemical reactions

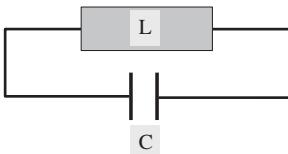


with an inflow of M and an outflow of N , show that the steady state is given by

$$v_1 = v_2 = \cdots = v_n$$

in which the v_k are velocities of the indicated reactions.

- 17.5** Consider an ideal capacitor C in series with an inductance L .



The voltage across the capacitor is $V_C = -Q/C$; the voltage across the inductance is $V_L = -L \frac{dI}{dt}$. For the shown circuit, the sum of these two voltages must be zero, i.e. $V_C + V_L = 0$. Using this fact, write a differential equation for Q and show that the quantity $(LI^2/2 + Q^2/2C)$ is constant in time. (The conservation of energy here is similar to that of a simple harmonic oscillator.) If a resistor R is added to the circuit, show that the equation $dU/dt = -V_R I$ leads to the well-known equation $L \frac{d^2Q}{dt^2} + R \frac{dQ}{dt} + Q/C = 0$ of an LCR circuit.

- 17.6** Using Equations (17.1.28) and (17.1.29) obtain the time variation of $I(t)$ and $Q(t)$ in a real capacitor and a real inductance. Using these expressions in Equations (17.1.25) and (17.1.26) obtain the entropy production at any time t in these circuit elements with initial current I_0 and initial charge Q_0 .
- 17.7** Demonstrate the theorem of minimum entropy production for an arbitrary number of constrained and unconstrained thermodynamic forces.

- 17.8** Consider the chemical reaction $A \xrightleftharpoons[1]{X} \xrightleftharpoons[2]{B}$.

- (a) Show that the entropy production per unit volume is

$$\sigma(\delta_X) = R \left\{ \frac{(k_{1f}\delta_A - k_{1r}\delta_X)^2}{k_{1f}[A]_{eq}} + \frac{(k_{2f}\delta_X - k_{2r}\delta_B)^2}{k_{2f}[X]_{eq}} \right\}$$

in which $\delta_A = [A] - [A]_{eq}$, $\delta_B = [B] - [B]_{eq}$, $\delta_X = [X] - [X]_{eq}$.

- (b) Show that σ attains a minimum value for

$$\delta_X = \frac{k_{1f}\delta_A + k_{2r}\delta_B}{k_{1r} + k_{2f}}$$

Part V

Order Through Fluctuations

18

Nonlinear Thermodynamics

18.1 Far-from-Equilibrium Systems

Systems that are subject to a flow of energy and matter can be driven far from thermodynamic equilibrium, into the ‘nonlinear’ regime. In the nonlinear regime, the thermodynamic flows J_α are no longer linear functions of thermodynamic forces F_α . In the case of chemical reactions, we have seen that a system is in the linear regime if the affinities A_k are small compared to RT , i.e. $|A_k/RT| \ll 1$. The value of RT at $T = 300$ K is about 2.5 kJ mol^{-1} . Since the affinities of chemical reactions can easily reach the range $10\text{--}100\text{ kJ mol}^{-1}$, the nonlinear regime is easily reached for chemical processes (Exercise 18.1). It is more difficult to reach the nonlinear regime for transport processes such as heat conduction and diffusion.

In Nature, far-from-equilibrium systems are ubiquitous. The Earth as a whole is an open system subject to the constant flow of energy from the Sun. This influx of solar energy sustains the biosphere, and is ultimately responsible for maintaining an atmosphere out of thermodynamic equilibrium (Exercise 18.2). Every living cell lives through the flow of matter and energy.

As we shall see in the following sections, far-from-equilibrium states can lose their stability and evolve to one of the many states available to the system. Irreversible processes and the boundary conditions do not uniquely specify the nonequilibrium state to which the system will evolve; driven by internal fluctuations or other small external influences, the system leaves the unstable state and evolves to one of the many possible new states. These new states can be highly organized and are called **dissipative structures**.

Dissipative structures behave in an unpredictable way. Small external influences play a significant role; causes that determine the behavior of the system are no longer within the system. It becomes extremely difficult, if not impossible, to approximate such systems as isolated or closed systems. As for the certainty of Newtonian and Laplacian planetary motion and the uniqueness of equilibrium states, both begin to fade; we see instead a probabilistic Nature that generates new organized structures, a Nature that can create living organisms.

18.2 General Properties of Entropy Production

In the linear regime we saw that the stationary states are those in which the total entropy production $P = \int_V \sigma dV$ reaches a minimum. This criterion also assured the stability of the stationary state. In the

far-from-equilibrium nonlinear regime, there is no such general principle for determining the state of the system. Far-from-equilibrium states can become unstable and evolve to new organized states and we will identify the thermodynamic conditions under which this may happen.

We begin by noting some general properties of the total entropy production P . These are statements regarding the time evolution of change δP due to small changes in the forces δF_k and the flows δJ_k . Let P be the entropy production in a nonequilibrium stationary state. Since $P = \int_V \sigma dV = \int_V \sum_k F_k J_k dV$, the rate of change in P can be written as

$$\begin{aligned} \frac{dP}{dt} &= \int_V \left(\frac{d\sigma}{dt} \right) dV = \int_V \left(\sum_k \frac{dF_k}{dt} J_k \right) dV + \int_V \left(\sum_k F_k \frac{dJ_k}{dt} \right) dV \\ &\equiv \frac{d_F P}{dt} + \frac{d_J P}{dt} \end{aligned} \quad (18.2.1)$$

in which $d_F P/dt$ is the change due to the changes in F_k and $d_J P/dt$ is the change due to the changes in J_k . Two general properties can now be stated [1–3]:

- a. In the linear regime:

$$\boxed{\frac{d_F P}{dt} = \frac{d_J P}{dt}} \quad (18.2.2)$$

- b. For time-independent boundary conditions, even outside the linear regime:

$$\boxed{\frac{d_F P}{dt} \leq 0} \quad (18.2.3)$$

($d_F P/dt = 0$ at the stationary state).

In contrast to the variation dG in the Gibbs free energy G , $d_F P$ is not a differential of a state function. Hence the fact that $d_F P$ can only decrease does not tell us how the state will evolve.

The first of the above relations follows from the linear relations $J_k = \sum_i L_{ki} F_i$ and the Onsager reciprocal relations $L_{ki} = L_{ik}$. First we note that

$$\sum_k dF_k J_k = \sum_{ki} dF_k L_{ki} F_i = \sum_{ki} (dF_k L_{ik}) F_i = \sum_i dJ_i F_i \quad (18.2.4)$$

Using this result in the definitions of $d_F P$ and $d_J P$ in Equation (18.2.1), we immediately see that

$$\frac{d_F P}{dt} = \int_V \left(\sum_k \frac{dF_k}{dt} J_k \right) dV = \int_V \left(\sum_k F_k \frac{dJ_k}{dt} \right) dV = \frac{d_J P}{dt} = \frac{1}{2} \frac{dP}{dt} \quad (18.2.5)$$

The general property (18.2.3) when applied to Equation (18.2.5) gives us the result we have seen in the previous chapter:

$$\frac{dP}{dt} = 2 \frac{d_F P}{dt} < 0 \quad \text{in the linear regime} \quad (18.2.6)$$

This shows, once again, that a perturbation in the total entropy production P from its stationary state value will monotonically decrease to its stationary state value, in accordance with the principle of minimum entropy production. A simple proof of Equation (18.2.3) is given in Appendix 18.1.

We see that we now have two inequalities, $P \geq 0$ and $d_F P \leq 0$. The second inequality is an important evolution criterion. Let us indicate briefly two consequences for a homogeneous system of unit volume. If only one concentration, say X , is involved in the evolution, $d_F P = v(X) (\partial A / \partial X) dX \equiv dW$. The variable W , thus defined, is then a ‘kinetic potential’. However, this is rather an exceptional case. The interesting consequence is that time-independent constraints may lead to states that are not stationary, states that oscillate in time. We shall see examples of such systems in Chapter 19, but let us consider here a simple example of a far-from-equilibrium chemical system where the dependence of velocities on affinities are antisymmetric, i.e. $v_1 = lA_2$, $v_2 = -lA_1$ (Onsager’s relations are not valid for systems far from equilibrium). The derivative $d_F P/dt$ in this case becomes

$$\frac{1}{V} \frac{d_F P}{dt} = v_1 \frac{dA_1}{dt} + v_2 \frac{dA_2}{dt} = lA_2 \frac{dA_1}{dt} - lA_1 \frac{dA_2}{dt} \leq 0 \quad (18.2.7)$$

By introducing the polar coordinates $A_1 = r \cos \theta$ and $A_2 = r \sin \theta$, it is easy to see that this equation can be written as

$$\frac{1}{V} \frac{d_F P}{dt} = -lr^2 \frac{d\theta}{dt} \leq 0 \quad (18.2.8)$$

The system rotates irreversibly in a direction determined by the sign of l . An example of such a system is the well-known Lotka–Volterra ‘prey–predator’ interaction given as an exercise (Exercise 18.9). We can also apply this inequality to derive a *sufficient condition* for the stability of a steady state. If all fluctuations $\delta_F P > 0$ then the steady state is stable. However, here it is more expedient to use the Lyapunov theory of stability to which we turn now.

18.3 Stability of Nonequilibrium Stationary States

A very general criterion for stability of a state was formulated by Lyapunov [4]. We shall obtain the conditions for the stability of a nonequilibrium state using Lyapunov’s theory.

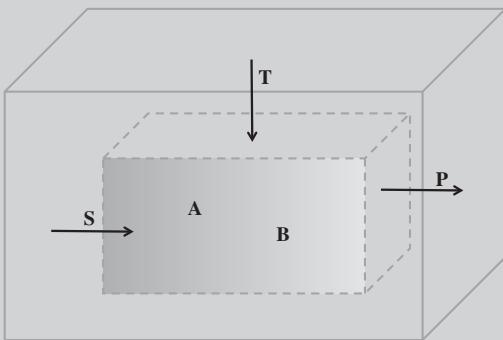
18.3.1 Lyapunov’s Theory of Stability

Lyapunov’s formulation gives conditions for stability in precise mathematical terms (with clear intuitive meaning). Let X_s be a stationary state of a physical system. In general, X may be an r -dimensional vector with components X_k , $k = 1, 2, \dots, r$. We shall denote the components of X_s by X_{sk} . Let the time evolution of X be described by an equation

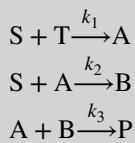
$$\frac{dX_k}{dt} = Z_k(X_1, X_2, \dots, X_r; \lambda_j) \quad (18.3.1)$$

in which the λ_j are parameters that may or may not be independent of time. A simple example of such an equation is given in Box 18.1. In general, if the X_k are functions not only of time t but also of positions x , then Equation (18.3.1) will be a partial differential equation in which Z_k will be a partial differential operator.

Box 18.1 Kinetic equations and Lyapunov stability theory: an example



Consider the open chemical system shown above with the following chemical reactions:



For simplicity, we assume that the reverse reactions can be ignored. If the system is subject to an inflow of S and T and an outflow of P such that the concentrations of these species are maintained constant, we have the following kinetic equations for the concentrations of A and B:

$$\begin{aligned} X_1 &\equiv [A], \quad X_2 \equiv [B] \\ \frac{dX_1}{dt} &= k_1[S][T] - k_2[S]X_1 - k_3X_1X_2 \equiv Z_1(X_j, [S], [T]) \\ \frac{dX_2}{dt} &= k_2[S]X_1 - k_3X_1X_2 \equiv Z_2(X_j, [S], [T]) \end{aligned}$$

In this system, [S] and [T] correspond to the parameters λ_j in Equation (18.3.1). For a given value of these parameters, the stationary states X_{s1} and X_{s2} are easily found by setting $dX_1/dt = dX_2/dt = 0$:

$$X_{s1} = \frac{k_1[T]}{2k_2}, \quad X_{s2} = \frac{k_2[S]}{k_3}$$

The stability of this stationary state is determined by examining the evolution of the perturbations δX_1 and δX_2 from this stationary state. A possible Lyapunov function L , for example, is

$$L(\delta X_1, \delta X_2) = [(\delta X_1)^2 + (\delta X_2)^2] > 0$$

If it can be shown that $dL(\delta X_1, \delta X_2)/dt < 0$, then the stationary state (X_{s1}, X_{s2}) is stable.

The stationary state X_{sk} is the solution to the set of coupled equations

$$\frac{dX_k}{dt} = Z_k(X_{s1}, X_{s2}, \dots, X_{sr}; \lambda_j) = 0 \quad (k = 1, 2, \dots, r) \quad (18.3.2)$$

The stability of the stationary state can be understood by looking at the behavior of a small perturbation δX_k . To establish the stability of a state, first a *positive function* $L(\delta X)$ of δX , which may be called a ‘distance’, is defined in the space spanned by X_k . If this ‘distance’ between X_{sk} and the perturbed state $(X_{sk} + \delta X_k)$ steadily decreases in time, the stationary state is stable. Thus state X_{sk} is stable if

$$\boxed{L(\delta X_k) > 0 \quad \frac{dL(\delta X_k)}{dt} < 0} \quad (18.3.3)$$

A function L that satisfies Equation (18.3.3) is called a **Lyapunov function**. If the variables X_k are functions of position (as concentrations n_k in a nonequilibrium system can be), L is called a **Lyapunov functional** – a ‘functional’ is a mapping of a set of functions to a number, real or complex. The notion of stability is not restricted to stationary states; it can also be extended to periodic states [4]. However, since we are interested in the stability of nonequilibrium stationary states, we shall not deal with the stability of periodic states at this point.

18.3.2 Second Variation of Entropy – $\delta^2 S$ as a Lyapunov Functional

We have already seen that the second variation of entropy is a function that has a definite sign for any thermodynamic system in local equilibrium. By considering the entropy density $s(\mathbf{x})$ as a function of the energy density $u(\mathbf{x})$ and the concentrations $n_k(\mathbf{x})$, we can write ΔS , the change in entropy from the stationary value, in the form

$$\begin{aligned} \Delta S &= \int \left[\left(\frac{\partial s}{\partial u} \right)_{n_k} \delta u + \sum_k \left(\frac{\partial s}{\partial n_k} \right)_u \delta n_k \right] dV \\ &\quad + \frac{1}{2} \int \left[\left(\frac{\partial^2 s}{\partial u^2} \right) (\delta u)^2 + 2 \sum_k \left(\frac{\partial^2 s}{\partial u \partial n_k} \right) \delta u \delta n_k + \sum_{ij} \left(\frac{\partial^2 s}{\partial n_i \partial n_j} \right) \delta n_i \delta n_j \right] dV \\ &= \delta S + \frac{1}{2} \delta^2 S \end{aligned} \quad (18.3.4)$$

Since we are considering a nonequilibrium stationary state, the thermodynamic forces and the corresponding flows of energy, \mathbf{J}_u , and matter, \mathbf{J}_k , do not vanish. Hence the first variation $\delta S \neq 0$. The second variation, $\delta^2 S$, has a definite sign because the integrand, which is the second variation of entropy of elemental volume that is locally in equilibrium, is negative (Equation (12.4.10)):

$$\frac{1}{2} \delta^2 S < 0 \quad (18.3.5)$$

Appendix 18.2 contains the derivation of the following general result:

$$\boxed{\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV} \quad (18.3.6)$$

In Chapter 14 (Equation (14.1.16)) we obtained the same equation for perturbations from the equilibrium state. Equation (18.3.6) shows that the time derivative of $\delta^2 S$ has the same form even under nonequilibrium conditions. The difference is that near equilibrium $\sum_k \delta F_k \delta J_k = \sum_k F_k J_k > 0$; but it is not necessarily so far from equilibrium. We shall refer to this quantity as **excess entropy production**, but, strictly speaking, it is the increase in entropy production only near the equilibrium state; for a perturbation from a nonequilibrium state, the increase in entropy production is equal to $\delta P = \delta_F P + \delta_J P$.

Expressions (18.3.5) and (18.3.6) would define a Lyapunov functional, $L = -\delta^2 S/2$ if the stationary state were such that $\sum_k \delta F_k \delta J_k > 0$. Thus, a nonequilibrium stationary state is stable if

$$\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV > 0 \quad (18.3.7)$$

If this inequality is violated, it only means that the system *may* be unstable; i.e. $\sum_k \delta F_k \delta J_k < 0$ is a necessary but not a sufficient condition for instability.

18.3.3 Using the Stability Criterion

Since $\delta^2 S < 0$ under both equilibrium and nonequilibrium conditions, the stability of a stationary state is assured if

$$\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV > 0 \quad (18.3.8)$$

Let us apply this condition to simple chemical systems to understand when a nonequilibrium system may become unstable.

First, let us consider the following reaction:



Assuming these reactions are elementary steps, we write the forward and reverse rates as

$$R_f = k_f[A][B] \quad \text{and} \quad R_r = k_r[C][D] \quad (18.3.10)$$

We assume this system is maintained out of equilibrium by suitable flows. As we have seen in Section 9.5, for a chemical reaction the affinity A and the velocity of reaction v are given by $A = RT \ln(R_f/R_r)$ and $v = (R_f - R_r)$. The time derivative of $\delta^2 S$, the ‘excess entropy production’ (18.3.8), can be written in terms of $\delta F = \delta A/T$ and $\delta J = \delta v$. For a perturbation $\delta[B]$ from the stationary state, it is easy to show that (Exercise 18.4)

$$\frac{1}{2} \frac{d\delta^2 S}{dt} = \int_V \sum_\alpha \delta J_\alpha \delta F_\alpha dV = \int_V \sum_\alpha \frac{\delta A}{T} \delta v dV = R k_f \int_V \frac{[A]_s}{[B]_s} (\delta[B])^2 dV > 0 \quad (18.3.11)$$

in which the subscript s indicates the nonequilibrium stationary state values of the concentrations. Since $d\delta^2 S/dt$ is positive, the stationary state is stable.

The situation is different, however, for an *autocatalytic* reaction such as



which appears in a reaction scheme called the ‘Brusselator’, which we will consider in the next chapter. For this reaction, we can consider a nonequilibrium stationary state in which the concentrations are $[X]_s$ and $[Y]_s$ and a perturbation δX . Using the forward and reverse rates $R_f = k_f[X]^2[Y]$ and $R_r = k_r[X]^3$ in the expressions $A = RT \ln(R_f/R_r)$ and $v = (R_f - R_r)$, we can once again calculate the excess entropy production to obtain

$$\frac{1}{2} \frac{d\delta^2 S}{dt} = \int_V \frac{\delta A}{T} \delta v dV = -R \int_V (2k_f[X]_s[Y]_s - 3k_r[X]_s^2) \frac{(\delta X)^2}{[X]_s} dV \quad (18.3.13)$$

The excess entropy production can now become negative, particularly if $k_f \gg k_r$. Hence the stability is no longer assured and the stationary state *may* become unstable.

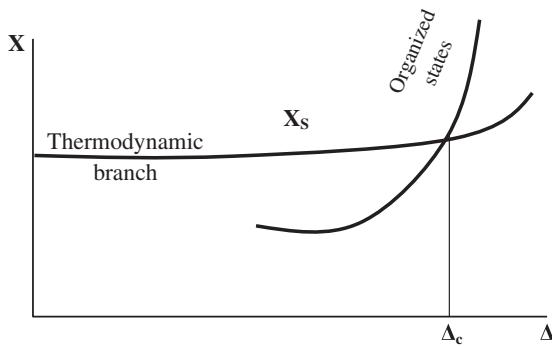


Figure 18.1 Each value of X represents a state of the system. The distance from equilibrium is represented by the parameter Δ . When $\Delta = 0$ the system is in a state of thermodynamic equilibrium. When Δ is small, the system is in a near-equilibrium state, which is an extrapolation of the equilibrium state; this family of states is called the thermodynamic branch. In some systems, such as those with autocatalysis, when Δ reaches a critical value Δ_c , the states belonging to the thermodynamic branch become unstable. When this happens, the system makes a transition to a new branch, which may correspond to organized states.

The above discussion can be summarized through a stability diagram, as shown in Figure 18.1. The value of the parameter Δ is a measure of the distance from equilibrium. For each value of Δ the system will relax to a stationary state, denoted by X_s . The equilibrium state corresponds to $\Delta = 0$; X_s is a continuous extension of the equilibrium state and is called the **thermodynamic branch**. As long as condition (18.3.8) is satisfied, the thermodynamic branch is stable; if it is violated, the thermodynamic branch *may* become unstable. If it does become unstable, the system makes a transition to a new branch, which is generally an organized structure.

If the kinetic equations of the systems are known, there is a well-defined mathematical method to determine at what point the stationary state will become unstable. This is the linear stability analysis we will discuss in the following section. Nonequilibrium instabilities give rise to a great variety of structures, which we will discuss in the next chapter.

18.4 Linear Stability Analysis

In general, the rate equations of a homogeneous chemical system take the general form:

$$\frac{dX_k}{dt} = Z_k(X_1, \dots, X_n; \lambda_j) \quad (18.4.1)$$

where the X_k correspond to concentrations, such as $[X]$ and $[Y]$ in Equation (18.3.12), and λ_j corresponds to concentrations that are maintained at a constant nonequilibrium value. We begin by assuming that a stationary solution X_k^0 of Equation (18.4.1) is known. This means

$$Z_k(X_1^0, \dots, X_n^0, \lambda_j) = 0 \quad (18.4.2)$$

We would like to know if this stationary solution will be stable to small perturbations x_i . Linear stability analysis provides the answer in the following way. Consider a small perturbation x_k :

$$X_k = X_k^0 + x_k(t) \quad (18.4.3)$$

Now the Taylor expansion of $Z_k(X_i)$ gives

$$Z_k(X_i^0 + x_i) = Z_k(X_i^0) + \sum_j \left(\frac{\partial Z_k}{\partial X_j} \right)_0 x_j + \dots \quad (18.4.4)$$

in which the subscript 0 indicates that the derivative is evaluated at the stationary state X_i^0 . In linear stability analysis, only the linear terms in x_j are retained; the higher-order terms are neglected by assuming the x_j are small. Substituting Equation (18.4.4) into Equation (18.4.1), since X_i^0 is a stationary state, we obtain for $x_k(t)$ the linear equation

$$\frac{dx_k}{dt} = \sum_j \Lambda_{kj}(\lambda) x_j \quad (18.4.5)$$

in which $\Lambda_{kj}(\lambda) = (\partial Z_k / \partial X_j)_0$ is a function of the parameter λ . In matrix notation, Equation (18.4.5) can be written as

$$\frac{d\mathbf{x}}{dt} = \Lambda \mathbf{x} \quad (18.4.6)$$

in which the vector $\mathbf{x} = (x_1, x_2, x_3, \dots, x_n)$ and Λ_{kj} are the elements of the matrix Λ . The matrix Λ is sometimes referred to as the **Jacobian matrix**.

The general solution of Equation (18.4.6) can be written if the eigenvalues and the eigenvectors of the matrix Λ are known. Let ω_k be the eigenvalues and ψ_k the corresponding eigenvectors:

$$\Lambda \psi_k = \omega_k \psi_k \quad (18.4.7)$$

In general, for an n -dimensional matrix there are n eigenvalues and n eigenvectors. (Note that ψ_k is a vector and the subscript k indicates different vectors.) If the eigenvalues ω_k and the eigenvectors ψ_k are known, it is easy to see that, corresponding to each eigenvector and its eigenvalue, we have the following solution to Equation (18.4.6):

$$\mathbf{x} = e^{\omega_k t} \psi_k \quad (18.4.8)$$

This can be easily seen by substituting Equation (18.4.8) into Equation (18.4.6). Since a linear combination of solutions of a linear equation is also a solution, the general solution to Equation (18.4.6) can be written as

$$\mathbf{x} = \sum_k c_k e^{\omega_k t} \psi_k \quad (18.4.9)$$

in which the coefficients c_k are determined by \mathbf{x} at $t = 0$. Now the question of stability depends on whether the perturbation \mathbf{x} will grow or decay with time. Clearly, this depends on the eigenvalues ω_k : if one or more of the eigenvalues have a positive real part, the associated solutions (18.4.8) will grow exponentially. The corresponding eigenvectors are called **unstable modes**. Since a random perturbation will be of the form (18.4.9), which includes the unstable modes, the existence of a single eigenvalue with a positive real part is sufficient to make the perturbation grow with time. If all the eigenvalues have negative real parts, any small perturbation \mathbf{x} in the vicinity of the stationary solution will exponentially decay or regress to zero. (This need not be true for large perturbations \mathbf{x} for which the approximation (18.4.5) is not valid.)

Thus, a necessary and sufficient condition for the stability of a stationary state is that all eigenvalues of the associated Jacobian matrix, Λ , have negative real parts. An eigenvalue with a positive real part implies instability.

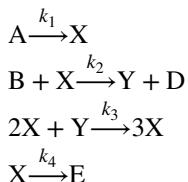
The example given below illustrates the application of the linear stability theory to a chemical system. As we have seen in the previous section, thermodynamic considerations lead us to the conclusion that instability

can arise only when the system is far from thermodynamic equilibrium and, generally, when autocatalysis is present.

The exponential growth of the perturbation does not continue indefinitely; the growth eventually stops due to the nonlinear terms. Through this process, the system makes a transition from an unstable state to a stable state. Thus, driven by instability, the system makes a transition to a new state. This new state is often an organized state, a state with lower entropy. These organized states can be maintained indefinitely as long as the flows are maintained.

18.4.1 An Example

We shall illustrate the use of linear stability theory with the following reaction scheme:



in which we assume A and B are maintained at a constant value while D and E are removed so that all four concentrations are maintained at a constant value. Furthermore, we completely ignore the reverse reactions because we assume their rates to be extremely small. This leads to the following set of kinetic equations that we will study in more detail in the following chapter.

Instead of using X_1 and X_2 , we shall use concentrations [X] and [Y] for the system variables:

$$\frac{d[X]}{dt} = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] = Z_1 \quad (18.4.10)$$

$$\frac{d[Y]}{dt} = k_2[B][X] - k_3[X]^2[Y] = Z_2 \quad (18.4.11)$$

Here [A] and [B] are the parameters (concentrations that are maintained at fixed values) corresponding to λ (Equation (18.4.1)). One can easily obtain the stationary solutions to this equation (Example 18.6):

$$[X]_s = \frac{k_1}{k_4}[A], \quad [Y]_s = \frac{k_4 k_2}{k_3 k_1} \frac{[B]}{[A]} \quad (18.4.12)$$

The Jacobian matrix evaluated at the stationary state is

$$\begin{bmatrix} \frac{\partial Z_1}{\partial [X]} & \frac{\partial Z_1}{\partial [Y]} \\ \frac{\partial Z_2}{\partial [X]} & \frac{\partial Z_2}{\partial [Y]} \end{bmatrix} = \begin{bmatrix} -k_2[B] + 2k_3[X]_s[Y]_s - k_4 & k_3[X]_s^2 \\ k_2[B] - 2k_3[X]_s[Y]_s & -k_3[X]_s^2 \end{bmatrix} = \Lambda$$

The product $[X]_s [Y]_s$ in the above matrix can be simplified using Equations (18.4.12) and the resulting matrix has the form:

$$\begin{bmatrix} k_2[B] - k_4 & k_3[X]_s^2 \\ -k_2[B] & -k_3[X]_s^2 \end{bmatrix} = \Lambda \quad (18.4.13)$$

The stationary state (18.4.12) becomes unstable when the real parts of the eigenvalues of (18.4.13) become positive. The **eigenvalue equation** or the **characteristic equation** of a matrix Λ , whose solutions are the eigenvalues, is

$$\text{Det}[\Lambda - \lambda I] = 0 \quad (18.4.14)$$

in which ‘Det’ stands for the determinant. For a 2×2 matrix such as (18.4.13) it is easy to see that the characteristic equation is

$$\lambda^2 - (\Lambda_{11} + \Lambda_{22})\lambda + (\Lambda_{11}\Lambda_{22} - \Lambda_{21}\Lambda_{12}) = 0 \quad (18.4.15)$$

in which Λ_{ij} are the elements of the matrix Λ . If all the matrix elements Λ_{ij} are real, as is the case for chemical systems, the solutions of the characteristic equation must be complex conjugate pairs because coefficients in the equation are real. For the matrix (18.4.13) we shall consider the case of a complex conjugate pair. We shall look at these solutions as functions of the concentration $[B]$ and investigate whether their real parts, which are initially negative, can become positive due to an appropriate change in $[B]$. The point at which the real parts reach zero will be the point of transition from stability to instability.

For Equation (18.4.15), since the coefficient of the linear term is the negative of the sum of the roots (Exercise 18.7), if λ_{\pm} are the two roots, we have

$$\lambda_+ + \lambda_- = (\Lambda_{11} + \Lambda_{22}) = k_2[B] - k_4 - k_3[X]_s^2 \quad (18.4.16)$$

If the real parts of this complex conjugate pair, λ_{\pm} , are negative then $k_2[B] - k_4 - k_3[X]_s^2 < 0$; if they are positive then $k_2[B] - k_4 - k_3[X]_s^2 > 0$.¹ Thus the condition that requires positive real parts for the onset of instability leads to

$$[B] > \frac{k_4}{k_2} + \frac{k_3}{k_2}[X]_s^2$$

or

$$[B] > \frac{k_4}{k_2} + \frac{k_3}{k_2} \frac{k_1^2}{k_4} [A]^2 \quad (18.4.17)$$

where we have used Equation (18.4.12) for $[X]_s$. Thus, for a fixed value of $[A]$, as the value of $[B]$ increases, when condition (18.4.17) is satisfied, the stationary state (18.4.12) becomes unstable. In the next chapter we will see that this instability leads to oscillations.

Linear stability analysis does not provide a means of determining how the system will evolve when a state becomes unstable. To understand the system’s behavior fully, the full nonlinear equation has to be considered. Often we encounter nonlinear equations for which solutions cannot be obtained analytically. However, with the availability of powerful desktop computers and software, numerical solutions can be obtained without much difficulty. To obtain numerical solutions to nonlinear equations considered in the following chapter, *Mathematica* codes are provided at the end of Chapter 19.

¹If λ_{\pm} are real roots, $\lambda_+ + \lambda_- > 0$ implies that at least one of the roots is positive.

Appendix 18.1 A General Property of $d_F P/dt$

In this appendix we show that, regardless of the distance from equilibrium,

$$\frac{d_F P}{dt} \leq 0 \quad (\text{A18.1.1})$$

The validity of (A18.1.1) depends on the validity of the local equilibrium. In Chapter 12 we have seen that the second-order variation of entropy $\delta^2 S$ is negative because quantities such as the molar heat capacity C_V , isothermal compressibility κ_T and $-\sum_{i,j}(\partial A_i/\partial \xi_j)\delta \xi_i \delta \xi_j$ are positive. This condition remains valid for an elemental volume δV , which is in local equilibrium. We can see the relation between the derivative $d_F P/dt$ and quantities such as $-\sum_{i,j}(\partial A_i/\partial \xi_j)\delta \xi_i \delta \xi_j$, which have a definite sign, as follows.

A18.1.1 Chemical Reactions

Consider a closed homogeneous nonequilibrium system undergoing a chemical reaction at uniform constant temperature. The affinities A_k are functions of the extents of reaction ξ_j and

$$\frac{\partial A_k}{\partial t} = \sum_j \left(\frac{\partial A_k}{\partial \xi_j} \right) \left(\frac{\partial \xi_j}{\partial t} \right) = \sum_j \left(\frac{\partial A_k}{\partial \xi_j} \right) v_j \quad (\text{A18.1.2})$$

Therefore:

$$\frac{d_F P}{dt} = \frac{1}{T} \sum_{k,j} \left(\frac{\partial A_k}{\partial \xi_j} \right) v_j v_k \leq 0 \quad (\text{A18.1.3})$$

which follows from the general relation $-\sum_{i,j}(\partial A_i/\partial \xi_j)\delta \xi_i \delta \xi_j \geq 0$ valid for a system in local equilibrium (12.4.5). This proof can be extended to open systems following along the lines of the proof for isothermal diffusion given below.

A18.1.2 Isothermal Diffusion

In this case we begin with

$$\frac{d_F P}{dt} = - \int \sum_k \mathbf{J}_k \cdot \frac{\partial}{\partial t} \nabla \left(\frac{\mu_k}{T} \right) dV = - \int \frac{1}{T} \sum_k \mathbf{J}_k \cdot \nabla \left(\frac{\partial \mu_k}{\partial t} \right) dV \quad (\text{A18.1.4})$$

Using the identity $\nabla \cdot (f \mathbf{J}) = f \nabla \cdot \mathbf{J} + \mathbf{J} \cdot \nabla f$, the right-hand side can be written as

$$- \int \frac{1}{T} \mathbf{J}_k \cdot \nabla \left(\frac{\partial \mu_k}{\partial t} \right) dV = - \int \frac{1}{T} \nabla \cdot \left[\mathbf{J}_k \left(\frac{\partial \mu_k}{\partial t} \right) \right] dV + \int \frac{1}{T} \left(\frac{\partial \mu_k}{\partial t} \right) \nabla \cdot \mathbf{J}_k dV \quad (\text{A18.1.5})$$

Using Gauss's theorem, the first term on the right-hand side can be converted into a surface integral. Since we assume that the value of μ_k is time independent at the boundary, i.e. the boundary conditions are time independent, this surface integral vanishes. Using the relations

$$\frac{\partial \mu_k}{\partial t} = \sum_j \frac{\partial \mu_k}{\partial n_j} \frac{\partial n_j}{\partial t} \quad \text{and} \quad \frac{\partial n_k}{\partial t} = -\nabla \cdot \mathbf{J}_k \quad (\text{A18.1.6})$$

the second term can be written as

$$\int \frac{1}{T} \left(\frac{\partial \mu_k}{\partial t} \right) \nabla \cdot \mathbf{J}_k dV = \frac{-1}{T} \int \sum_j \frac{\partial \mu_k}{\partial n_j} \left(\frac{\partial n_j}{\partial t} \right) \left(\frac{\partial n_k}{\partial t} \right) dV \quad (\text{A18.1.7})$$

Combining Equations (A18.1.7), (A18.1.5) and (A18.1.4), we arrive at

$$\frac{d_F P}{dt} = \frac{-1}{T} \int \sum_{jk} \frac{\partial \mu_k}{\partial n_j} \left(\frac{\partial n_j}{\partial t} \right) \left(\frac{\partial n_k}{\partial t} \right) dV \leq 0$$

The right-hand side of this expression is negative because

$$-\sum_{jk} \frac{\partial \mu_k}{\partial n_j} \left(\frac{\partial n_j}{\partial t} \right) \left(\frac{\partial n_k}{\partial t} \right) \leq 0$$

is valid for systems in local equilibrium (Equation (12.4.9)). The general validity of Equation (18.2.3) is proved in the literature [1].

Appendix 18.2 General Expression for the Time Derivative of $\delta^2 S$

The relation

$$\frac{d}{dt} \frac{\delta^2 S}{2} = \int_V \sum_k \delta F_k \delta J_k dV \quad (\text{A18.2.1})$$

can be obtained as follows. We begin by taking the time derivative of $\delta^2 S/2$ as defined in Equation (18.3.4). For notational simplicity, we shall denote the time derivatives of a quantity x by $\dot{x} \equiv \partial x / \partial t$. The time derivative of $\delta^2 S$ can be written as

$$\begin{aligned} \delta^2 \dot{S} &= \int \left[\left(\frac{\partial^2 s}{\partial u^2} \right) 2\delta u(\delta \dot{u}) + 2 \sum_k \left(\frac{\partial^2 s}{\partial u \partial n_k} \right) (\dot{u} \delta n_k + \delta u \delta \dot{n}_k) \right. \\ &\quad \left. + 2 \sum_k \left(\frac{\partial^2 s}{\partial n_i \partial n_k} \right) \delta \dot{n}_i \delta n_k \right] dV \end{aligned} \quad (\text{A18.2.2})$$

in which the factor 2 appears in the last term because we used the relation

$$\frac{\partial^2 s}{\partial n_i \partial n_k} = \frac{\partial^2 s}{\partial n_k \partial n_i}$$

Next, noting that $(\partial s / \partial u)_{n_k} = 1/T$ and $(\partial s / \partial n_k)_u = -\mu_k/T$, we can write Equation (A18.2.2) as

$$\begin{aligned} \delta^2 \dot{S} &= \int 2 \left[\left(\frac{\partial}{\partial u} \frac{1}{T} \right) \delta u(\delta \dot{u}) + \sum_k \left(\frac{\partial}{\partial n_k} \frac{1}{T} \right) \delta \dot{u} \delta n_k \right] dV \\ &\quad + \int 2 \left[\sum_k \frac{\partial}{\partial u} \left(\frac{-\mu_k}{T} \right) \delta u \delta \dot{n}_k + \sum_{ik} \frac{\partial}{\partial n_i} \left(\frac{-\mu_k}{T} \right) \delta n_i \delta \dot{n}_k \right] dV \end{aligned} \quad (\text{A18.2.3})$$

We now observe that, since u and n_k are independent variables, we can write

$$\delta \left(\frac{1}{T} \right) = \sum_k \left(\frac{\partial}{\partial n_k} \frac{1}{T} \right) \delta n_k + \left(\frac{\partial}{\partial u} \frac{1}{T} \right) \delta u \quad (\text{A18.2.4})$$

$$\delta \left(\frac{\mu_i}{T} \right) = \sum_k \left(\frac{\partial}{\partial n_k} \frac{\mu_i}{T} \right) \delta n_k + \left(\frac{\partial}{\partial u} \frac{\mu_i}{T} \right) \delta u \quad (\text{A18.2.5})$$

Equations (A18.2.4) and (A18.2.5) enable us to reduce (A18.2.3) to the simple form

$$\delta^2 \dot{S} = 2 \int \left[\delta \left(\frac{1}{T} \right) \delta \dot{u} + \sum_k \delta \left(\frac{-\mu_k}{T} \right) \delta \dot{n}_k \right] dV \quad (\text{A18.2.6})$$

This relation can be written in terms of the changes in thermodynamic forces $\delta \nabla(1/T)$ and $\delta \nabla(-\mu_k/T)$ and the corresponding flows $\delta \mathbf{J}_u$ and $\delta \mathbf{J}_k$, using the balance equations for energy density u and the concentrations n_k :

$$\frac{\partial u}{\partial t} = \dot{u} = -\nabla \cdot \mathbf{J}_u \quad (\text{A18.2.7})$$

$$\frac{\partial n_k}{\partial t} = \dot{n}_k = -\nabla \cdot \mathbf{J}_k + \sum_i v_{ki} v_i \quad (\text{A18.2.8})$$

in which v_{ki} is the stoichiometric coefficient of reactant k in reaction i and v_i is the velocity of reaction i . If we denote the stationary state densities and flows by u_s , n_{ks} , \mathbf{J}_{us} , \mathbf{J}_{ks} and v_{is} , we have $\dot{u}_s = -\nabla \cdot \mathbf{J}_{us} = 0$ and $\dot{n}_s = -\nabla \cdot \mathbf{J}_{ks} + \sum_i v_{ki} v_{is} = 0$. Consequently, for a perturbation $u = u_s + \delta u$, $\mathbf{J}_u = \mathbf{J}_{us} + \delta \mathbf{J}_u$, etc., from the stationary state, we have

$$\delta \dot{u} = -\nabla \cdot \delta \mathbf{J}_u \quad (\text{A18.2.9})$$

$$\delta \dot{n}_k = -\nabla \cdot \delta \mathbf{J}_k + \sum_i v_{ki} \delta v_i \quad (\text{A18.2.10})$$

We substitute these expressions for $\delta \dot{u}$ and $\delta \dot{n}_k$ into (A18.2.6) and use the identity

$$\nabla \cdot (f \mathbf{J}) = f \nabla \cdot \mathbf{J} + \mathbf{J} \cdot \nabla f \quad (\text{A18.2.11})$$

in which f is a scalar function and \mathbf{J} is a vector field, and we use Gauss's theorem

$$\int_V (\nabla \cdot \mathbf{J}) dV = \int_{\Sigma} \mathbf{J} \cdot d\mathbf{a} \quad (\text{A18.2.12})$$

in which Σ is the surface enclosing the volume V and $d\mathbf{a}$ is the element of surface area. All this allows Equation (A18.2.6) to be written as follows:

$$\begin{aligned} \frac{1}{2} \delta^2 \dot{S} &= - \int_{\Sigma} \delta \left(\frac{1}{T} \right) \delta \mathbf{J}_u \cdot d\mathbf{a} + \int_V \delta \nabla \left(\frac{1}{T} \right) \delta \mathbf{J}_u dV \\ &\quad + \int_{\Sigma} \sum_k \delta \left(\frac{\mu_k}{T} \right) \delta \mathbf{J}_k \cdot d\mathbf{a} - \int_V \sum_k \delta \nabla \left(\frac{\mu_k}{T} \right) \delta \mathbf{J}_k dV \\ &\quad + \int_V \left[\sum_i \delta \left(\frac{A_i}{T} \right) \delta v_i \right] dV \end{aligned} \quad (\text{A18.2.13})$$

In obtaining this equation, we have used the relation $\sum_k v_{ki} \delta(\mu_k/T) = -\delta(A_i/T)$. The flows at the surface are fixed by the boundary conditions and are not subject to fluctuations, so the surface terms vanish. This leads us to the required result:

$$\begin{aligned} \frac{1}{2} \delta^2 \dot{S} &= \int_V \delta \nabla \left(\frac{1}{T} \right) \delta \mathbf{J}_u dV - \int_V \sum_k \delta \nabla \left(\frac{\mu_k}{T} \right) \delta \mathbf{J}_k dV + \int_V \left[\sum_i \delta \left(\frac{A_i}{T} \right) \delta v_i \right] dV \\ &= \int_V \sum_{\alpha} \delta F_{\alpha} \delta J_{\alpha} dV \end{aligned} \quad (\text{A18.2.14})$$

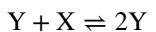
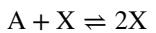
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Exercises

- 18.1** Calculate the affinities of the following reaction systems for a range of concentrations (or partial pressures) of the reactants and the products and compare them with RT at $T = 298$ K. Determine the ranges in which the system is thermodynamically in the linear regime using appropriate data from tables.
- (a) Racemization reaction $L \rightleftharpoons D$ (L and D are enantiomers).
 - (b) Reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (with partial pressures $P_{N_2O_4}$ and P_{NO_2}).
- 18.2** (a) What factors would you identify to conclude that the Earth's atmosphere is not in thermodynamic equilibrium?
 (b) Through an appropriate literature search, determine whether the atmospheres of Mars and Venus are in chemical equilibrium.
- 18.3** For the chemical reaction $A \rightleftharpoons B$, verify the general property $d_F P \leq 0$.
- 18.4** (a) Obtain inequality (18.3.11) for a perturbation $\delta[B]$ from the stationary states of reaction (18.3.9).
 (b) Obtain the 'excess entropy production' (18.3.13) for a perturbation $\delta[X]$ from the stationary states of reaction (18.3.12).
- 18.5** Obtain the excess entropy production and analyze the stability of the stationary states for the following reaction schemes:
- (a) $W \rightleftharpoons X \rightleftharpoons Z$, in which the concentrations of W and Z are maintained fixed at a nonequilibrium value.
 - (b) $W + X \rightleftharpoons 2X$, $X \rightleftharpoons Z$, in which the concentrations of W and Z are maintained fixed at a nonequilibrium value.
- 18.6** Show that the stationary states of Equations (18.4.10) and (18.4.11) are Equations (18.4.12).
- 18.7** For a polynomial equation of the type $\omega^n + A_1\omega^{n-1} + A_2\omega^{n-2} + \dots + A_n = 0$ show that coefficient $A_1 = -(\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n)$ and coefficient $A_n = (-1)^n (\lambda_1 \lambda_2 \lambda_3 \dots \lambda_n)$, where λ_k are roots.
- 18.8** For the following equations, obtain the stationary states and analyze their stability as a function of the parameter λ assuming A , B and C are positive:
- (a) $\frac{dx}{dt} = -Ax^3 + C\lambda x$
 - (b) $\frac{dx}{dt} = -Ax^3 + Bx^2 + C\lambda x$
 - (c) $\frac{dx}{dt} = \lambda x - 2xy$, $\frac{dy}{dt} = -y + xy$
 - (d) $\frac{dx}{dt} = -5x + 6y + x^2 - 3xy + 2y^2$, $\frac{dy}{dt} = -\lambda x - 14y + 2x^2 - 5xy + 4y^2$

18.9 Consider the reaction scheme:



Far from equilibrium, we only keep the forward reactions and we assume A and E are fixed. Using the linear stability theory, show that the perturbations around the nonequilibrium steady state lead to oscillations in [X] and [Y], as was discussed in Section 18.2. This model was used by Lotka and Volterra to describe the ‘struggle of life’ (see V. Volterra, *Theorie Mathématique de la Lutte pour la Vie*, 1931, Gauthier Villars: Paris). Here X is the prey (lamb) and Y is the predator (wolf). This model of the prey–predator interaction shows that the populations X and Y will exhibit oscillations.

19

Dissipative Structures

19.1 The Constructive Role of Irreversible Processes

One of the most profound lessons of nonequilibrium thermodynamics is the dual role of irreversible processes: as destroyers of order near equilibrium and as creators of order far from equilibrium. For far-from-equilibrium systems, there are no general extremum principles that predict the state to which it will evolve. The lack of extremum principles that uniquely predict the state to which a nonequilibrium system will evolve is a fundamental aspect of nonequilibrium systems. In stark contrast to equilibrium systems, which evolve to a state that minimizes a free energy, nonequilibrium systems can evolve unpredictably; their state cannot always be uniquely specified by macroscopic rate equations. This is because, for a given set of nonequilibrium conditions, it is often possible to have more than one state. As a result of random fluctuations, or other random factors such as small inhomogeneities or imperfections, the system evolves to one of the many possible states. Which one of these states a particular system will evolve to is, in general, not predictable. The new states thus attained are often ‘ordered states’ that possess spatiotemporal organization. Patterns in fluid flow, inhomogeneities in concentrations exhibiting geometrical patterns with great symmetry or periodic variations of concentrations are examples of such ordered states. Because of its fundamental character, we shall refer to the general phenomenon of a nonequilibrium system evolving to an ordered state as a result of fluctuations as **order through fluctuations** [1, 2].

In nonequilibrium systems, oscillating concentrations and geometrical concentration patterns can be a result of chemical reactions and diffusion, the same dissipative processes that, in an isolated system, wipe out inhomogeneities and drive the system to a stationary, timeless homogeneous state of equilibrium. Since the creation and maintenance of organized nonequilibrium structures are due to dissipative processes, they are called **dissipative structures** [3].

The two concepts of *dissipative structures* and *order through fluctuations* encapsulate the main aspects of nonequilibrium order that we describe in this chapter.

19.2 Loss of Stability, Bifurcation and Symmetry Breaking

In the previous chapter we have seen that the stability of the thermodynamic branch is no longer assured when a system is driven far from equilibrium. In Section 18.3 we have seen how a necessary condition (18.3.7) for

a system to become unstable can be obtained by using the second variation of entropy, $\delta^2 S$. Beyond this point, we are confronted with a multiplicity of states and unpredictability. To understand the precise conditions for instability and the subsequent behavior of a system, we need to use the specific features of the system, such as the rates of chemical reactions and the hydrodynamic equations. There are, however, some general features of far-from-equilibrium systems that we will summarize in this section. A detailed discussion of dissipative structures will be presented in the following sections.

The loss of stability of a nonequilibrium state can be analyzed using the general theory of stability for solutions of a nonlinear differential equation. Here we encounter the basic relationship between the loss of stability, multiplicity of solutions and symmetry. We also encounter the phenomenon of ‘bifurcation’ or ‘branching’ of new solutions of a differential equation from a particular solution. We shall first illustrate these general features for a simple nonlinear differential equation and then show how they are used to describe far-from-equilibrium systems.

19.2.1 An Elementary Example of Bifurcation and Symmetry Breaking

Consider the equation

$$\frac{d\alpha}{dt} = -\alpha^3 + \lambda\alpha \quad (19.2.1)$$

in which λ is a parameter. Our objective is to study the stationary solutions of this equation as a function of λ . Equation (19.2.1) possesses a simple twofold symmetry: it remains invariant when α is replaced by $-\alpha$. This means that if $\alpha(t)$ is a solution, then $-\alpha(t)$ is also a solution. If $\alpha(t) \neq -\alpha(t)$, then there are two solutions to the equation. In this way, symmetry and multiplicity of solutions are related.

The stationary states of this differential equation are

$$\alpha = 0, \quad \alpha = \pm\sqrt{\lambda} \quad (19.2.2)$$

Note the multiplicity of solutions related to symmetry. When a solution does not possess the symmetries of the differential equation, i.e. when $\alpha \neq -\alpha$, it is said to be a solution with a **broken symmetry** or a solution that has broken the symmetry. In this case, the solution $\alpha = 0$ is invariant when α is replaced by $-\alpha$, but the solution $\alpha = \pm\sqrt{\lambda}$ is not. Hence $\alpha = \pm\sqrt{\lambda}$ is said to have broken the symmetry of the differential equation. (Though this idea may seem rather trivial in this simple case, it has a rather important and nontrivial significance for nonequilibrium systems.)

Let us assume that, for physical reasons, we are seeking only real solutions of Equation (19.2.1). When $\lambda < 0$ there is only one real solution, but when $\lambda > 0$ there are three solutions, as shown in Figure 19.1. The new solutions for $\lambda > 0$ branch or bifurcate from the solution $\alpha = 0$. The value of λ at which new solutions bifurcate

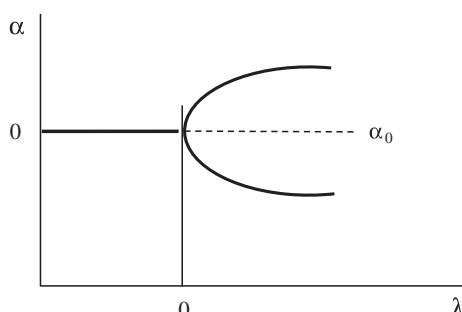


Figure 19.1 The bifurcation of solutions $\alpha = 0$ and $\alpha = \pm\sqrt{\lambda}$ to Equation (19.2.1) as a function of the parameter λ . The dashed line represents an unstable solution.

is called the **bifurcation point**. In Figure 19.1, $\lambda = 0$ is the bifurcation point. A similar bifurcation of new solutions from a given solution occurs generally in nonlinear equations, be they a simple algebraic equation as above, a set of coupled ordinary differential equations or more complex partial differential equations.

Turning to the question of stability, we shall now see that the solution $\alpha = 0$ becomes unstable precisely at the point where new solutions $\alpha = \pm\sqrt{\lambda}$ emerge. As we have seen earlier, a stationary solution α_s is locally stable if a small perturbation $\delta(t)$ from the solution decays to the stationary state. Thus we must look at the time evolution of $\alpha = \alpha_s + \delta(t)$ to determine if α_s is stable or not. Substituting $\alpha = \alpha_s + \delta(t)$ into Equation (19.2.1), and keeping only terms of the first order in δ , we obtain

$$\frac{d\delta}{dt} = -3\alpha_s^2\delta + \lambda\delta \quad (19.2.3)$$

For the stationary state $\alpha_s = 0$, we see that the solution is stable if $\lambda < 0$, because $\delta(t)$ decays exponentially. On the other hand, if $\lambda > 0$ the solution is locally unstable because $\delta(t)$ grows exponentially. At the same time, if we use Equation (19.2.3) to analyze the stability of the stationary states $\alpha_s = \pm\sqrt{\lambda}$, we find that they are stable. These stability properties of the stationary states mean that, as λ moves from a value less than zero to a value greater than zero, the solution $\alpha = 0$ becomes unstable and the system makes a transition to one of the two new solutions that bifurcate at $\lambda = 0$. To which of the two possible states the system will evolve is not deterministic; it depends on the random fluctuations in the system. The loss of stability implies that a random fluctuation will grow and drive the system to one of the two states, $\alpha_s = +\sqrt{\lambda}$ or $\alpha_s = -\sqrt{\lambda}$.

The bifurcation of new solutions at exactly the point where one solution loses stability is not a coincidence, it is a general property of the solutions of nonlinear equations. (This general relation between bifurcation and stability of solutions of nonlinear equations can be explained using *topological degree theory*, which is beyond the scope of this discussion.)

19.2.2 General Theory of Bifurcation

In far-from-equilibrium systems the loss of stability of the thermodynamic branch and the transition to a dissipative structure follows the same general features shown in the above simple example. The parameter such as λ corresponds to constraints – e.g. flow rates or concentrations maintained at a nonequilibrium value – that keep the system away from equilibrium. When λ reaches a particular value, the thermodynamic branch becomes unstable but at the same time new solutions now become possible; driven by fluctuations, the system makes a transition to one of the new states. As we did in Section 18.4, let us specify the state of the system by X_k , $k = 1, 2, \dots, n$ which, in general, may be functions of both position \mathbf{r} and time t . Let the equation that describes the spatiotemporal evolution of the system be

$$\frac{\partial X_k}{\partial t} = Z_k(X_i, \lambda) \quad (19.2.4)$$

Here λ is the nonequilibrium constraint. If the system under consideration is a homogeneous chemical system, then Z_k is specified by the rates of chemical reactions. For an inhomogeneous system, Z_k may contain partial derivatives to account for diffusion and other transport processes. It is remarkable that, whatever the complexity of Z_k , the loss of stability of a solution of Equation (19.2.4) at a particular value of λ and bifurcation of new solutions at this point are similar to those of Equation (19.2.1). As in the case of Equation (19.2.1), the symmetries of Equation (19.2.4) are related to the multiplicity of solutions. For example, in an isotropic system, the equations should be invariant under the inversion $\mathbf{r} \rightarrow -\mathbf{r}$. In this case, if $X_k(\mathbf{r}, t)$ is a solution then $X_k(-\mathbf{r}, t)$ will also be a solution; if $X_k(\mathbf{r}, t) \neq X_k(-\mathbf{r}, t)$ then there are two distinct solutions which are mirror images of each other.

Let X_{sk} be a stationary solution of Equation (19.2.4). The stability of this state can be analyzed as before by considering the evolution of $X_k = X_{sk} + \delta_k$, where δ_k is a small perturbation. If δ_k decays exponentially,

then the stationary state is stable. This generally happens when λ is less than a ‘critical value’ λ_c . When λ exceeds λ_c it may happen that the perturbations δ_k , instead of decaying exponentially, grow exponentially, thus making the state X_{sk} unstable. Precisely at λ_c , new solutions to Equation (19.2.4) will appear. As we will see in detail in the following sections, in the vicinity of λ_c , the new solutions often take the form

$$X_k(\mathbf{r}, t; \lambda) = X_{sk}(\lambda_c) + \alpha_k \psi_k(\mathbf{r}, t) \quad (19.2.5)$$

in which $X_{sk}(\lambda_c)$ is the stationary state when $\lambda = \lambda_c$, α_k are a set of ‘amplitudes’ that are to be determined and $\psi_k(r, t)$ are functions that can be obtained from Z_k in Equation (19.2.4). The general theory of bifurcation provides a means of obtaining the time evolution of the amplitudes α_k through a set of equations of the type (see Reference [4] and references therein)

$$\frac{d\alpha_k}{dt} = G(\alpha_k, \lambda) \quad (19.2.6)$$

These are called the **bifurcation equations**. In fact, though Equation (19.2.1) is an equation in its own right, it is also a bifurcation equation for systems that break a twofold symmetry. The multiplicity of solutions to Equation (19.2.6) corresponds to the multiplicity of solutions to the original equation (19.2.4).

In this manner, instability, bifurcation, multiplicity of solutions and symmetry are all interrelated. We shall now give a few detailed examples of instability of the thermodynamic branch leading to dissipative structures.

19.3 Chiral Symmetry Breaking and Life

The chemistry of life as we know it is founded on a remarkable asymmetry. A molecule whose geometrical structure is not identical to its mirror image is said to possess **chirality**, or handedness. Mirror-image structures of a chiral molecule are called **enantiomers**. Just as we distinguish the left and the right hand, the two mirror-image structures are identified as L- and D-enantiomers (L for ‘levo’ and D for ‘dextro’; R and S is another convention of identifying the two enantiomers). Amino acids, the building blocks of proteins, and deoxyribose in DNA are chiral molecules. In the entire biosphere, almost all amino acids that take part in the chemistry of life are L-amino acids (Figure 19.2) and the riboses in DNA and RNA are D-riboses (Figure 19.3). As Francis Crick noted in his book *Life Itself*, ‘The first great unifying principle of biochemistry is that the key molecules have the same hand in all organisms.’ This is all the more remarkable because chemical reactions show equal preference for the two mirror-image forms (except for very small differences due to parity-nonconserving electroweak interactions [5–7]).

Biochemistry’s hidden molecular asymmetry was discovered by Louis Pasteur in 1857. Nearly 150 years later, its true origin remains elusive and it is a subject of active research. Nevertheless, we can see how such a state might be realized in the framework of dissipative structures. First, we note that such an asymmetry can

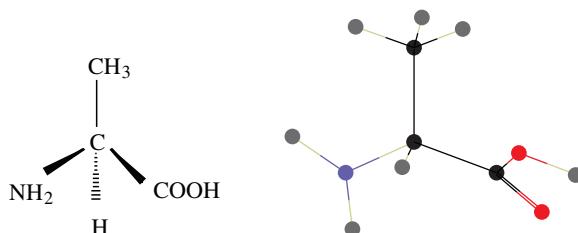


Figure 19.2 Proteins are made exclusively of L-amino acids. The amino acid shown is L-alanine. In other L-amino acids, different groups of atoms take the place of CH_3 .

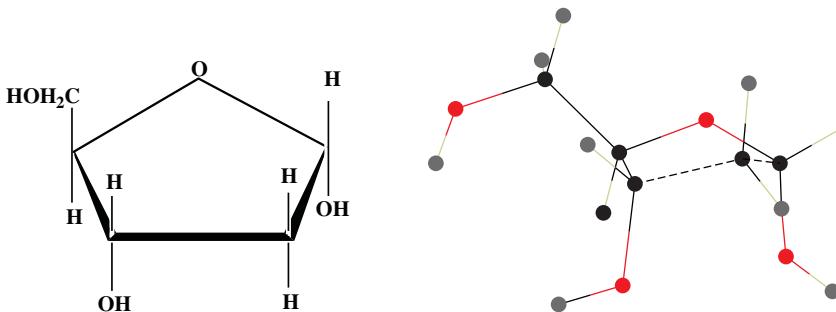


Figure 19.3 The 2-deoxy-D-ribose shown above is a basic chiral building block of DNA. Its mirror image structure, 2-deoxy-L-ribose, is excluded from the chemistry of life.

arise only under far-from-equilibrium conditions; at equilibrium, the concentrations of the two enantiomers must be equal. The maintenance of this asymmetry requires constant catalytic production of the preferred enantiomer in the face of interconversion between enantiomers, called **racemization**. (Racemization drives the system to the equilibrium state in which the concentrations of the two enantiomers will become equal.) Second, following the paradigm of order through fluctuations, we will presently see how, in systems with appropriate chiral autocatalysis, the thermodynamic branch, which contains equal amounts of L- and D-enantiomers, can become unstable. The instability is accompanied by the bifurcation of asymmetric states, or states of broken symmetry, in which one enantiomer dominates. Driven by random fluctuations, the system makes a transition to one of the two possible states.

In 1953 F.C. Frank [8] devised a simple model reaction scheme with chiral autocatalysis that could amplify a small initial asymmetry. We shall modify this reaction scheme so that its nonequilibrium aspects, instability and bifurcation of symmetry breaking states can be clearly seen (Figure 19.4). It includes chirally autocatalytic reactions:



Each enantiomer of X is produced directly from the achiral¹ reactants S and T, as shown in reactions (19.3.1) and (19.3.3) and autocatalytically, as shown in reactions (19.3.2) and (19.3.4). In addition, the two enantiomers react with one another and turn into an inactive dimer, P. Due to symmetry, the rate constants for the direct reactions, (19.3.1) and (19.3.3), as well as the autocatalytic reactions, (19.3.2) and (19.3.4), must be equal.

¹ Objects that do not possess a sense of handedness are called achiral. The molecule NH₃ is an example of an achiral molecule.

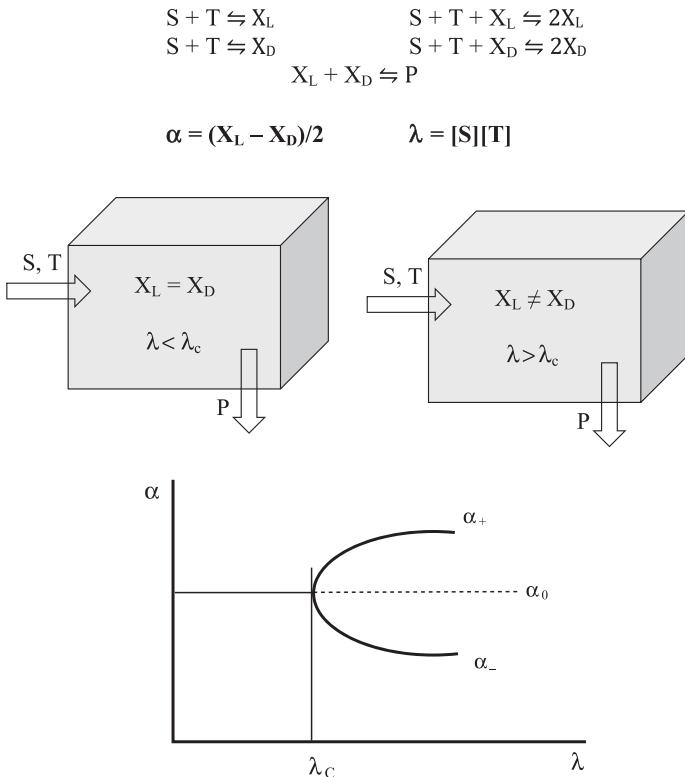


Figure 19.4 A simple autocatalytic reaction scheme in which X_L and X_D are produced with equal preference. However, in an open system, this leads to a dissipative structure in which $X_L \neq X_D$, a state of broken symmetry. A bifurcation diagram shows some general features of transitions to dissipative structures.

It is easy to see that, at equilibrium, the system will be in a *symmetric state*, i.e. $[X_L] = [X_D]$ (Exercise 19.3). Now let us consider an open system into which S and T are pumped and from which P is removed. For mathematical simplicity, we assume that the pumping is done in such a way that the concentrations $[S]$ and $[T]$ are maintained at a fixed level, and that due to removal of P the reverse reaction in (19.3.5) may be ignored. Such an approximation does not limit its conclusions in any significant way – as can be seen in the numerical simulations using the *Mathematica* codes that include the reverse reaction (see Appendix 19.1). The kinetic equations of this system are

$$\frac{d[X_L]}{dt} = k_{1f}[S][T] - k_{1r}[X_L] + k_{2f}[X_L][S][T] - k_{2r}[X_L]^2 - k_3[X_L][X_D] \quad (19.3.6)$$

$$\frac{d[X_D]}{dt} = k_{1f}[S][T] - k_{1r}[X_D] + k_{2f}[X_D][S][T] - k_{2r}[X_D]^2 - k_3[X_L][X_D] \quad (19.3.7)$$

Since the equilibrium constants of the direct reaction and the catalyzed reaction should be the same; the rate constants must be such that $(k_{1f}/k_{1r}) = (k_{2f}/k_{2r})$. To make the symmetric and asymmetric states explicit, it is convenient to define the following variables:

$$\lambda = [S][T], \quad \alpha = \frac{[X_L] - [X_D]}{2}, \quad \beta = \frac{[X_L] + [X_D]}{2} \quad (19.3.8)$$

When Equations (19.3.6) and (19.3.7) are rewritten in terms of α and β (Exercise 19.4), we have

$$\frac{d\alpha}{dt} = -k_{1r}\alpha + k_{2f}\lambda\alpha - 2k_{2r}\alpha\beta \quad (19.3.9)$$

$$\frac{d\beta}{dt} = k_{1f}\lambda - k_{1r}\beta - k_{2f}\lambda\beta - k_{2r}(\beta^2 + \alpha^2) - k_3(\beta^2 - \alpha^2) \quad (19.3.10)$$

The stationary states of these equations can be obtained after a little calculation (by setting $d\alpha/dt = d\beta/dt = 0$). A complete analytic study of the solutions of Equations (19.3.9) and (19.3.10) and their stability is somewhat lengthy and can be found in the literature [4]. We shall only state the main results of this analysis. With the *Mathematica* code provided in Appendix 19.1, the reader can explore the properties of the equation quite easily and verify the phenomenon of chiral symmetry breaking in this system (Figure 19.5).

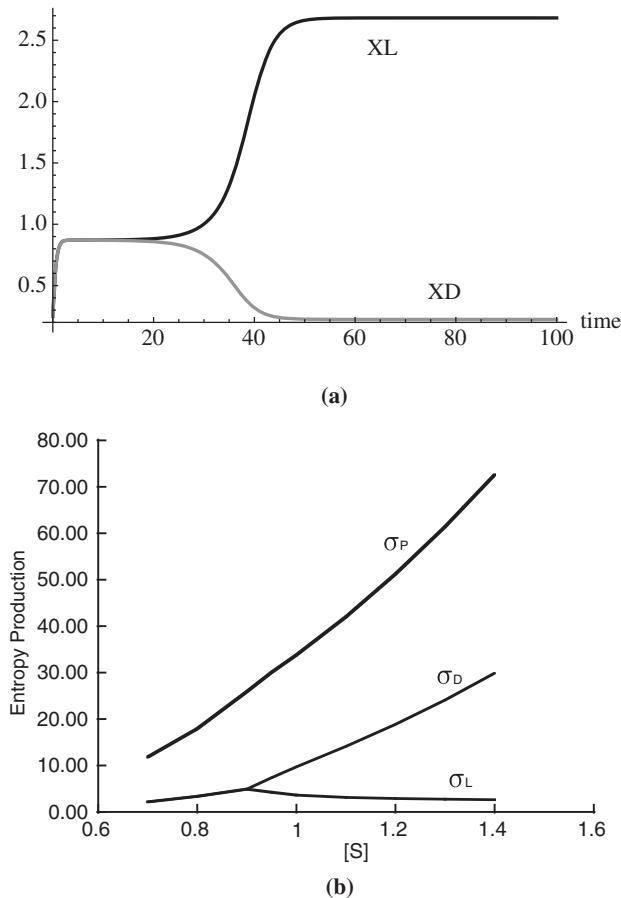


Figure 19.5 (a) Time evolution of X_L and X_D obtained using Mathematica Code A given in Appendix 19.1. For $\lambda > \lambda_c$ a small initial fluctuation in X_L grows to establish a state of broken symmetry in which the concentrations of X_L and X_D are unequal. (b) Steady-state entropy production in the reaction model (19.3.1) to (19.3.5) as a function of $[S]$, where σ_P is the entropy production due to reaction (19.3.5), σ_D is the entropy production due to reaction (19.3.3) and (19.3.4) and σ_L is the entropy production due to reactions (19.3.1) and (19.3.2). The numerical values used in the model are: $k_{1f} = 0.5$; $k_{1r} = 0.2$; $k_{2f} = 0.5$; $k_{2r} = (k_{1r}/k_{1f})k_{2f}$; $k_{3f} = 1.5$; $k_{3r} = 10^{-3}$; $[P] = 0.5$; $[T] = [S]$, and $[S]$ varies in the shown range.

For small values of λ the stable stationary state is

$$\alpha_s = 0 \quad (19.3.11)$$

$$\beta_s = \frac{2k_{2r}\beta_a + \sqrt{(2k_{2r}\beta_a)^2 + 4(k_{2r} + k_3)k_{1f}\lambda}}{2(k_{2r} + k_3)} \quad (19.3.12)$$

in which

$$\beta_a = \frac{k_{2f}\lambda - k_{1r}}{2k_{2r}}$$

This is a *symmetric* solution in which $[X_L] = [X_D]$ (as indicated by the subscript s). Using the stability analysis described in the previous chapter, it can be shown that this symmetric solution becomes unstable when λ is greater than a critical value λ_c . The value of λ_c is given by

$$\lambda_c = \frac{s + \sqrt{s^2 - 4k_{2f}^2 k_{1r}^2}}{2k_{2f}^2} \quad (19.3.13)$$

where

$$s = 2k_{2f}k_{1r} + \frac{4k_{2r}^2 k_{1r}}{k_3 - k_{2r}} \quad (19.3.14)$$

For the system of equations (19.3.9) and (19.3.10) it is possible to obtain an asymmetric stationary solution analytically:

$$\alpha_a = \pm \sqrt{\beta_a^2 - \frac{k_{1f}\lambda}{k_3 - k_{2r}}} \quad (19.3.15)$$

$$\beta_a = \frac{k_{2f}\lambda - k_{1r}}{2k_{2r}} \quad (19.3.16)$$

in which the subscript a stands for *asymmetric*. (We recommend the reader to use *Mathematica* code A in Appendix 19.1 to verify all these properties of the system.)

The simplest process that demonstrates chiral symmetry breaking is in the crystallization of NaClO_3 under far-from-equilibrium conditions [9]. During the last two decades, other chirally autocatalytic reactions were discovered through the mechanism of catalysis in these systems but are not as simple as the one presented in the above model [10]. These chirally autocatalytic reactions are capable of amplifying extremely small initial asymmetries. The simple model, however, leads to interesting conclusions regarding the sensitivity of bifurcation discussed below.

19.3.1 Entropy Production Is Chiral-Symmetry-Breaking Transitions

Dissipative structures are generated and maintained through irreversible processes that continuously generate entropy. Let us look at the entropy generation in the model system studied above. We assume each of the reactions (19.3.1) to (19.3.5) is an elementary step so that we can use the formula $(1/V)dS/dt = R(R_f - R_r) \ln(R_f/R_r)$, which gives the rate of entropy generated per unit volume by that reaction (see Equation (9.5.10); here R_f and R_r are the forward and reverse reaction rates and R is the gas constant. Though in the theoretical analysis we have ignored the reverse reaction (19.3.5), we shall include it in calculating the rate of entropy production to make the affinity of this reaction finite.

Using the numerical values specified in the caption of Figure 19.3b, we calculate the entropy production for each of the reactions in the above model. Our objective is to investigate how the rate of entropy production changes when the system moves from a region below the critical point, where system evolves to a symmetric steady state $[X_L] = [X_D]$, to a region above the critical point, where the system evolves to an asymmetric state, $[X_L] \neq [X_D]$. The values of $[S]$, $[T]$ and $[P]$ are the parameters of the system. Keeping $[P]$ at a fixed value and setting $[S] = [T]$, we obtain the steady-state rates of entropy production of each of the reactions in the model. We do the same for various values of $[S]$ and tabulate the entropy production rates for each value of $[S]$. The range of values of $[S]$ extends from the region below the critical point to a value above the critical point. Salient features of the results are shown graphically in Figure 19.5b. This graph shows the entropy production due to the reactions that produce X_L , (19.3.1) and (19.3.2), as σ_L ; similarly, σ_D is the corresponding entropy production for X_D . The entropy production due to the reaction that produces P is indicated as σ_P . The behavior of σ_L and σ_D is interesting: both increase identically till $[S]$ reaches the critical point and then they diverge. The entropy production due to the dominant X_L decreases above the critical point while that of X_D continues to increase. This indicates that the dominant species, X_L , is closer to its equilibrium value compared with X_D ; through the reaction $X_L + X_D \rightleftharpoons P$, the dominant X_L keeps the concentration of X_D at a low value and farther away from its equilibrium value. The bulk of the total entropy production of the system comes from the reaction producing P , as σ_P indicates. Furthermore, for the above model, by artificially making $X_L = X_D$ above the critical point one can show that the entropy production is lower for the asymmetric state. Thus, when the unstable symmetric state makes a transition to the asymmetric state above the critical point, then entropy production decreases. The rate of entropy production is in general not a widely studied topic. We encourage the reader to explore this aspect of nonequilibrium systems.

19.3.2 Nonequilibrium Symmetry Breaking and the Origin of Biomolecular Asymmetry

The above example shows how a far-from-equilibrium chemical system can generate and maintain chiral asymmetry, but it only provides a general framework in which we must seek the origins of biomolecular handedness. The origin of biomolecular handedness, or life's **homochirality**, remains to be explained [11, 12]. Here we shall confine our discussion to how the theory of nonequilibrium symmetry breaking contributes to this important topic. We cannot yet say with confidence whether chiral asymmetry arose in a prebiotic (i.e. before life) process and facilitated the evolution of life, or whether some primitive form of life that incorporated both L- and D-amino acids arose first and subsequent evolution of this life form led to the homochirality of L-amino acids and D-sugars. Both views have their proponents.

A related question is whether the dominance of L-amino acids in biochemistry was a matter of chance or whether it was a consequence of the extremely small but systematic chiral asymmetry due to electroweak interactions that are known to exist at the atomic and molecular levels [5–7, 13, 14]. Theories that support both views have been put forward but there is no general consensus on this matter either, mainly because there is a dearth of persuasive experimental evidence. However, the theory of nonequilibrium symmetry breaking provides a valuable means of assessing the plausible role of different models. For example, if we consider a prebiotic symmetry-breaking process that might have occurred in the oceans, it is possible to develop a general theory of symmetry breaking. A parameter λ , similar to the one in the above model, can be defined for any symmetry-breaking system. When $\lambda < \lambda_c$, the system will be in a symmetric state; for $\lambda > \lambda_c$ the symmetric state will become unstable and evolve to an asymmetric state. Furthermore, regardless of the complexities of the reaction scheme, based only on symmetry considerations, it is possible to describe the bifurcation of the chiral symmetry-breaking states with an equation of the following type [15, 16]:

$$\frac{d\alpha}{dt} = -A\alpha^3 + B(\lambda - \lambda_c)\alpha + Cg + \sqrt{\varepsilon f(t)} \quad (19.3.17)$$

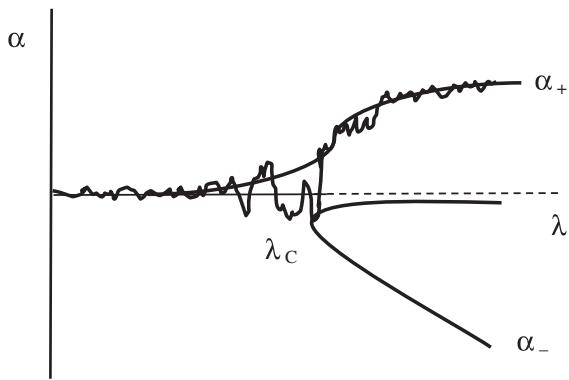


Figure 19.6 A symmetry-breaking transition or bifurcation in the presence of a small bias that favors one of the bifurcating branches. It can be analyzed through the general equation (19.3.17) and the probability of the system making a transition to the favored branch is given by Equation (19.3.18).

in which the coefficients A , B and C depend on the concentrations of the reactants and on the reaction rates (Figure 19.6). The parameter g is a small systematic bias, such as due to the electroweak force [6, 14] or other systematic chiral influences such as spin-polarized electrons that emerge from radioactive decay [17], or circularly polarized electromagnetic radiation emitted by certain stars that might fill large regions of space for long periods of time [11]. The systematic influence appears in the form of the rates of production or destruction of one enantiomer being larger than that of the other. The term $\sqrt{\epsilon}f(t)$ represents random fluctuations with the root-mean-square value $\sqrt{\epsilon}$. Since the assumptions about rates of production for biomolecules, their catalytic activities and their concentrations determine the coefficients A , B and C , rather than the details of the chemical reaction scheme, the model is constrained by our general understanding of the prebiotic chemistry. Equation (19.3.17) provides a way to assess whether a given prebiotic model can produce and maintain the required asymmetry in a reasonable amount of time.

Furthermore, Equation (19.3.17) can also give us a quantitative measure for the systematic chiral influence g . Detailed analysis [16, 18] of this equation has shown that the sensitivity of the bifurcation to the systematic influence depends on the rate at which the system moves through the critical point λ_c ; i.e. we assume that $\lambda = \lambda_0 + \gamma t$, so that the initial value of λ_0 is less than λ_c , but that λ gradually increases to a value larger than λ_c at an average rate γ . This process may correspond, for example, to a slow increase in the concentrations of biomolecules in the oceans. It has been shown [16, 18] that the probability P of the system making a symmetry-breaking transition to the asymmetric state favored by the systematic chiral influence g is given by

$$P = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^N e^{-x^2/2} dx \quad \text{where} \quad N = \frac{Cg}{\sqrt{\epsilon}/2} \left(\frac{\pi}{B\gamma} \right)^{1/4} \quad (19.3.18)$$

Although derived in the context of biomolecular handedness, this formula is generally valid for any system that breaks a twofold symmetry, such as mirror inversion. Using this formula, it is possible to understand the extraordinary sensitivity of bifurcation to small systematic biases that favor one enantiomer by increasing its production rate. Calculations show that L-amino acids have a lower ground-state energy [14]. For example, it can be estimated that the chiral asymmetry of the electroweak interaction can create differences of the order of one part in 10^{17} between the production rates of the enantiomers. Application of the above theory shows that if the autocatalytic production rate of the chiral molecules is faster than the racemization rates, then for a period in the range 10^4 to 10^5 years, the enantiomer favored by the electroweak force will dominate [16].

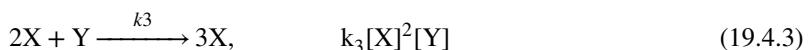
For such a scenario, there is currently no experimental evidence to show us how chiral autocatalysis with the required properties can originate in prebiotic chiral molecules.

Many different scenarios have been suggested for the possible origins of biomolecular handedness. An extensive review can be found in the literature [19]. Note that, even if one is considering a process of chiral asymmetry generation after ‘life’ arose, equations of the type (19.3.17) can still be used to describe the symmetry-breaking process, but this time the model will contain as ‘reactants’ the self-replicating unit of life.

19.4 Chemical Oscillations

Our next example of a dissipative structure illustrates how the breaking of time-translation symmetry leads to oscillatory behavior. Some early reports of concentration oscillations were discounted because it was widely believed that such behavior was not consistent with thermodynamics. That is why the report on oscillating reactions by Bray in 1921 and Belousov in 1958 were met with skepticism [20]. Although it is true that oscillations of the extent of reaction ξ about its equilibrium value will violate the Second Law, oscillations of concentration about a nonequilibrium value of ξ do not violate the Second Law. When it was realized that systems far from thermodynamic equilibrium could exhibit oscillations, interest in these and other oscillating reactions rose sharply and gave rise to a rich study of dissipative structures in chemical systems.

Developments in the theoretical understanding of instability for nonequilibrium states in the 1960s [3] stimulated the experimental study of autocatalytic chemical kinetics that could give rise to concentration oscillations through the phenomenon of bifurcation. In 1968 Prigogine and Lefever [21] developed a simple model that not only demonstrated clearly how a nonequilibrium system can become unstable and make a transition to an oscillatory state, but also proved to be a rich source for theoretical understanding of propagating waves and almost every other phenomenon observed in real chemical systems, most of which are extremely complex to study. Due to its impact on the study of dissipative structures, it is often called the **Brusselator** (after its place of origin, the Brussels School of Thermodynamics) or the ‘trimolecular model’ due to the trimolecular autocatalytic step in the reaction scheme. Because of its theoretical simplicity, we shall discuss this reaction first and then present the experimentally studied Belousov–Zhabotinsky reaction. The Brusselator reaction scheme and the corresponding rates are:



The net reaction of this scheme is $A + B \rightarrow D + E$. We assume that the concentrations of the reactants A and B are maintained at a desired nonequilibrium value through appropriate flows. The products D and E are removed as they are formed. We also assume that the reaction occurs in a solution that is well stirred and hence homogeneous. If we further assume that all the reverse reactions are so slow they can be neglected, we have the following rate equations for the species X and Y:

$$\frac{d[X]}{dt} = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] \equiv Z_1 \quad (19.4.5)$$

$$\frac{d[Y]}{dt} = k_2[B][X] - k_3[X]^2[Y] \equiv Z_2 \quad (19.4.6)$$

One can easily verify (Exercise 19.5) that the stationary solutions, $[X]_s$ and $[Y]_s$, to these equations are

$$[X]_s = \frac{k_1}{k_4} [A], \quad [Y]_s = \frac{k_4 k_2}{k_3 k_1} \frac{[B]}{[A]} \quad (19.4.7)$$

As was explained in Section 18.4, the stability of the stationary state depends on the eigenvalues of the Jacobian matrix

$$\begin{bmatrix} \frac{\partial Z_1}{\partial [X]} & \frac{\partial Z_1}{\partial [Y]} \\ \frac{\partial Z_2}{\partial [X]} & \frac{\partial Z_2}{\partial [Y]} \end{bmatrix} \quad (19.4.8)$$

evaluated at the stationary state (19.4.7). The explicit form of the Jacobian matrix that was derived in Chapter 18 is (see Equation (18.4.13)):

$$\begin{bmatrix} k_2[B] - k_4 & k_3[X]_s^2 \\ -k_2[B] & -k_3[X]_s^2 \end{bmatrix} = M \quad (19.4.9)$$

The example in Section 18.4 shows how the stationary state (19.4.7) becomes unstable when a complex conjugate pair of eigenvalues of the matrix M cross the imaginary axis; for the Brusselator this happens when

$$[B] > \frac{k_4}{k_2} + \frac{k_3 k_1^2}{k_2 k_4^2} [A]^2 \quad (19.4.10)$$

The system makes a transition to an oscillatory state and the resulting oscillations are shown in Figure 19.7. The steady states and the transition to oscillations can easily be investigated using the *Mathematica* codes provided in Appendix 19.1.

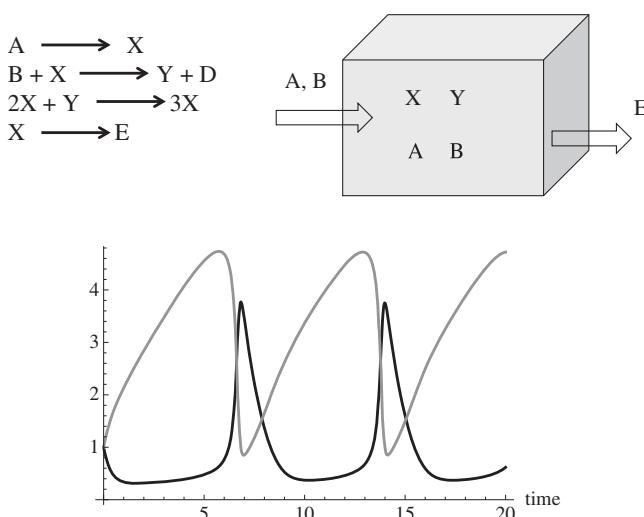
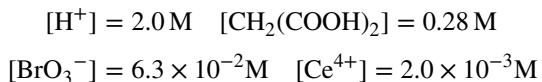


Figure 19.7 Brusselator model, model flow reactor and oscillations in $[X]$ and $[Y]$ obtained using Mathematica in Appendix 19.1.

19.4.1 The Belousov–Zhabotinsky Reaction

Once it became clear that concentration oscillations are not inconsistent with the laws of thermodynamics (as the theoretical models of oscillating reactions showed), interest grew in the neglected 1958 report by Belousov and the later experiments of Zhabotinsky reported in a 1964 article [22]. These experimental studies of Belousov and Zhabotinsky were conducted in the Soviet Union and made known to the Western world through the Brussels School of Thermodynamics. In the United States, the study of the Belousov–Zhabotinsky oscillations was taken up by Field, Körös and Noyes [23], who performed a thorough-study of the reaction mechanism in the early 1970s. This was an important landmark in the study of oscillating reactions. Field, Körös and Noyes identified the key steps in the rather complex **Belousov–Zhabotinsky reaction** and developed a model – which we shall refer to as the **FKN model** – consisting of only three variables that showed how the oscillations arise.

The Belousov–Zhabotinsky reaction is basically catalytic oxidation of an organic compound such as malonic acid, $\text{CH}_2(\text{COOH})_2$. The reaction occurs in an aqueous solution and is easily performed in a beaker by simply adding the following reactants in the concentrations shown:



After an initial ‘induction’ period, the oscillatory behavior can be seen in the variation of the concentration of the Ce^{4+} ion, due to which there is a change in color from colorless to yellow. Many variations of this reaction – with more dramatic variations of color – are known today. (A wealth of detail about the Belousov–Zhabotinsky may be found in the literature [24].)

Box 19.1 presents a simplified version of the reaction mechanism from which the FKN model was developed. Later models of the Belousov–Zhabotinsky reactions have included as many as 22 reaction steps. The FKN model of the Belousov–Zhabotinsky reaction makes the following identifications: A = BrO_3^- , X = HBrO_2 , Y = Br^- , Z = Ce^{4+} , P = $[\text{HBrO}]$ and B = [Org], an organic species that is oxidized. In modeling the reaction, $[\text{H}^+]$ is absorbed in the definition of the rate constant. The reaction scheme consists of the following steps and corresponding rates:

- Generation of HBrO_2



- Autocatalytic production of HBrO_2



- Consumption of HBrO_2



- Oxidation of the organic reactants



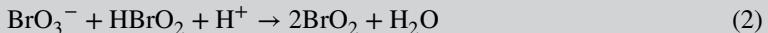
Box 19.1 The Belousov–Zhabotinsky reaction and the FKN model

The Field–Köros–Noyes (FKN) model of the Belousov–Zhabotinsky reaction consists of the following steps with A = BrO₃⁻, X = HBrO₂, Y = Br⁻, Z = Ce⁴⁺, P = HBrO and B = Org. In modeling the reaction, [H⁺] is absorbed in the definition of the rate constant.

- Generation of HBrO₂ : A + Y → X + P

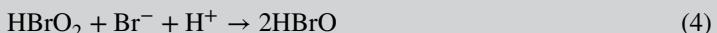


- Autocatalytic production of HBrO₂ : A + X → 2X + 2Z

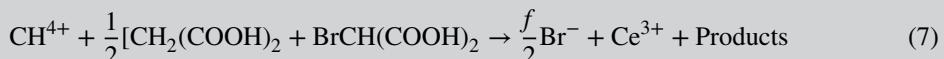
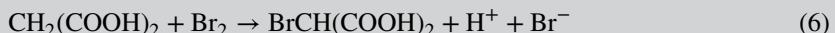


The net reaction, (2) + 2(3), is autocatalytic in HBrO₂. Since the rate-determining step is (2), the reaction is modeled as $\text{BrO}_3^- + \text{HBrO}_2 \xrightarrow{\text{H}^+, \text{Ce}^{3+}} + 2\text{Ce}^{4+} + 2\text{HBrO}_2$

- Consumption of HBrO₂ : X + Y → 2P and 2X → A + P



- Oxidation of the organic reactants: B + Z → (f/2)Y



The oxidation of the organic species is a complex reaction. It is approximated by a single rate determining step (7). In the FKN model, concentration [B] of the organic species is assumed to be constant. The value of the effective stoichiometric coefficient *f* is a variable parameter. Oscillations occur if *f* is in the range 0.5–2.4.

The corresponding rate equations are

$$\frac{d[X]}{dt} = k_1[A][Y] + k_2[A][X] - k_3[X][Y] - 2k_4[X]^2 \quad (19.4.16)$$

$$\frac{d[Y]}{dt} = -k_1[A][Y] - k_3[X][Y] + \frac{f}{2}k_5[B][Z] \quad (19.4.17)$$

$$\frac{d[Z]}{dt} = 2k_2[A][X] - k_5[B][Z] \quad (19.4.18)$$

Stationary states of this equation can be found after a little calculation (Exercise 19.7). To study its stability involves analyzing the roots of a third-degree equation. There are many analytical methods [25] to analyze the oscillatory behavior of such a system, but these details are outside our main objective of giving examples of oscillating chemical systems. The oscillatory behavior of these equations may be numerically studied quite

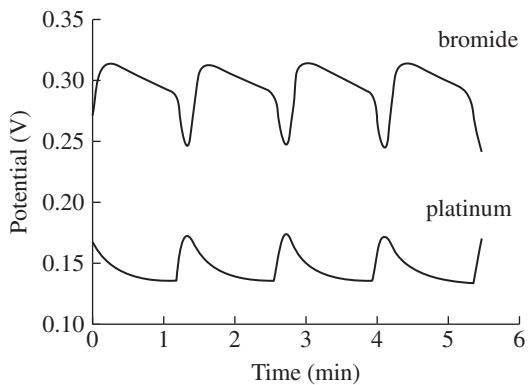


Figure 19.8 Experimentally observed oscillations in $[Br^-]$ for the Belousov–Zhabotinsky reaction; the concentrations were measured using electrodes. (Courtesy of John Pojman.)

easily using *Mathematica* Code C in Appendix 19.1 (Figures 19.8 and 19.9). For numerical solutions, one may use the following data [25]:

$$\begin{aligned} k_1 &= 1.28 \text{ mol}^{-1} \text{ L s}^{-1}, k_2 = 8.0 \text{ mol}^{-1} \text{ L s}^{-1}, \quad k_3 = 8.0 \times 10^5 \text{ mol}^{-1} \text{ L s}^{-1} \\ k_4 &= 2.0 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}, \quad k_5 = 1.0 \text{ mol}^{-1} \text{ L s}^{-1} \\ [B] &= [Org] = 0.02M, \quad [A] = [BrO_3^-] = 0.06M, \quad 0.5 < f < 2.4 \end{aligned} \quad (19.4.19)$$

The Belousov–Zhabotinsky reaction shows oscillations of great variety and complexity; it even exhibits chaos. In chaotic systems arbitrarily close initial conditions diverge exponentially; the system exhibits aperiodic behavior. A review by Epstein and Showalter [26] summarizes these aspects. It also produces propagating waves and multistability. A large number of very interesting phenomena have been studied using this reaction [24, 25].

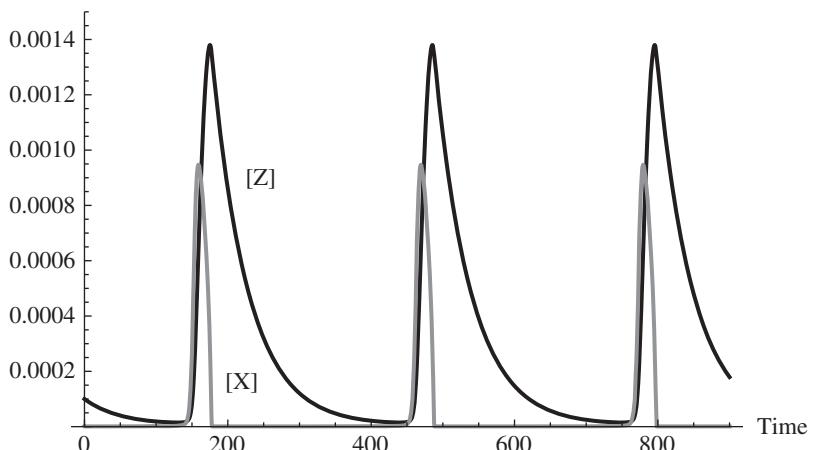


Figure 19.9 Oscillatory solutions obtained numerically using the FKN model of the Belousov–Zhabotinsky reaction: $[X] = [HBrO_2]$ and $[Z] = [Ce^{4+}]$. The plots were obtained using *Mathematica* codes in Appendix 19.1.

19.4.2 Other Oscillating Reactions

During the last two decades, many more oscillating chemical reactions have been discovered. Indeed, Irving Epstein and coworkers in the United States [27–29] and De Kepper and Boissonade in France [30] developed a systematic way of designing oscillating chemical reactions. In biochemical systems, one of the most interesting oscillating behaviors is found in the glycolytic reaction. A recent monograph by Albert Goldbeter [31] summarizes the vast amount of study on oscillatory biochemical systems.

19.5 Turing Structures and Propagating Waves

From the delicate beauty of the butterfly to the ‘fearful symmetry’ of the tiger, Nature is full of wondrous patterns, both animate and inanimate. How do these patterns arise? Dissipative processes in systems far from thermodynamic equilibrium may provide at least a partial answer.

The emergence of biological morphology during embryonic development – with hands and feet and eyes all in the right place – is a fascinating subject (a popular account of this subject is Lewis Wolpert’s *Triumph of the Embryo*, 1991, Oxford University Press). What mechanism produces the morphology of living organisms? In 1952 the British mathematician Alan Turing suggested a mechanism based on the processes of chemical reactions and diffusion [32]. He showed, by devising a simple model, how chemical reactions and diffusion can work in consonance to produce stable stationary patterns of concentrations. Turing proposed it to explain biological morphogenesis. Today we know that biological morphogenesis is a very complex process, too complex to be explained entirely by the processes of diffusion and chemical reactions. However, Turing’s observation has gained much attention since the 1970s due to the great interest in theoretical and experimental study of far-from-equilibrium chemical systems. In this section we will briefly describe a **Turing structure**, or a stationary **spatial dissipative structure**, using the Brusselator of Section 19.4.

For simplicity, we shall consider a system with one spatial dimension, with coordinate r , in which diffusion occurs (Figure 19.10). We assume the system extends from $-L$ to $+L$. We must also specify spatial boundary conditions; the usual boundary conditions are that either the concentrations of the reactants or their flows are maintained at a constant value at the boundaries (or even a combination of both). For our example, we shall assume that the flows of the reactants are zero at the boundaries. Since diffusion flow is proportional to the derivative $\partial C / \partial r$ (in which C is the concentration), the no-flow boundary conditions imply that the derivatives of the concentrations are zero at the boundaries.

When diffusion is included as a transport process, the kinetic equations (19.4.5) and (19.4.6) become

$$\frac{\partial[X]}{\partial t} = D_X \frac{\partial^2[X]}{\partial r^2} + k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] \quad (19.5.1)$$

$$\frac{\partial[Y]}{\partial t} = D_Y \frac{\partial^2[Y]}{\partial r^2} + k_2[B][X] - k_3[X]^2[Y] \quad (19.5.2)$$

The boundary conditions are

$$\left. \frac{\partial[X]}{\partial r} \right|_{r=-L} = \left. \frac{\partial[X]}{\partial r} \right|_{r=+L} = 0$$

in which D_X and D_Y are the diffusion coefficients and r is the spatial coordinate. As before, we assume that $[A]$ and $[B]$ are maintained at a fixed uniform value along the entire system (an assumption that simplifies the mathematics but which is difficult to achieve in practice). Diffusion usually homogenizes the concentration in a system, but when coupled with autocatalytic chemical reactions under far-from-equilibrium conditions, it actually generates inhomogeneities or patterns. For pattern formation, the diffusion coefficients must be different. If the diffusion coefficients are nearly equal, then diffusion does not cause an instability; diffusion

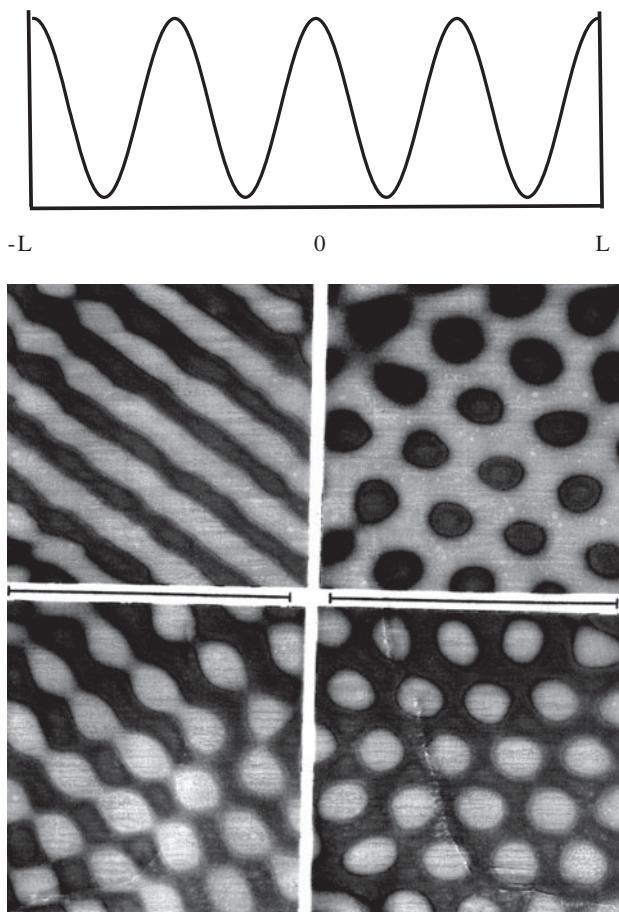


Figure 19.10 Above: Turing structure in a one-dimensional Brusselator model. Below: Turing structures observed in a chlorite–iodide–malonic acid reaction in an acidic aqueous solution (Courtesy of Harry L. Swinney). The size of each square is nearly 1 mm.

only tends to homogenize the instability that already exists. This can be seen as follows. We begin by considering the stability of the stationary state (19.4.7), the concentrations being homogeneous in the entire system:

$$[X]_s = \frac{k_1}{k_4} [A], \quad [Y]_s = \frac{k_4 k_2}{k_3 k_1} \frac{[B]}{[A]} \quad (19.5.3)$$

The stability of this solution depends on the behavior of a small perturbation. If δX and δY are the small perturbations from $[X]_s$ and $[Y]_s$, it is easy to see that equations linearized about the steady state (19.5.3) are

$$\frac{\partial}{\partial t} \begin{pmatrix} \delta X \\ \delta Y \end{pmatrix} = \begin{bmatrix} D_X \frac{\partial^2}{\partial r^2} & 0 \\ 0 & D_Y \frac{\partial^2}{\partial r^2} \end{bmatrix} \begin{pmatrix} \delta X \\ \delta Y \end{pmatrix} + M \begin{pmatrix} \delta X \\ \delta Y \end{pmatrix} \quad (19.5.4)$$

in which we have used the matrix defined in (19.4.9):

$$M = \begin{bmatrix} k_2[B] - k_4 & k_3[X]_s^2 \\ -k_2[B] & -k_3[X]_s^2 \end{bmatrix}$$

We will first see that a spatial structure will not arise when the diffusion coefficients are equal. If we assume $D_X = D_Y = D$, Equation (19.5.4) can be written as

$$\frac{\partial}{\partial t} \begin{pmatrix} \delta X \\ \delta Y \end{pmatrix} = D \frac{\partial^2}{\partial r^2} I \begin{pmatrix} \delta X \\ \delta Y \end{pmatrix} + M \begin{pmatrix} \delta X \\ \delta Y \end{pmatrix} \quad (19.5.5)$$

in which I is the identity matrix. For a *linear equation* of this type, the spatial part of the solutions can always be written as combinations of $\text{Sin } Kr$ and $\text{Cos } Kr$, in which the wavenumbers K are chosen so that the boundary conditions are satisfied. This means that if we understand the behavior of a perturbation of the type

$$\begin{pmatrix} \delta X(t) \\ \delta Y(t) \end{pmatrix} \text{ Sin } Kr \text{ and } \begin{pmatrix} \delta X(t) \\ \delta Y(t) \end{pmatrix} \text{ Cos } Kr \quad (19.5.6)$$

in which the spatial part is separated, then the behavior of all linear combinations of these basic solutions can be deduced. If we substitute (19.5.6) into (19.5.5), we obtain

$$\frac{\partial}{\partial t} \begin{pmatrix} \delta X(t) \\ \delta Y(t) \end{pmatrix} = (-DK^2 I + M) \begin{pmatrix} \delta X(t) \\ \delta Y(t) \end{pmatrix} \quad (19.5.7)$$

From this expression, it is clear that if λ_+ and λ_- are the eigenvalues of M , the addition of diffusion will only change the eigenvalues to $(\lambda_+ - DK^2)$ and $(\lambda_- - DK^2)$. Since it is the positivity of the real part of the eigenvalue that indicates instability, we see that diffusion does not generate a new instability; it only makes steady states more stable to perturbations with $K \neq 0$. So the solution to Equation (19.5.7) with $K = 0$ is the least stable state because its eigenvalues will have the largest real parts.

For the emergence of spatial patterns, the diffusion coefficients must be *unequal*. In a small region, if one species diffuses out more rapidly than the other, the growth of one species may be facilitated by the depletion of the other. If this happens, the homogeneous state will no longer be stable and inhomogeneities will begin to grow. When the diffusion coefficients are unequal, it is easy to see that in place of the matrix $(-K^2 DI + M)$ we have the matrix

$$\begin{bmatrix} k_2[B] - k_4 - K^2 D_X & k_3[X]_s^2 \\ -k_2[B] & -k_3[X]_s^2 - K^2 D_Y \end{bmatrix} \quad (19.5.8)$$

For an instability to produce stationary **spatial structures**, the two eigenvalues of this matrix must be real and at least one must become positive. If the eigenvalues are real and one becomes positive due to the variations in the parameters $[B]$ and $[A]$, then the unstable perturbation will be of the form

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \text{ Sin}(Kr)e^{\lambda_+ t} \text{ or } \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \text{ Cos}(Kr)e^{\lambda_+ t} \quad (19.5.9)$$

in which λ_+ is the eigenvalue with a positive real part. This indicates a growth of a spatial pattern $\sin Kr$ or $\cos Kr$ without any temporal oscillations; it will evolve to a stationary pattern or a Turing structure.

On the other hand, if the eigenvalues are a complex-conjugate pair, then the solutions to the perturbation equation (19.5.4) will be of the form

$$\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \text{ Sin}(Kr)e^{(\lambda_{\text{re}} \pm i\lambda_{\text{im}})t} \text{ or } \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \text{ Cos}(Kr)e^{(\lambda_{\text{re}} \pm i\lambda_{\text{im}})t} \quad (19.5.10)$$

in which $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$ is the eigenvector with the eigenvalue $\lambda = \lambda_{\text{re}} \pm i\lambda_{\text{im}}$, with its real and imaginary parts as shown. If the real part λ_{re} is positive, the perturbation (19.5.10) will grow. The unstable perturbation contains oscillations in time, due to the factor $e^{i\lambda_{\text{im}}t}$ as well as variations in space due to the factor $\sin Kr$ or $\cos Kr$. Such a perturbation corresponds to a **propagating wave**.

For matrix (19.5.8), the condition for one of its two real eigenvalues to cross zero can be obtained as follows. First we note that the determinant, Det, of a matrix is the product of the eigenvalues. If the eigenvalues are λ_+ and λ_- , we have

$$(\lambda_+ \lambda_-) = \text{Det} = (k_2[B] - k_4 - K^2 D_X) (-k_3[X]_s^2 - K^2 D_Y) + (k_2[B])(k_3[X]_s^2) \quad (19.5.11)$$

Before the onset of the instability, both eigenvalues are negative and hence $\text{Det} > 0$. Let us assume that when the parameter $[B]$ is varied, λ_+ crosses zero and becomes positive. Then, at the point where $\lambda_+ = 0$, we have $\text{Det} = 0$ and when $\lambda_+ > 0$ we have $\text{Det} < 0$. Thus the condition for the instability may be stated as

$$\text{Det} = (k_2[B] - k_4 - K^2 D_X)(-k_3[X]_s^2 - K^2 D_Y) + (k_2[B])(k_3[X]_s^2) < 0 \quad (19.5.12)$$

Using $[X]_s = (k_1/k_4)[A]$ this inequality can be rewritten as

$$[B] > \frac{1}{k_2}[k_4 + K^2 D_X] \left[1 + \frac{k_3 k_1^2 [A]^2}{k_4^2} \frac{1}{K^2 D_Y} \right] \quad (19.5.13)$$

This then is the condition under which a Turing structure will arise in the Brusselator model. As $[B]$ increases, the lowest value $[B]_c$ for which (19.5.13) is satisfied will trigger an instability. The value of $[B]_c$ can be found by plotting

$$[B]_c = \frac{1}{k_2}[k_4 + K^2 D_X] \left[1 + \frac{k_3 k_1^2 [A]^2}{k_4^2} \frac{1}{K^2 D_Y} \right] \quad (19.5.14)$$

as a function of K^2 . As shown in Figure 19.11, this plot has a minimum. When $[B]$ reaches this minimum value, the corresponding K_{\min} will be the wavenumber of the stationary pattern. The minimum occurs at the following values (Exercise 19.9):

$$K_{\min}^2 = A \sqrt{\frac{k_3 k_1^2}{k_4 D_X D_Y}} \quad \text{and} \quad [B]_c = [B]_{\min} = \frac{1}{k_2} \left[\sqrt{k_4} + A \sqrt{\frac{D_X k_3 k_1^2}{D_Y k_4^2}} \right]^2 \quad (19.5.15)$$

Experimentally, traveling waves have been observed in the Belousov–Zhabotinsky reaction (Figure 19.12) but only recently have the Turing patterns been realized in the laboratory [33].

The examples shown in this chapter are only a small part of the rich variety of behavior encountered in far-from-equilibrium chemical systems. Here our objective is only to show a few examples; an extensive description would form a book in itself! At the end of the chapter there is a list of monographs and conference proceedings that give a detailed descriptions of oscillations, propagating waves, Turing structures, pattern formation on catalytic surfaces, multistability and chaos (both temporal and spatiotemporal). Dissipative structures have also been found in other fields such as hydrodynamics and optics.

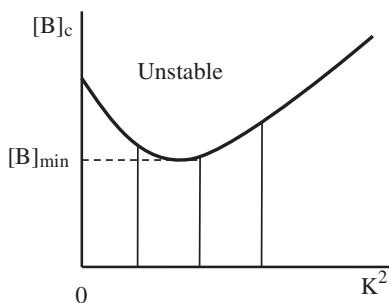


Figure 19.11 Stability diagram showing the value of $[B]$ and the corresponding value of K^2 that will become unstable and grow. The values of K that are consistent with the boundary conditions are discrete modes characterized by an integer m . As $[B]$ increases, when it is just above $[B]_{min}$, the mode m that becomes unstable first grows into a spatial structure.

19.6 Dissipative Structures and Machines

Having studied some examples of dissipative structures, it is interesting to compare them with machines/computers or *designed structures*, for there are some notable and interesting fundamental differences that have been insightfully noted by Robert Rosen [34].

First, we note that most designed structures are based on time-reversible mechanics, classical or quantum; i.e. their mathematical description is based on the reversible dynamical processes. The ideal designed structure

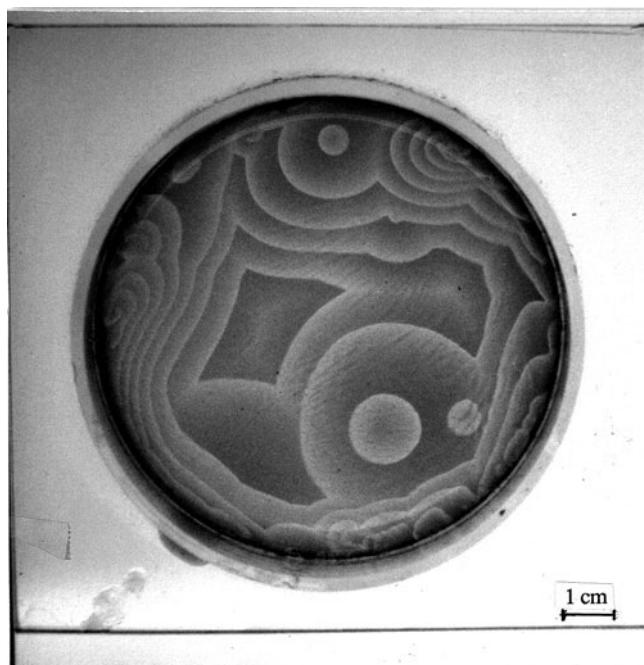


Figure 19.12 Traveling waves in the Belousov–Zhabotinsky reaction.

does not include irreversible processes; for its best performance, entropy-generating dissipative processes must be minimized. In stark contrast, the very existence of dissipative structures depends on dissipative processes. Their mathematical description is based on irreversible thermodynamic processes. Their behavior is not time symmetric.

Second, the structure of a designed structure originates from processes external to the system and so is its function: every designed structure is designed to perform a specific set of functions, as are its components. In computers, ‘machine intelligence’ is, in fact, ‘borrowed intelligence’; the algorithms that enable it to perform its function originate in processes external to the system. Even if a computer can generate an algorithm, it can do so only because it has been supplied with a higher-level algorithm that enables it to do so. In contrast, the structure in dissipative structures originates from processes within. Their behavior, if it could be interpreted as a ‘function’, is entirely a consequence of self-organization. In a complex dissipative structure, one may associate ‘functions’ to various subsystems, but those functions are entirely self-generated. If one could associate an ‘algorithm’ for its behavior, that too originates from within.

Finally, thermodynamic stability of dissipative structure means dissipative processes restore the structure if it is perturbed or ‘damaged’ – within bounds, of course. This bestows them with the property of ‘self-healing’. This is clearly not the case with machines or computers.

From these observations, one may surmise that dissipative structures are more akin to biological organisms than are machines and computers. The machine paradigm is inappropriate as a theory of biological organism. This aspect will be discussed further in the concluding Chapter 21.

19.7 Structural Instability and Biochemical Evolution

We conclude this chapter with a few remarks on another kind of instability often called ‘structural instability’ and its relevance to biochemical evolution. In the previous sections we have seen instabilities giving rise to organized states. These instabilities arose in a given set of chemical reactions. In nonequilibrium chemical systems, instability may also arise by the introduction of a new chemical species that gives rise to new reactions; these new reactions may destabilize the system and drive it to a new state of organization. In this case the ‘structure’ of the chemical reaction network is itself subject to changes. Each new species alters the reaction kinetics and this may drastically alter the state of the system; i.e. due to the appearance of a new chemical species the system may become unstable and evolve to a new state.

This type of structural instability can be seen most easily in the evolution of self-replicating molecules with a steady supply of monomers. Let us consider a set of autocatalytic polymers that are capable of self-replication through a template mechanism. In this case, each new polymer is a new autocatalytic species. Let us further assume that this self-replication is subject to random errors or mutations. Each mutation of a self-replicating molecule introduces a new species and new chemical reactions. Thus if we write a set of kinetic equations for such a system, each time a random mutation occurs, the set of equations itself will change. Under a given set of nonequilibrium conditions or ‘environment’ some (or perhaps most) of the mutations may not produce a polymer whose rate of self-replication is larger than those of others. The appearance of such a new species may cause a small change in the population of various polymers but no significant change will arise. However, some of the mutations might give rise to a polymer with a high rate of self-replication. This would correspond to fluctuation to which the system is unstable. The new polymer may now dominate the system and alter the population significantly. This of course corresponds to Darwinian evolution at the molecular level, the paradigm of the ‘survival of the fittest’. Many detailed studies of such structural instabilities and molecular evolution have been conducted [35–38]. These models are beyond the scope of this text but we will note an interesting thermodynamic feature summarized in Figure 19.13. Each new structural instability generally increases the dissipation or the rate of entropy production in the system because it increases the number of

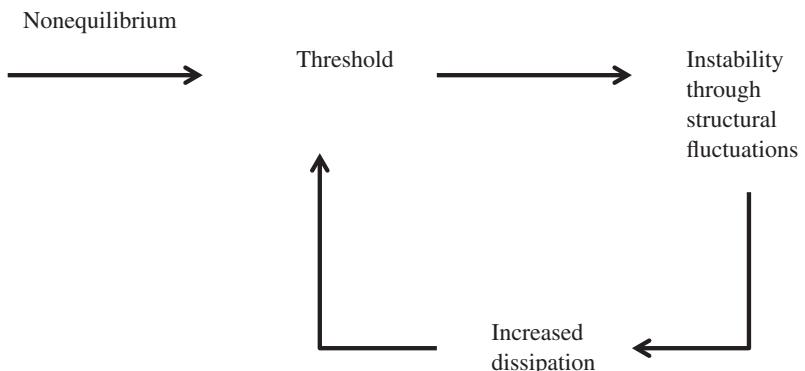


Figure 19.13 Structural instabilities during molecular evolution give rise to new processes that tend to increase entropy production.

reactions. This is in contrast to the near-equilibrium situations discussed in Chapter 17 in which the entropy production tends to a minimum. Structural instability may progressively drive far-from-equilibrium systems to higher rates of entropy production and higher states of order. Needless to say, biochemical evolution and the origin of life is a very complex process that we are only beginning to understand. However, now we see instability, fluctuation and evolution to organized states as a general nonequilibrium process whose most spectacular manifestation is the evolution of life.

Appendix 19.1 Mathematica Codes

The following codes give the numerical solutions for the kinetic equations for the systems discussed in this chapter. As in Chapter 9, **NDSolve** is used to obtain numerical solutions. The results can be plotted using the **Plot** command. Numerical output can be exported to graphing software using the **Export** command.

CODE A: CHIRAL SYMMETRY BREAKING

```
(*Code to show chiral symmetry breaking. Kinetic constants are
chosen such that the equilibrium constant, (kf/kr), for direct and
catalyzed reactions are equal*)
```

```
k1f=0.5;k1r=0.2;k2f=0.5;k2r=(k1r/k1f)*k2f;k3f=1.5;k3r=10^-3;
S=1.25;T=S;P=0.5;

R1f:=k1f*S*T;R1r:=k1r*XL[t];
R2f:=k2f*S*T*XL[t];R2r:=k2r*(XL[t])^2;
R3f:=k1f*S*T;R3r:=k1r*XD[t];
R4f:=k2f*S*T*XD[t];R4r:=k2r*(XD[t])^2;
R5f:=k3f*XL[t]*XD[t];R5r:=k3r*P;

(* Initial values of XL and XD are set at steady state values for S=0.5 *)

Soln1=NDSolve[{XL'[t]==R1f-R1r+R2f-R2r-R5f+R5r,
    XD'[t]==R3f-R3r+R4f-R4r-R5f+R5r,
```

```

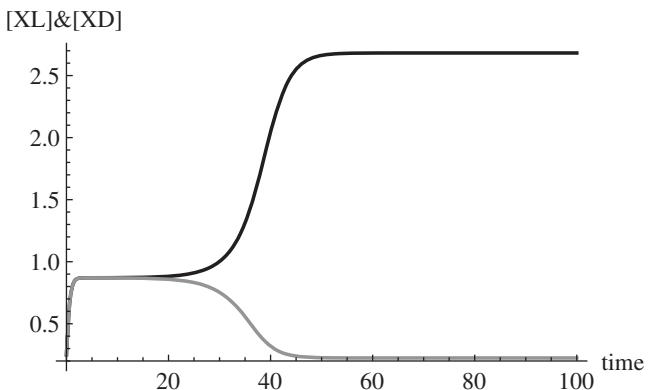
XL[0]==0.2502,XD[0]==0.2500},{XL,XD},{t,0,2000},
MaxSteps->10000]

tmax=100;

Plot[Evaluate[{XL[t],XD[t]}/.Soln1],{t,0,tmax},
AxesLabel->{"time","[XL]&[XD]"},
AxesStyle->Directive[Black,14],
PlotStyle->{{Black,Thick},{Gray,Thick}},PlotRange->All]

{ {XL->InterpolatingFunction[{{0.,2000.}},<>],
  XD->InterpolatingFunction[{{0.,2000.}},<>]} }

```



To write output files for spreadsheets, use the **Export** command and the file format List. For more detail see the *Mathematica* help file for the **Export** command. In the command below, the output filename is: `data1.txt`. This file can be read by most spreadsheets and graphing software.

The command `X[t]/.Soln1` specifies that `X[t]` is to be evaluated using `Soln1` defined above. `TableForm` outputs data in a convenient form.

```

Export["data1.txt",Table[{t,{XL[t],XD[t]}/.Soln1},{t,1,50}]//TableForm, "List"]

```

`data1.txt`

To obtain a table of t versus $X(t)$ the following command can be used.

```

Table[{t,{XL[t],XD[t]}/.Soln1},{t,1,5}]//TableForm

```

1	0.774193	0.773908
2	0.860958	0.860593
3	0.86964	0.869178
4	0.870507	0.869924
5	0.870658	0.869922

The rate of entropy production due to each of the reactions in the above scheme can be calculated using the following code. The Plot command plots the total rate of entropy production. The Table command outputs a table of the rates of entropy production for each reaction at the last three time points.

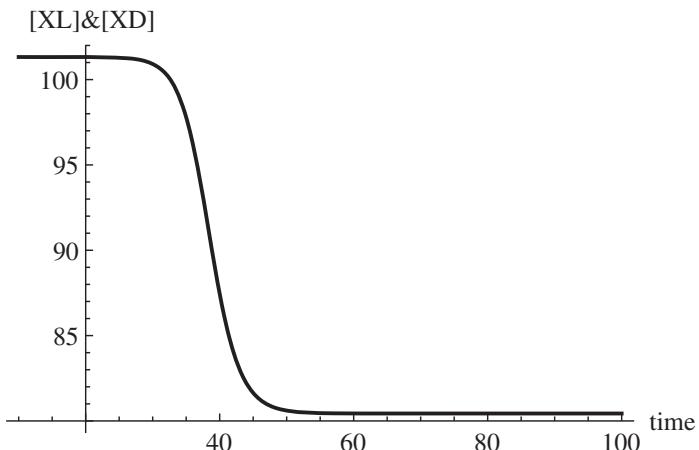
```

RR=8.314;
Sig1:=RR*(R1f-R1r)*Log[R1f/R1r];
Sig2:=RR*(R2f-R2r)*Log[R2f/R2r];
Sig3:=RR*(R3f-R3r)*Log[R3f/R3r];
Sig4:=RR*(R4f-R4r)*Log[R4f/R4r];
Sig5:=RR*(R5f-R5r)*Log[R5f/R5r];
SigTot:=Sig1+Sig2+Sig3+Sig4+Sig5;

Plot[Evaluate[SigTot/.Soln1], {t,10,tmax},
AxesLabel->{"time", "[XL]&[XD]"},
AxesStyle->Directive[Black,14],
PlotStyle->{Black,Thick},PlotRange->All]

Table[TableForm[{Evaluate[{t,SigTot,Sig1,Sig2,Sig3,Sig4,Sig5}
/.Soln1}], {t,tmax-2,tmax}]

```



98	99	100
80.4352	80.4352	80.4352
0.765395	0.765395	0.765395
2.05282	2.05282	2.05282
17.4965	17.4965	17.4965
3.92293	3.92293	3.92293
56.1976	56.1976	56.1976

CODE B: THE BRUSSELATOR

The following is the code for the Brusselator. Since no reverse reactions are involved, we shall not use the subscripts f and r for the reaction rates and rate constants.

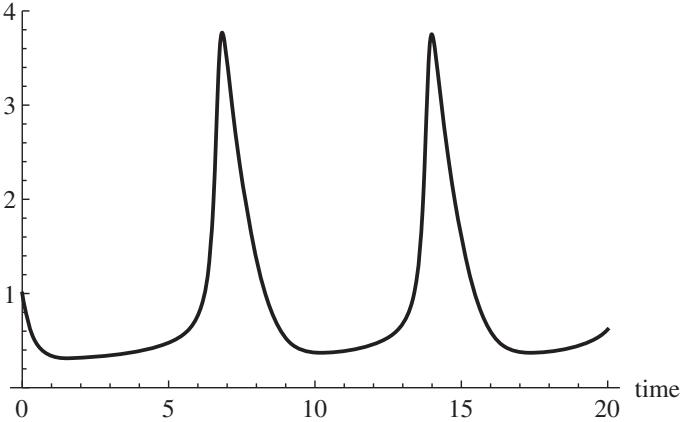
```
(* Chemical Kinetics: The Brusselator *)

k1=1.0; k2=1.0; k3=1.0; k4=1.0; A=1.0; B=3.0;
R1:=k1*A; R2:=k2*B*X[t]; R3:=k3*(X[t]^2)*Y[t];
R4:=k4*X[t];

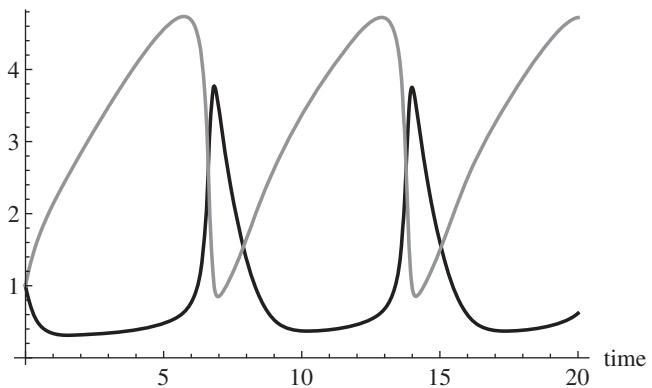
Soln2=NDSolve[{X'[t]== R1-R2+R3-R4,
                 Y'[t]== R2-R3,
                 X[0]==1.0,Y[0]==1.0},
                {X,Y},{t,0,20},
                MaxSteps->500]

{{X->InterpolatingFunction[{{0.,20.}},<>],
  Y->InterpolatingFunction[{{0.,20.}},<>]}}

Plot[Evaluate[{X[t]}/.Soln2],{t,0,20},PlotRange->{0,4},
      PlotStyle->{Black,Thick},
      AxesLabel->{"time"},
      AxesStyle->Directive[Black,14]]



```



```
Table[{t, Evaluate[{x[t], y[t]}/.soln2]}, {t, 0, 10, 1}]
//TableForm
```

	0	1.	1.
0	0.336806	2.13473	
1	0.316947	2.83679	
2	0.344197	3.48043	
3	0.389963	4.0695	
4	0.476012	4.556	
5	0.766335	4.6843	
6	3.45363	0.851828	
7	1.36836	1.6496	
8	0.526035	2.63	
9	0.373265	3.36134	

CODE C: THE BELUSOV-ZHABOTINSKY REACTION

The following is the FKN model of the Belousov–Zhabotinsky reaction. Since no reverse reactions are involved, we shall not use the subscripts f and r for the reaction rates and rate constants.

```
(* The Belousov-Zhabotinsky Reaction/FKN Model *)
(* X=HBrO2      Y=Br-      Z=Ce4+      B=Org      A=BrO3-  *)

k1=1.28; k2=8.0; k3=8.0*10^5; k4=2*10^3; k5=1.0;
A=0.06; B=0.02; f=1.5;

R1:=k1*A*Y[t];   R2:=k2*A*X[t];   R3:=k3*X[t]*Y[t];
R4:=k4*X[t]^2;   R5:=k5*B*Z[t];

Soln3=NDSolve[{X'[t]== R1+R2-R3-2*R4,
                 Y'[t]== -R1-R3+(f/2)*R5,
                 Z'[t]== 2*R2-R5,
```

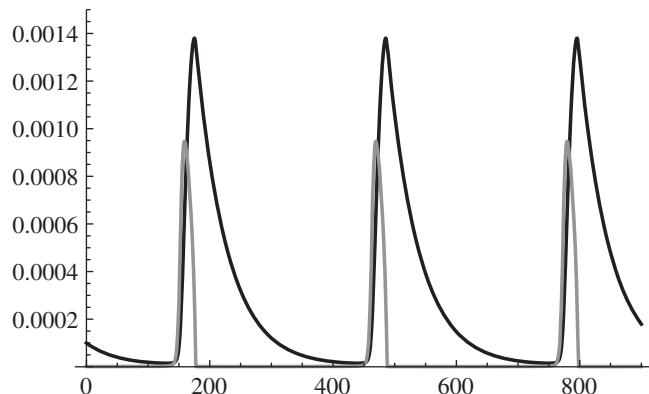
```

x[0]==2*10^-7,y[0]==0.00002,z[0]==0.0001},
{x,y,z},{t,0,1000}, MaxSteps->2000]

{{x->InterpolatingFunction[{{0.,1000.}},<>],
y->InterpolatingFunction[{{0.,1000.}},<>],
z->InterpolatingFunction[{{0.,1000.}},<>]}

Plot[Evaluate[{z[t],10*x[t]}/.Soln3],{t,0,900},
PlotRange->{0.0,1.5*10^-3},
PlotStyle->{{Black,Thick},{Gray,Thick}},
AxesStyle->Directive[Black,14]]

```



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Further Reading

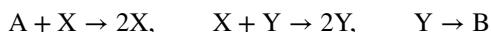
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Exercises

- 19.1** Analyze the stability of solutions $\alpha = 0$ and $\alpha = \pm\sqrt{\lambda}$ for Equation (19.2.1) and show explicitly that when $\lambda > 0$ the solution $\alpha = 0$ becomes unstable whereas the solutions $\alpha = \pm\sqrt{\lambda}$ are stable.
- 19.2** Write a *Mathematica* or *Maple* code to obtain the solutions of the equations in Exercise 19.1. Plot these solutions as a function of time for various initial conditions and show explicitly that the solutions evolve to stable stationary states.
- 19.3** For the reaction scheme (19.3.1) to (19.3.5), using the principle of detailed balance, verify that the concentrations of X_L and X_D will be equal at equilibrium.
- 19.4** Using the variables α , β and λ defined in (19.3.8), show that the kinetic equations (19.3.6) and (19.3.7) can be written in the forms of (19.3.9) and (19.3.10).
- 19.5** Show that Equation (19.4.7) are the stationary states of the kinetic equations of the Brusselator equations (19.4.5) and (19.4.6).
- 19.6 (a)** Write the kinetic equations for [X] and [Y], assuming that [A] and [B] are fixed, for the following scheme (called the Lotka–Volterra model):



- (b)** Obtain its steady states and analyze their stability as a function of the parameters [A] and [B].
- 19.7 (a)** Using the dimensionless variables defined by

$$x = \frac{[X]}{X_0}, \quad y = \frac{[X]}{Y_0}, \quad z = \frac{[Z]}{Z_0} \text{ and } \tau = \frac{t}{T_0}$$

in which

$$X_0 = \frac{k_2[A]}{2k_4}, \quad Y_0 = \frac{k_2[A]}{k_3}, \quad Z_0 = \frac{(k_2[A])^2}{k_4 k_5[B]}, \quad T_0 = \frac{1}{k_5[B]}$$

show that the kinetic equations (19.4.16) to (19.4.18) can be written as

$$\varepsilon \frac{dx}{d\tau} = qy - xy + x(1 - x)$$

$$\varepsilon' \frac{dx}{d\tau} = -qy - xy + fz$$

$$\frac{dz}{d\tau} = x - z$$

in which

$$\varepsilon = \frac{k_5[B]}{k_2[A]}, \quad \varepsilon' = \frac{2k_5k_4[B]}{k_3k_2[A]} \quad \text{and} \quad q = \frac{2k_1k_4}{k_3k_2}$$

(See Tyson, J.J., Scaling and reducing the Field–Körös–Noyes mechanism of the Belousov–Zhabotinsky reaction, *J. Phys. Chem.*, **86** (1982), 3006–3012.)

- (b)** Find the stationary states of this set of equations.

- 19.8** Using *Mathematica* Code C in Appendix 19.1, obtain the range of values for the parameter f in which oscillations occur. Also plot the relation between the period of oscillations and the value of f .
- 19.9** Show that the minimum of Equation (19.5.14) occurs at the values given by Equation (19.5.15).

20

Elements of Statistical Thermodynamics

Introduction

In the kinetic theory of the nineteenth century, the ideas Daniel Bernoulli published a century earlier in his *Hydrodynamica* came to fruition. When the atomic nature of matter became evident, James Clerk Maxwell, Ludwig Boltzmann and others began to formulate the kinetic theory of gases. Kinetic theory demonstrated how random molecular motion gives rise to pressure in accordance with the ideal gas law, $pV = NRT$ (as discussed in Section 1.6). It gave us the precise relationship between temperature and molecular motion: the average kinetic energy of a molecule is directly proportional to the temperature, $\langle mv^2/2 \rangle = (3/2)k_B T$. The concepts introduced through kinetic theory could also explain other properties of gases, such as heat conductivity, diffusion and viscosity [1], the so-called **transport properties**. Once the connection between the temperature and energy of an individual molecule was established, the relationship between energy as formulated in thermodynamics and mechanical energy of a molecule became clear. The thermodynamic energy of a system is the sum of all the energies of the molecules. Random molecular motion distributes the total energy of the system into all possible **modes of motion**, i.e. translation, rotation and vibration, and the amount of energy in each mode of motion depends on the temperature. If the average energy of a single molecule is known, then the total energy of the system can be calculated; in turn, the average energy of a molecule is related to the system's temperature. The success of these developments still left one big question unanswered: what is the microscopic explanation of entropy? What is the relationship between entropy and molecular properties? Boltzmann's answer to that question, which has already been introduced in earlier chapters, is $S = k_B \ln W$. This fundamental formula opened the way for the formulation of **statistical thermodynamics**, a theory that relates thermodynamic quantities to the statistical properties of molecules.

In this chapter, we introduce the reader to the basic formalism of statistical thermodynamics and illustrate how thermodynamic properties of some simple systems can be related to statistical properties of molecules. We will begin by giving the reader a brief overview of the theory.

In previous chapters the thermodynamic quantities were written as functions of moles N and gas constant R . In this chapter, it is more convenient to use molecular quantities, \tilde{N} the number of particles and the Boltzmann constant k_B . Conversion to N and R may be done by noting that $\tilde{N} = NN_A$ and $R = N_A k_B$. Also, when discussing general statistical thermodynamic concepts that are valid for electrons, atoms or molecule, we shall use the term 'particles'.



Ludwig Boltzmann (1844–1906).
(Reproduced by courtesy of the AIP Emilio Segré Visual Archives, Segré Collection.)

20.1 Fundamentals and Overview

On the one hand, quantum mechanics describes the behavior of electrons, atoms and molecules with remarkable success through the concepts of quantum states, quantized energies and energy eigenstates. On the other hand, an equally successful thermodynamics describes the macroscopic behavior of matter in terms of variables such as entropy S , Helmholtz energy F and chemical potential μ . Statistical thermodynamics relates these two theories. It enables us to calculate thermodynamic quantities, such as the Helmholtz energy F , given all the energy states of constituent particles: electrons, atoms or molecules as the case might be.

In quantum theory, particles such as electrons, atoms or molecules are described by their quantum states $|\psi\rangle$. Among these states are energy eigenstates, states with definite energy. Statistical thermodynamics uses these ‘energy eigenstates’ $|E_k\rangle$, associated with an energy E_k , in which the subscript $k = 1, 2, 3, \dots$ indexes the quantized energies. There could be several states that have the same energy; the energy level is then said to be ‘degenerate’. A **microstate** of a system is the detailed specification of the state of every particle in the system. For a given total energy U there are a large number of different ways in which that energy can be distributed among the particles in the system. In general, there are a large number of microstates that correspond to a given thermodynamic state. Boltzmann’s fundamental postulate is that entropy is related to the number of microstates W through

$$S = k_B \ln W \quad (20.1.1)$$

in which the constant k_B is now named after Boltzmann. W is sometimes called the **thermodynamic probability**, a term introduced by Max Planck. In Chapter 3 (Box 3.2) we considered simple examples to illustrate how W is calculated. We will discuss more such examples in the following sections. For a brief overview

of statistical thermodynamics, we shall focus on two basic relations that follow when Equation (20.1.1) is applied to systems in thermodynamic equilibrium.

- Statistical thermodynamics uses the concept of statistical ensembles, a large collection of \tilde{N} identical particles or entire systems, to calculate average values. There is an alternative way of expressing Equation (20.1.1). For an ensemble of particles or systems, if P_k is the probability that the particle or system is in state k , then in Section 20.4 we show that S can also be written as

$$S = -\tilde{N}k_B \sum_k P_k \ln P_k \quad (20.1.2)$$

- When a system is in thermodynamic equilibrium at a temperature T , the probability $P(E_i)$ that a particle will occupy a state with energy E_i is

$$P(E_i) = \frac{1}{q} e^{-E_i/k_B T} \quad (20.1.3)$$

The term

$$q = \sum_i e^{-E_i/k_B T} \quad (20.1.4)$$

is the **normalization constant**; it is introduced so that $\sum_i P(E_i) = 1$, as required by the very definition of probability. Expression (20.1.3) for the probability of a state k is called the **Boltzmann probability distribution**. In many situations, it is found that several distinct states have the same energy. If $g(E_i)$ is the number of states having the same energy E_i , then the probability that a particle has an energy E_i occupying any one of the $g(E_i)$ states is

$$P(E_i) = \frac{1}{q} g(E_i) e^{-E_i/k_B T}, \quad \text{where } q = \sum_i g(E_i) e^{-E_i/k_B T} \quad (20.1.5)$$

and $g(E_i)$ is called the **degeneracy** of the energy level E_i .

Statistical thermodynamics of equilibrium systems is based on the fundamental expressions (20.1.2) and (20.1.3). Thus, given the quantum energy levels E_k , and their degeneracies $g(E_k)$, the average value of the energy of a single particle, which we shall denote by $\langle E \rangle$, is calculated using Equation (20.1.3):

$$\langle E \rangle = \sum_{i=1}^m E_i P(E_i) \quad (20.1.6)$$

To calculate the average energy of a system of \tilde{N} particles, an ensemble of systems is used (the reason for using an ensemble of systems is explained in Section 20.4). In this case, the total energy of all the particles U_i takes the place of E_i in Equation (20.1.6), in which $P(U_i)$ is the corresponding probability. The ensemble average $\langle U \rangle = U$ is the energy of the system. The entropy of the system can be calculated using Equation (20.1.2). From these two quantities, the Helmholtz energy $F = U - TS$ and other thermodynamic quantities can be obtained.

In the following sections we shall see that thermodynamic quantities can be obtained from q defined in Equation (20.1.4). Because of its importance, it is given a name, **the partition function**.¹ To be more precise

¹The letter z is also used for the partition function, because in German the sum (20.1.4) is called Zustandsumme (which means ‘state sum’).

with terminology, q defined above is called the ‘single-particle canonical partition function’. The partition function of a system of \tilde{N} particles is usually denoted by Q . For \tilde{N} identical noninteracting particles, q and Q have the following relation:

$$Q = \frac{q^{\tilde{N}}}{\tilde{N}!} \quad (20.1.7)$$

For interacting particles, Q is a more complicated function of T , V and \tilde{N} . Expressing Q as a function of V , T and \tilde{N} , and using Equation (20.1.2), one can derive the following general relation between Q and the Helmholtz energy F :

$$F = -k_B T \ln Q(V, T, \tilde{N}) \quad (20.1.8)$$

From the Helmholtz energy, other thermodynamic quantities can be calculated:

$$\mu(p, T) = \left(\frac{\partial F}{\partial N} \right)_{V, T}, \quad p = - \left(\frac{\partial F}{\partial V} \right)_{T, N}, \quad S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} \quad (20.1.9)$$

Statistical thermodynamics of a system usually begins with the calculation of the partition function Q . If Q can be obtained in a convenient analytic form, then all thermodynamic quantities can be calculated from it. This is the basic framework of equilibrium statistical thermodynamics. In the following sections we develop this formalism and present illustrative applications.

20.2 Partition Function Factorization

When the total energy of a particle can be written as a sum of independent energies with independent quantum numbers, the partition function can be expressed as a product of partition functions. The total energy of a molecule consists of energies of translation, rotation, vibration and the energies in the electronic and nuclear states. We can write the total energy E as the sum

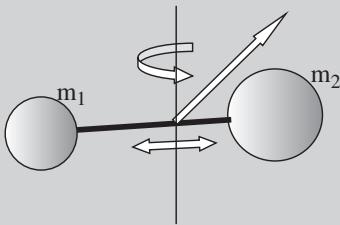
$$E = E^{\text{trans}} + E^{\text{rot}} + E^{\text{vib}} + E^{\text{elec}} + E^{\text{nuc}} \quad (20.2.1)$$

in which the superscripts stand for translation, rotation, etc. Each of the energies is quantized and has independent quantum numbers. (Depending on the conditions, the energies may also depend on external factors, such as gravitational and electromagnetic fields, but those terms are not included in the above expression.) The above expression assumes that energy of each type of motion is independent of another. Though this may be a good approximation in many situations, it is not strictly true. For example, the rotational energy of a molecule may depend on its vibrational state; in such situations, one could deal with the combined vibrational–rotational energy levels. For simplicity, we shall assume that energy levels of each type of motion have independent quantum numbers. In this case, the single molecule partition function can be factorized:

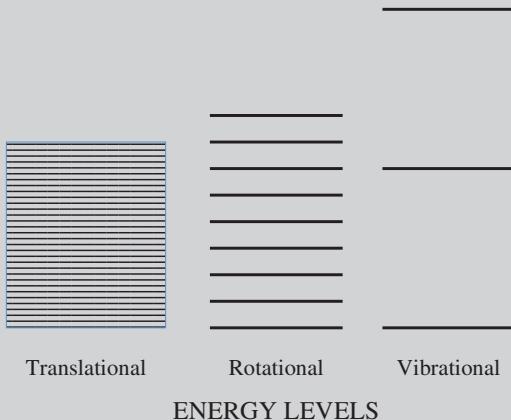
$$\begin{aligned} q &= \sum_{j, k, l, m, n} g(E_j)g(E_k)g(E_l)g(E_m)g(E_n)e^{-\beta(E_j^{\text{trans}} + E_k^{\text{rot}} + E_l^{\text{vib}} + E_m^{\text{elec}} + E_n^{\text{nuc}})} \\ &= \sum_j g(E_j)e^{-\beta E_j^{\text{trans}}} \sum_k g(E_k)e^{-\beta E_k^{\text{rot}}} \sum_l g(E_l)e^{-\beta E_l^{\text{vib}}} \sum_m g(E_m)e^{-\beta E_m^{\text{elec}}} \sum_n g(E_n)e^{-\beta E_n^{\text{nuc}}} \end{aligned} \quad (20.2.2)$$

For each molecule, quantum theory gives us the energy levels of each mode of motion. As shown in Box 20.1, the spacing of energy levels increases from translation to rotation to vibration. Translational energy levels are very closely spaced compared with the average thermal energy of a molecule, which is of the order of $k_B T$. The electronic energies generally have a much larger spacing than vibrational energies. If the ground-state energy is taken to be zero, then the electronic partition function is close to unity.

Box 20.1 Energy levels associated with different types of motion



Energy levels of a molecule are given for various types of motion. Translational energy levels are very closely spaced compared with rotational energies, which are more closely spaced than vibrational energies. The energy level spacing shown is not to scale; these are just meant to give a qualitative idea.



- Translational energy levels of a particle of mass m in a box of sides l_x , l_y and l_z (volume $V = l_x l_y l_z$) are specified by quantum numbers n_x , n_y and n_z :

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right), \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

in which $h = 6.626 \times 10^{-34}$ J s is Planck's constant.

- Energy levels for rotation about an axis with moment of inertia I are specified by the quantum number L :

$$E_L = \frac{\hbar^2}{2I} L(L+1), \quad L = 0, 1, 2, 3, \dots, \quad g(E_L) = 2L+1 \quad \text{and} \quad \hbar = h/2\pi$$

- Vibrational energy levels of a diatomic molecule with reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$ and force constant k are specified by the quantum number v :

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right), \quad \omega = \sqrt{\frac{k}{\mu}}, \quad v = 0, 1, 2, 3, \dots$$

The energy of the nucleus is also quantized and the spacing is so large that transition from an excited state to the ground state is through the emission of high-energy γ rays or the ejection of α or β particles (the latter being electrons or positrons). Transitions between nuclear states do not occur as a result of thermal collisions between atoms and molecules, so we can assume that the nuclei are in their ground states (except for radioactive nuclei). However, at temperatures that are encountered in the interior of stars, transitions between nuclear states must be considered. Box 20.1 lists commonly used expressions for the energy levels in molecules. With these energy levels, the corresponding partition functions can be calculated.

20.3 The Boltzmann Probability Distribution and Average Values

To illustrate the use of the Boltzmann probability distribution (20.1.5) let us consider \tilde{N} particles whose energy can be any of the m possible values E_1, E_2, \dots, E_m . At equilibrium, let $\tilde{N}_1, \tilde{N}_2, \dots, \tilde{N}_m$ be the number of particles in these energy levels, which implies $\tilde{N} = \tilde{N}_1 + \tilde{N}_2 + \dots + \tilde{N}_m$. The probability that we will find a particle in energy level E_k is proportional to \tilde{N}_k , the number of particles in that state. According to the Boltzmann principle:

$$P(E_k) = \frac{g(E_k)e^{-E_k/k_B T}}{q} = \frac{\tilde{N}_k}{\tilde{N}} \quad (20.3.1)$$

\tilde{N}_k is often called the **occupation number** of the state with energy E_k . From Equation (20.3.1), it follows that the relative number of particles in energy states E_k and E_l is

$$\frac{\tilde{N}_k}{\tilde{N}_l} = \frac{g(E_k)}{g(E_l)} e^{-(E_k - E_l)/k_B T} \quad (20.3.2)$$

Thus, the ratio of occupation numbers is a function of the difference in the energies and the ratio of the corresponding degeneracies.

The average value of a variable or physical property can be calculated using the Boltzmann probability distribution. We shall denote the average value of a quantity X by $\langle X \rangle$. Thus, the average energy of a single particle $\langle E \rangle$ is

$$\langle E \rangle = \frac{\sum_{k=1}^m E_k \tilde{N}_k}{\tilde{N}} = \sum_{k=1}^m E_k P(E_k) \quad (20.3.3)$$

The total energy of all particles is $U = \tilde{N}\langle E \rangle$.

More generally, the average values of any physical property X can be calculated if its value in the state $|E_k\rangle$, which we denote by X_k , is known:

$$\langle X \rangle = \frac{\sum_{k=1}^m X_k \tilde{N}_k}{\tilde{N}} = \sum_{k=1}^m X_k P(E_k) \quad (20.3.4)$$

The average value of any function of X , $f(X)$, can similarly be calculated using

$$\langle f(X) \rangle = \frac{\sum_{k=1}^m f(X_k) \tilde{N}_k}{\tilde{N}} = \sum_{k=1}^m f(X_k) P(E_k) \quad (20.3.5)$$

For example, the average value of $\langle E^2 \rangle$ is

$$\langle E^2 \rangle = \sum_{k=1}^m E_k^2 P(E_k) \quad (20.3.6)$$

The standard deviation in E is defined as $(\Delta E)^2 \equiv \langle (E - \langle E \rangle)^2 \rangle$. An elementary calculation shows that

$$(\Delta E)^2 \equiv \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \quad (20.3.7)$$

In this manner, statistical quantities such as the average and standard deviation of physical variables associated with an equilibrium system can be calculated. When an ensemble of systems is considered, the energy E_k is replaced by the total energy U_i .

20.4 Microstates, Entropy and the Canonical Ensemble

A macroscopic thermodynamic state of a system corresponds to a large number of ‘microstates’. For instance, if the total energy of an ensemble of \tilde{N} particles (molecules, electrons, etc.) in a volume V is specified, then this energy can be distributed among the \tilde{N} particles in a number of ways. Each distinct distribution of the energy among the \tilde{N} particles corresponds to a microstate. We now show how expression (20.1.2) is derived from the fundamental formula

$$S = k_B \ln W \quad (20.4.1)$$

in which W is the number of microstates corresponding to the given thermodynamic state (also called a macrostate). To illustrate how W is calculated, let us consider an ensemble of \tilde{N} particles each of which can be in any one of the m states. These could be ‘numbered particles’ on a crystal lattice. A microstate specifies the energy state of each particle. As in the previous sections, we assume \tilde{N}_k particles are in a state with energy E_k . The number of microstates W is the number of distinct ways in which the \tilde{N} particles can be distributed in m states. W can be calculated as follows (Figure 20.1). First, we note that if a particle, say particle 26, is

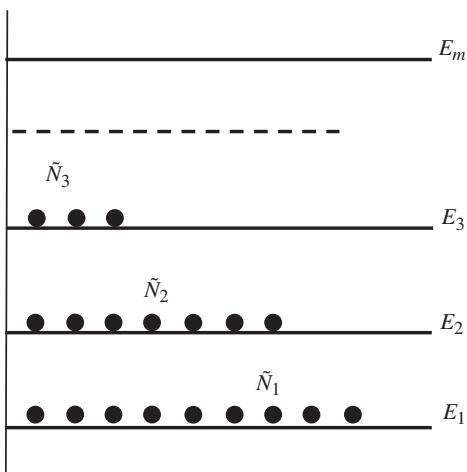


Figure 20.1 An ensemble of \tilde{N} particles distributed in m energy levels. \tilde{N}_k particles are in the energy level E_k and $P_k = \tilde{N}_k/\tilde{N}$ is the probability that a particle will occupy a state with energy E_k . The entropy of the system $S = -\tilde{N}k_B \sum_k P_k \ln P_k$.

in energy state E_5 and another particle, say particle 14, is in energy state E_2 , then an interchange of these two particles gives a different microstate; but if both particles 26 and 14 are in the same energy state, say E_5 , then interchanging them does not give a new microstate. Thus, only permutations that do not correspond to an interchange of particles with the same energy E_k correspond to distinct microstates. The number of all possible permutations is $\tilde{N}!$ The number of permutations of particles with the same energy E_k is $\tilde{N}_k!$ Thus, the total number of microstates W is given by

$$W = \frac{\tilde{N}!}{\tilde{N}_1! \tilde{N}_2! \dots \tilde{N}_m!} \quad (20.4.2)$$

The entropy S is

$$S = k_B \ln W = k_B \ln \left(\frac{\tilde{N}!}{\tilde{N}_1! \tilde{N}_2! \dots \tilde{N}_m!} \right) \quad (20.4.3)$$

We assume \tilde{N}_k is large. Then, for the term $\ln(\tilde{N}_k!)$ we can use Stirling's approximation (see Appendix 20.1):

$$\ln(a!) \approx a \ln a - a \quad (20.4.4)$$

Using this approximation one can show that (Exercise 20.1)

$$\ln W = - \sum_k \tilde{N}_k \ln \left(\frac{\tilde{N}_k}{\tilde{N}} \right) = -\tilde{N} \sum_k \left(\frac{\tilde{N}_k}{\tilde{N}} \right) \ln \left(\frac{\tilde{N}_k}{\tilde{N}} \right) \quad (20.4.5)$$

Since $\tilde{N}_k/\tilde{N} = P_k$, the probability of occupying a state with energy E_k , we immediately see that

$$S = k_B \ln W = -k_B \tilde{N} \sum_k \left(\frac{\tilde{N}_k}{\tilde{N}} \right) \ln \left(\frac{\tilde{N}_k}{\tilde{N}} \right) = -k_B \tilde{N} \sum_k P_k \ln P_k \quad (20.4.6)$$

which is Equation (20.1.2) if we replace $P(E_k)$ with P_k . We derived (20.4.6), the relationship between entropy and probability, from Equation (20.4.1) without any assumption about the system being in equilibrium. Hence, this definition of entropy is valid for nonequilibrium systems as well. Sometimes it is considered the definition of statistical entropy and used in contexts other than thermodynamics, such as information theory.

In Chapter 5 we noted that the entropy reaches its maximum value when the energy of a system U is constant. Now, we show that the Boltzmann equilibrium distribution (20.1.3) maximizes S when the total energy is constant. In other words, we show that, with the constraint of fixed total energy, S will reach its maximum value when $P_k \propto e^{-\beta E_k}$. This result can be obtained by using Lagrange's method of finding the maximum of a function subject to constraints. Our constraints are the constancy of total energy E and the total number of particles \tilde{N} . They can be expressed as

$$E = \sum_k E_k \tilde{N}_k = \tilde{N} \sum_k E_k (\tilde{N}_k / \tilde{N}) = \tilde{N} \sum_k E_k P_k \quad (20.4.7a)$$

$$\tilde{N} = \sum_k \tilde{N}_k \quad (20.4.7b)$$

in which we have used $P_k = \tilde{N}_k/\tilde{N}$. Lagrange's method now stipulates that, to maximize $-\sum_k P_k \ln P_k$ with the constraints (20.4.7), one needs to maximize the function

$$I = - \sum_k P_k \ln P_k + \lambda \left(E - \tilde{N} \sum_k E_k P_k \right) + \xi \left(\tilde{N} - \sum_k \tilde{N}_k \right) \quad (20.4.8)$$

in which λ and ξ are arbitrary constants whose values can be determined by additional requirements. Now it is straightforward to see that the condition $\partial I/\partial P_k = 0$ leads to the relation

$$\ln P_k = -\lambda \tilde{N} E_k + 1 - \xi$$

As a function of E_k , we can now write

$$P_k = C e^{-\beta E_k} \quad (20.4.9)$$

in which $C = \exp(1 - \xi)$ and $\beta = \lambda \tilde{N}$. This is essentially the Boltzmann distribution (20.1.2) once we identify $\beta = 1/k_B T$. That β must be $1/k_B T$ can be deduced by calculating the average kinetic energy of a particle and equating it to $3k_B T/2$, as required by kinetic theory. Since $\sum_k P_k = 1$, we see that $C = 1/q$ by comparing Equation (20.4.9) with Equation (20.1.3). Equation (20.4.9) is valid for every state that has energy E_k . Taking into account the degeneracy $g(E_k)$, the probability that the system will occupy any one of the $g(E_k)$ states with energy E_k can be written as

$$P(E_i) = \frac{1}{q} g(E_i) e^{-E_i/k_B T} \quad (20.4.10)$$

If each state with energy E_i is counted separately, then the degeneracy factor need not be included. In expression (20.4.6) the P_k values are the probabilities of occupying a particular state with energy E_k .

20.4.1 The Canonical Ensemble

In the following sections we will see that thermodynamic quantities of a system are calculated using the concept of a statistical ensemble. In deriving Equation (20.4.10) it was assumed that the number of particles \tilde{N}_k occupying a state k is large. This is a good assumption for rotational and vibrational states of molecules, but it is not valid for the occupation of translational states. Translational energies are very closely spaced. At ordinary temperatures, the average kinetic energy $3k_B T/2$ is much larger than the energy spacing of the translational quantum states. For example, if we assume $T = 298$ K, then a simple calculation for N_2 gas in a cube of side 10 cm shows (Example 20.1) that there are roughly 10^{29} states with energy less than $3k_B T/2$. At ordinary pressures, this is much larger than the number of N_2 molecules; hence, most translational states are unoccupied. Thus, we cannot assume that \tilde{N}_k is large. In such cases we use the concept of an ensemble of systems. The energy U of each system in the ensemble is itself subject to fluctuations, and in that respect is similar to the energy of a single particle. The system's energy can take values U_1, U_2, \dots with probabilities P_1, P_2, \dots ; i.e. the probability $P(U_k)$ that the total energy U of a system in the ensemble has a particular value U_k can be defined just as $P(E_k)$ was defined for a single particle. *It is assumed that the thermodynamic properties of a single system are the same as the average properties of the ensemble.*

One such ensemble is the **canonical ensemble** shown in Figure 20.2. It consists of a large number \tilde{N} of identical systems in contact with a thermal reservoir at a temperature T . In this figure, \tilde{N}_k is the number of systems (not particles) with total energy U_k . Each system's energy can take values U_k with probabilities $P(U_k)$. The thermodynamic energy of a system is the average energy calculated using this ensemble. With this formalism, we see that all the calculations done above for a single particle could be carried out for the canonical ensemble with the following result:

$$P(U_k) = \frac{1}{Q} e^{-U_k/k_B T}, \quad Q = \sum_i e^{-U_i/k_B T} \quad (20.4.11)$$

We note here that U_i is the total energy of all the particles of the system at a given temperature T . The partition function Q of a canonical ensemble is called the **canonical partition function**. The entropy of a system is

$$S = -k_B \sum_k P(U_k) \ln P(U_k) \quad (20.4.12)$$

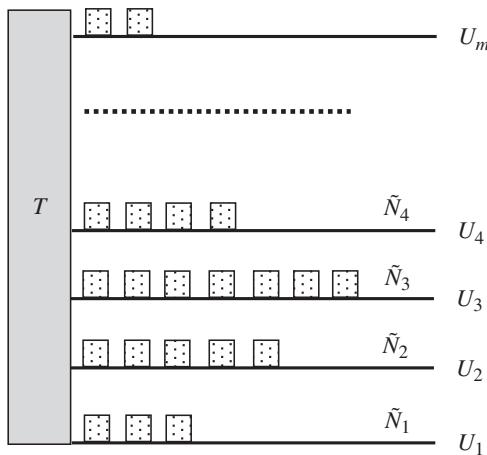


Figure 20.2 A canonical ensemble is a large set of \tilde{N} identical systems in contact with a temperature reservoir. The system's total energy U can take many possible values, U_1, U_2, \dots, U_m . At any instant, the ensemble of systems is distributed among the possible energy states, \tilde{N}_k systems with energy U_k . $P_k = \tilde{N}_k/\tilde{N}$ is the probability that a system's energy will be U_k . The entropy of the system $S = -k_B \sum_k P_k \ln P_k$.

In the following section, we shall see how thermodynamic quantities can be obtained from these two expressions.

20.5 Canonical Partition Function and Thermodynamic Quantities

There is a general procedure for calculating thermodynamic quantities from the partition functions. The partition function for a system of \tilde{N} particles is

$$Q = \sum_i e^{-U_i \beta}, \quad \beta = 1/k_B T \quad (20.5.1)$$

in which we have introduced a convenient notation $\beta = 1/k_B T$. The total energy $U_i = \sum_k \tilde{N}_k^i E_k$, in which \tilde{N}_k^i is the number of molecules in state k with energy E_k . The superscript i indexes a particular set of \tilde{N}_k^i whose total energy adds up to U_i . The value of each \tilde{N}_k^i can vary from 0 to \tilde{N} , the total number of molecules in the system, but $\sum_k \tilde{N}_k^i = \tilde{N}$. The entropy of the system is

$$\begin{aligned} S &= -k_B \sum_i P(U_i) \ln P(U_i) = -k_B \sum_i P(U_i) \ln(e^{-\beta U_i}/Q) \\ &= -k_B \sum_i P(U_i)(-\beta U_i - \ln Q) = k_B \beta \sum_i P(U_i) U_i + k_B \ln Q \sum_i P(U_i) \\ &= \frac{U}{T} + k_B \ln Q \end{aligned} \quad (20.5.2)$$

where we have used $U = \sum_i P(U_i)U_i$ and $\sum_i P(U_i) = 1$. From Equation (20.5.2), it follows that $F \equiv U - TS = -k_B T \ln Q$. When we compute Q explicitly in the following sections, we will see that Q is a function of the system volume V , the temperature T and \tilde{N} . Making this explicit, we write

$$F(V, T, \tilde{N}) = -k_B T \ln Q(V, T, \tilde{N}) \quad (20.5.3)$$

The total energy U can also be calculated directly from the partition function Q . It is easy to verify that

$$U = -\frac{\partial \ln Q}{\partial \beta} \quad (20.5.4)$$

Using Equations (20.5.3) and (20.5.4), other thermodynamic quantities could be calculated. For example, the chemical potential $\mu = (\partial F / \partial N)_{V,T}$ and $p = -(\partial F / \partial V)_{N,T}$.

20.6 Calculating Partition Functions

For simple systems, such as an ideal gas of noninteracting particles and the vibrational and rotational states of a diatomic molecule, the partition functions can be calculated without much difficulty. In these cases, the partition function Q of the entire system can be related to the partition function of a single particle or molecule. The calculation of the translational partition function is done as follows.

20.6.1 Translational Partitions Function

For a gas of \tilde{N} identical noninteracting particles the total energy $U_i = \sum_k \tilde{N}_k^i E_k$, in which E_k is the translational energy of state and \tilde{N}_k^i are the number of particles in that state. We have already noted (Section 20.4) that translational states are sparsely occupied. Therefore, most of the \tilde{N}_k^i are zero and the partition function for the translational states is a sum that looks like

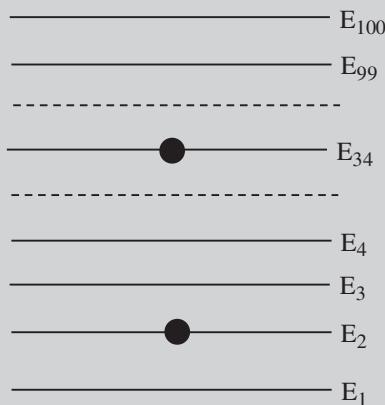
$$\begin{aligned} Q_{\text{trans}} &= \sum_i e^{-\beta U_i} = \sum_i e^{-\beta} \sum_k \tilde{N}_k^i E_k \\ &= e^{-\beta(1 \cdot E_1 + 0 \cdot E_2 + 0 \cdot E_3 + 1 \cdot E_4 + \dots)} + e^{-\beta(0 \cdot E_1 + 0 \cdot E_2 + 1 \cdot E_3 + 1 \cdot E_4 + \dots)} + \dots \end{aligned} \quad (20.6.1)$$

The terms in this sum can be interpreted as terms in a single-particle partition function. Each of the factors $e^{-\beta E_k}$ is a term in the single-particle partition function $q = \sum_k e^{-\beta E_k}$. Since the number of available translational states is much larger than the number of particles, an overwhelming number of terms correspond to only one particle in a translational state. Hence, the right-hand side of Equation (20.6.1) can be approximated as the product of \tilde{N} partition functions $q = \prod_k q_{\text{trans}}^{N_k}$. However, as explained in Box 20.2, such a product will have permutations between particles that are not in Q_{trans} . The overcounting is corrected by dividing $q^{\tilde{N}}$ by $\tilde{N}!$. This leads to the relation

$$Q_{\text{trans}} = \frac{q_{\text{trans}}^{\tilde{N}}}{\tilde{N}!} \quad (20.6.2)$$

Box 20.2 Relation between q and Q

The approximation $Q_{\text{trans}} = q^{\tilde{N}}/\tilde{N}!$ can be made clear by considering 100 translational states occupied by two identical particles. Every pair of energy states that the two particles occupy corresponds to a state of the system. In identifying distinct system states, every pair of energies should be counted only once; exchanging the two particles does not result in a different system state because the particles are identical.



For two particles and 100 states, there are $100 \times 99/2! = 4500$ system states in which the two particles occupy different energy states, but there are only 100 in which both particles are in the same system state. The corresponding terms in Q are

$$(a) \quad Q = \sum_{i>k}^{100} \sum_{k=1}^{100} e^{-\beta(E_i+E_k)} + \sum_{k=1}^{100} e^{-\beta 2E_k}$$

In the first term, $i > k$ assures that each pair of energy states is included only once. The single-particle partition function $q = \sum_{k=1}^{100} e^{-\beta E_k}$. Comparing Q with

$$q^2 = \sum_{i=1}^{100} e^{-\beta E_i} \sum_{k=1}^{100} e^{-\beta E_k} = \sum_{i=1}^{100} \sum_{k=1}^{100} e^{-\beta(E_i+E_k)}$$

we see that, when $i \neq k$, each pair of E_i and E_k occurs twice in q^2 but only once in Q . In q^2 , exchange of particles is counted as a different system state. We compensate for this overcounting by dividing q^2 by $2!$ and get

$$(b) \quad \frac{q^2}{2!} = \frac{1}{2} \sum_{i=1}^{100} \sum_{k=1}^{100} e^{-\beta(E_i+E_k)} = \sum_{i>k}^{100} \sum_{k=1}^{100} e^{-\beta(E_i+E_k)} + \frac{1}{2} \sum_{k=1}^{100} e^{-\beta 2E_k}$$

Comparing (a) and (b), we see that they differ only in the second term, which corresponds to two particles in the same energy state. Since such states are far fewer than those in which the two particles are in different energy states, the difference between (a) and (b) is not significant. The above argument can be extended to \tilde{N} particles by replacing $2!$ with $\tilde{N}!$. Thus, when the number of available states far exceeds the number of particles, $Q_{\text{trans}} = q_{\text{trans}}^{\tilde{N}}/\tilde{N}!$ is a very good approximation.

Our task now is to calculate the single-particle translational partitions function q_{trans} . As shown in Box 20.1, for a gas of particles with mass m in a cubical box of sides l_x, l_y, l_z , the translational states are specified by the quantum numbers n_x, n_y, n_z with energies

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left[\left(\frac{n_x}{l_x} \right)^2 + \left(\frac{n_y}{l_y} \right)^2 + \left(\frac{n_z}{l_z} \right)^2 \right]$$

To obtain q_{trans} , the following sum is to be evaluated:

$$q_{\text{trans}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta C[(n_x/l_x)^2 + (n_y/l_y)^2 + (n_z/l_z)^2]} = \sum_{n_x=1}^{\infty} e^{-\beta C(n_x/l_x)^2} \sum_{n_y=1}^{\infty} e^{-\beta C(n_y/l_y)^2} \sum_{n_z=1}^{\infty} e^{-\beta C(n_z/l_z)^2}$$

in which $C = h^2/8m$. Each of these sums can be approximated by an integral because the energy level spacing is very small. The sum over n_x can be written as the integral (which is evaluated using the table of integrals in Appendix 20.1):

$$\sum_{n_x=1}^{\infty} e^{-\beta C(n_x/l_x)^2} = \int_0^{\infty} e^{-\beta C(n_x/l_x)^2} dn_x = \frac{1}{2} \left(\frac{\pi l_x^2}{\beta C} \right)^{1/2} = \frac{l_x}{h} (2\pi m k_B T)^{1/2}$$

When similar integrals for n_y and n_z are evaluated, the partition function can be written as

$$q_{\text{trans}} = \frac{l_x l_y l_z}{h^3} (2\pi m k_B T)^{3/2} = \frac{V}{h^3} (2\pi m k_B T)^{3/2} \quad (20.6.3)$$

in which the volume of the system $V = l_x l_y l_z$. The translational partition function of the gas is thus

$$Q_{\text{trans}} = \frac{1}{\tilde{N}!} \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right]^{\tilde{N}} \quad (20.6.4)$$

This expression can be given another interpretation leading to another form in which Q_{trans} is often written. Since the average kinetic energy of a gas particle is $3k_B T/2$, the average momentum of particles at temperature T is $(3mk_B T)^{1/2}$. The de Broglie wavelength ($\lambda = h/p$) associated with this momentum equals $h/(3mk_B T)^{1/2}$. For this reason, a **thermal wavelength** $\Lambda = h/(2\pi m k_B T)^{1/2}$ is defined (replacing 3 with 2π). In terms of Λ , the partition function Q_{trans} can be written in the following simple form:

$$Q_{\text{trans}} = \frac{1}{\tilde{N}!} \left[\frac{V}{\Lambda^3} \right]^{\tilde{N}}, \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (20.6.5)$$

20.6.2 Thermodynamic Quantities

For particles that have no internal structure or for particles whose internal energy at the temperature of interest can be neglected, all the energy is translational (kinetic energy). A monatomic ideal gas is an example. The Helmholtz energy of a gas of such particles is

$$F(V, T, \tilde{N}) = -k_B T \ln Q_{\text{trans}} = -k_B T \tilde{N} \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right] + k_B T \ln \tilde{N}!$$

Using Stirling's approximation, $\ln(\tilde{N}!) \simeq \tilde{N} \ln \tilde{N} - \tilde{N}$, the above expression can be written as

$$\begin{aligned} F(V, T, \tilde{N}) &= -k_B T \left\{ \tilde{N} \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right] - \tilde{N} \ln \tilde{N} + \tilde{N} \right\} \\ &= -k_B \tilde{N} T \left\{ \ln \left[\frac{V}{\tilde{N} h^3} (2\pi m k_B T)^{3/2} \right] + 1 \right\} \end{aligned} \quad (20.6.6)$$

Since the gas constant $R = k_B N_A$ and amount in moles $N = \tilde{N}/N_A$, the above F can be expressed as

$$F(V, T, N) = -RNT \left\{ \ln \left[\frac{V}{NN_A h^3} (2\pi m k_B T)^{3/2} \right] + 1 \right\} \quad (20.6.7)$$

Other thermodynamic quantities can now be obtained from F . For example, since $p = -(\partial F/\partial V)_{T,N}$, it follows that

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{RTN}{V} \quad (20.6.8)$$

which is the ideal gas equation. Similarly, since entropy $S = -(\partial F/\partial T)_{V,N}$, a simple calculation shows that the ideal gas entropy is

$$S = N \left\{ R \ln \left[\frac{V}{NN_A h^3} (2\pi m k_B T)^{3/2} \right] + \frac{5R}{2} \right\} \quad (20.6.9)$$

This expression was obtained in 1911 by O. Sackur and H. Tetrode in the early stages of the development of quantum theory. It is called the **Sackur-Tetrode equation** for the entropy of an ideal gas. It shows us that quantum theory (Planck's constant being its signature) gives the absolute value of entropy without any arbitrary constants. In Chapter 3 we derived the following expression for the entropy of an ideal gas:

$$S(V, T, N) = N \left[s_0 + R \ln \left(\frac{V}{N} \right) + C_V \ln T \right] \quad (20.6.10)$$

in which s_0 was an undetermined constant. Comparing Equations (20.6.9) and (20.6.10), we see that $C_V = 3R/2$ and

$$s_0 = R \ln \left[\frac{(2\pi m k_B)^{3/2}}{N_A h^3} \right] + \frac{5R}{2}$$

We have noted that the energy U of the system can be obtained from Q using relation (20.5.4), $U = -(\partial \ln Q / \partial \beta)$, in which $\beta = 1/k_B T$. Because $\ln Q = -F/k_B T$, using Equation (20.6.6), Q can be expressed in terms of β thus:

$$\ln Q = \tilde{N} \left\{ \ln \left[\frac{V}{\tilde{N} h^3} (2\pi m / \beta)^{3/2} \right] + 1 \right\}$$

From this, it follows that the energy of an ideal gas of particles whose energy is entirely translational is

$$U = -\frac{\partial \ln Q}{\partial \beta} = \frac{3}{2} \tilde{N} k_B T = \frac{3}{2} NRT \quad (20.6.11)$$

From the fundamental quantities U and S , all thermodynamic quantities of an ideal gas of structureless particles are obtained.

20.6.3 Rotational Partition Function

For molecules, we must consider energy and entropy associated with rotational motion. At ordinary temperatures, a large number of rotational states above the lowest energy state are occupied by molecules (this can be seen by comparing $k_B T$ with rotational energy levels). For simplicity, we consider a diatomic molecule whose atoms have masses m_1 and m_2 , as shown in Box 20.1. Since the rotational energies are $E_L = (\hbar^2/2I)L(L+1)$ with degeneracy $g(E_L) = 2L + 1$, the single-molecule partition function is

$$q_{\text{rot}} = \sum_{L=0}^{\infty} (2L+1)e^{-\beta(\hbar^2/2I)L(L+1)} \quad (20.6.12)$$

For diatomic molecules with masses m_1 and m_2 , the reduced mass μ is defined as

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (20.6.13)$$

If the distance between the two nuclei (bond length) is R , then the moment of inertia I is given by

$$I = \mu R^2 \quad (20.6.14)$$

To compare the rotational energy-level spacing with $k_B T$, a characteristic temperature $\theta_{\text{rot}} \equiv \hbar^2/2Ik_B$ is defined. Then the rotational partition function q_{rot} is written as

$$q_{\text{rot}} = \sum_{L=0}^{\infty} (2L+1)e^{-L(L+1)\theta_{\text{rot}}/T} \quad (20.6.15)$$

Using bond length data, and assuming R equals the bond length, the moment of inertia I and θ_{rot} can be calculated. For H_2 it is found that $\theta_{\text{rot}} = 87.5$ K and $\theta_{\text{rot}} = 2.1$ K for O_2 . At very low temperatures, i.e. when $T \ll \theta_{\text{rot}}$, this sum can be approximated by

$$q_{\text{rot}} = 1 + 3e^{-2\theta_{\text{rot}}/T} + 5e^{-6\theta_{\text{rot}}/T} + \dots \quad (20.6.16)$$

At high temperatures, i.e. when $T \gg \theta_{\text{rot}}$, the sum (20.6.15) may be approximated by the following integral:

$$\begin{aligned} q_{\text{rot}} &= \int_0^{\infty} (2L+1)e^{-L(L+1)\theta_{\text{rot}}/T} dL \\ &= \int_0^{\infty} e^{-L(L+1)\theta_{\text{rot}}/T} d[L(L+1)] = \frac{T}{\theta} = \frac{2Ik_B T}{\hbar^2} \end{aligned} \quad (20.6.17)$$

For diatomic molecules with identical atoms, such as H_2 or N_2 , the quantum theory of identical particles stipulates that only half the rotational states are allowed. Hence, a factor of 2 has to be introduced in the denominator of the above expression. In general, when identical atoms are present in a molecule, a **symmetry number** σ must be included in the expression for the partition function. Thus, the general expression for the partition function for a rotation around a given axis with moment of inertia I is

$$q_{\text{rot}} = \frac{2Ik_B T}{\sigma \hbar^2} \quad (20.6.18)$$

The symmetry number σ for a larger molecule is determined by the symmetries of the molecule. It is equal to the number of proper rotations, including the identity, in the symmetry group of the molecule.

20.6.4 Vibrational Partition Function

Molecules also have vibrational motions that stretch and bend bonds. Each vibration is associated with frequency $\nu = \omega/2\pi$. Box 20.1 lists expressions for the energy levels for the vibrational motion:

$$E_\nu = \hbar\omega \left(\nu + \frac{1}{2} \right), \quad \nu = 0, 1, 2, \dots \quad (20.6.19)$$

Using this expression, the partition function for vibrational energies can easily be calculated because the energy levels are equally spaced. We shall assume that the degeneracy of the energy levels is 1. Then, the vibrational partition function is

$$q_{\text{vib}} = \sum_{\nu=0}^{\infty} e^{-\beta\hbar\omega[\nu+(1/2)]} = e^{-\beta\hbar\omega/2} \sum_{\nu=0}^{\infty} x^\nu$$

where $x = e^{-\beta\hbar\omega}$. Since $x < 1$, the series on the right-hand side can be summed:

$$q_{\text{vib}} = e^{-\beta\hbar\omega/2} \sum_{\nu=0}^{\infty} x^\nu = e^{-\beta\hbar\omega/2} \frac{1}{1-x}$$

Thus, the single-molecule vibrational partition function is

$$q_{\text{vib}} = e^{-\beta\hbar\omega/2} \frac{1}{1 - e^{-\beta\hbar\omega}} \quad (20.6.20)$$

At ordinary temperatures, the level spacing between vibrational energy states is generally larger than the thermal energy $k_B T$. Hence, only very few energy states higher than the ground state are occupied by molecules. As was done for rotational states, this aspect can be quantified by defining a characteristic vibrational temperature $\theta_{\text{vib}} \equiv \hbar\omega/k_B$. Then the partition function (20.6.20) can be written as

$$q_{\text{vib}} = e^{-\theta_{\text{vib}}/2T} \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} \quad (20.6.21)$$

The characteristic vibrational temperatures for some diatomic molecules are:²

$\theta_{\text{vib}} (\text{K})$	H ₂	N ₂	O ₂	Cl ₂	HCl	CO	NO
6210	3340	2230	810	4140	3070	2690	

(20.6.22)

Thus, at T in the range 200–400 K, only a few of the lowest vibrational states are occupied. The characteristic temperatures for electronic states are even higher, so electronic states are mostly in their lowest or ground state.

Combining all the partition functions for a diatomic molecule, we can write

$$q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} = \frac{V}{h^3} (2\pi m k_B T)^{3/2} \frac{2Ik_B T}{\sigma\hbar^2} e^{-\theta_{\text{vib}}/2T} \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} \quad \text{and } Q = \frac{q^N}{N} \quad (20.6.23)$$

From this partition function, thermodynamic quantities U , p , μ , etc., can be calculated (see Exercises). The total energy of the system is the sum of energies in each mode of motion $U = U^{\text{trans}} + U^{\text{rot}} + U^{\text{vib}} + U^{\text{elec}}$. The heat capacity $C_V = (\partial U / \partial T)_V$. By expressing U as the sum of energies, we can know the contribution of each of the modes of motion, i.e. translation, rotation, vibration, etc., to the heat capacity C_V .

²Source: T.L. Hill, *Introduction to Statistical Thermodynamics*, 1960, Addison-Wesley: Reading, MA.

20.7 Equilibrium Constants

The formalism of statistical thermodynamics can also be used to relate equilibrium constants of chemical reactions to partitions functions. In doing so, we relate molecular energies to equilibrium constants. Let us consider the simple reaction



At equilibrium, the chemical potentials of X and Y are equal. We use the subscripts X and Y to represent the quantities for the two species. The chemical potential of X is $\mu_X = (\partial F_X / \partial N_X)_{T,V}$; and since $F_X = -k_B T \ln Q_X$, in which $Q_X = q_X^{\tilde{N}_X} / \tilde{N}_X!$, we can establish a relationship between the q_X and μ_X . Here, \tilde{N} is the number of molecules and N is the amount in moles. Since Q is expressed as a function of \tilde{N} , we note that $\mu_X = (\partial F_X / \partial N_X) = (\partial F_X / \partial \tilde{N}_X)(\partial \tilde{N}_X / \partial N) = N_A(\partial F_X / \partial \tilde{N}_X)$.

When considering a system of reactants and products that interconvert, care must be taken to use the same scale of energy for all molecules when computing partition functions. In the calculations of q presented in the previous sections, generally the zero of energy was taken to be the lowest energy or ground state of that molecule. When more than one molecule is involved, their energies must be measured using a common zero. The lowest energy of a molecule can then have a nonzero value with respect to the common zero. As shown in Figure 20.3, the lowest energy states of X and Y can be different. We shall use E_X^0 and E_Y^0 to represent the lowest energies of X and Y, respectively, in the common energy scale. This means that the energies of X will all get an additive term E_X^0 and this in turn adds a factor $\exp(-\beta E_X^0)$ to q_X . Thus, with respect to the common zero of energy:

$$Q_X = \frac{(q_X e^{-\beta E_X^0})^{\tilde{N}_X}}{\tilde{N}_X!} = \frac{q_X^{\tilde{N}_X}}{\tilde{N}_X!} e^{-\beta \tilde{N}_X E_X^0} \quad (20.7.2)$$

The Helmholtz energy F is

$$F_X = -k_B T \ln Q_X = -k_B T (\tilde{N}_X \ln q_X - \tilde{N}_X \ln \tilde{N}_X + \tilde{N}_X - \beta \tilde{N}_X E_X^0) \quad (20.7.3)$$

and a simple calculation shows that

$$\mu_X = \left(\frac{\partial F_X}{\partial N_X} \right)_{T,V} = N_A \left(\frac{\partial F_X}{\partial \tilde{N}_X} \right)_{T,V} = -N_A k_B T \left[\ln \left(\frac{q_X}{\tilde{N}_X} \right) - \beta E_X^0 \right] \quad (20.7.4)$$

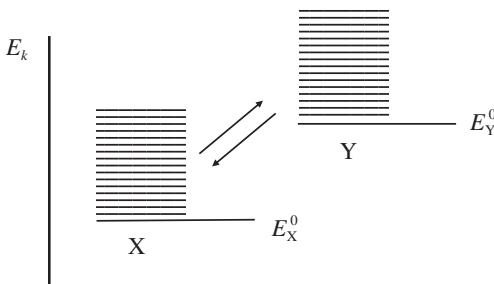


Figure 20.3 Energy levels of two molecules X and Y on a single energy scale. E_X^0 and E_Y^0 are the ground states on the single energy scale.

This expression relates the chemical potential to the partition function and the number of molecules \tilde{N} . We can invert this equation and write

$$\tilde{N}_X = q_X e^{(\mu - N_A E_X^0)/RT} \quad (20.7.5)$$

or in units of moles of X:

$$N_X = \frac{q_X}{N_A} e^{(\mu - U_{0X})/RT} \quad (20.7.6)$$

in which $U_{0X} = N_A E_X^0$.

As a side remark, we note here that for a monatomic ideal gas $q_X = (V/h^3)(2\pi mk_B T)^{3/2}$. Using this expression in Equation (20.7.6), we find

$$\frac{N_X}{V} = \frac{(2\pi mk_B T)^{3/2}}{N_A h^3} e^{(\mu - U_{0X})/RT} = \frac{1}{N_A \Lambda^3} e^{(\mu - U_{0X})/RT} \quad (20.7.7)$$

Thus, the molar density is related to the chemical potential. Equation (20.7.7) is the same as relation (12.6.4) if we identify $z(T)$ in (12.6.4) with $(1/N_A \Lambda^3)$ and U_0 with $M_X c^2$. When the chemical potential is zero, the molar density is a function of T only.

For the reaction $X \rightleftharpoons{} Y$, let us assume when equilibrium is reached that the moles of X and Y are $N_{X,\text{eq}}$ and $N_{Y,\text{eq}}$ respectively. Using Equation (20.7.4) and equating the chemical potentials of the two species, we obtain

$$\mu_X = -RT \left[\ln \left(\frac{q_X}{N_{X,\text{eq}} N_A} \right) - \beta E_X^0 \right] = \mu_Y = -RT \left[\ln \left(\frac{q_Y}{N_{Y,\text{eq}} N_A} \right) - \beta E_Y^0 \right]$$

This expression can be rewritten as

$$\frac{N_{Y,\text{eq}}}{N_{X,\text{eq}}} = \frac{q_Y / N_A}{q_X / N_A} e^{-(U_{0Y} - U_{0X})/RT} \quad (20.7.8)$$

in which $U_{0X} = N_A E_X^0$ and $U_{0Y} = N_A E_Y^0$. Since the equilibrium concentrations $[X]_{\text{eq}} = N_{X,\text{eq}}/V$ and $[Y]_{\text{eq}} = N_{Y,\text{eq}}/V$, we can relate the equilibrium constant $K_c \equiv [Y]_{\text{eq}}/[X]_{\text{eq}}$ to the partition functions:

$$K_c = \frac{[Y]_{\text{eq}}}{[X]_{\text{eq}}} = \frac{N_{Y,\text{eq}}/V}{N_{X,\text{eq}}/V} = \frac{q_Y / N_A V}{q_X / N_A V} e^{-\Delta U_0 / RT} \quad (20.7.9)$$

in which $\Delta U_0 = U_{0Y} - U_{0X}$ is the difference in the ground-state energies of the reactants and products. The above result can be generalized to the reaction



$$K_c = \frac{[Z]_{\text{eq}}^c [W]_{\text{eq}}^d}{[X]_{\text{eq}}^a [Y]_{\text{eq}}^b} = \frac{(q_Z / N_A V)^c (q_W / N_A V)^d}{(q_X / N_A V)^a (q_Y / N_A V)^b} e^{-\Delta U_0 / RT} \quad (20.7.11)$$

in which $\Delta U_0 = (cU_{0Z} + dU_{0W} - aU_{0X} - bU_{0Y})$. Thus, if the partition functions and the ground-state energies of the reacting molecules are known, the equilibrium constants can be calculated. The term ΔU_0 is very nearly the heat released in the reaction; i.e. it is essentially the reaction enthalpy.

20.8 Heat Capacities of Solids

In Chapter 6 we noted that the heat capacities of solids at low temperatures are proportional to T^3 . This was experimentally established. At high temperatures, experiments showed that the molar heat capacities of most solids were nearly the same, close to $3R$. The latter is called the law of Dulong and Petit, after the nineteenth century physicists who proposed it. Classical theories of solids could not explain the behavior at low temperatures. Only the use of quantum theory was able to explain why the molar heat capacity of a solid decreased when the temperature decreased. During the early years of quantum theory, the first explanation of the observed low temperature behavior of heat capacities using the then new ideas of energy quantization came from Einstein. Einstein's theory was a big step toward theoretically explaining experimentally observed behavior at low temperatures. However, its predictions did not agree very well with experiments because of the simplifying approximations Einstein made. An improved theory was formulated by Peter Debye (1884–1966) which was able to explain the low temperature ' T^3 ' behavior'. We shall look at both theories.

20.8.1 Einstein's Theory of Solids

Solids have a crystalline lattice structure in which atoms are arranged as a regular crystal array. The kinetic energy of each atom is in its vibrational motion about its position in the lattice. To understand the heat capacity, we need to calculate the energy of the crystal; i.e. we need to calculate the total vibrational energy of all the atoms in the solid. Einstein made the simplifying assumption that all atoms vibrate at the same frequency ν and that energy levels of the vibrational motion are that of a simple harmonic oscillator:

$$E_n = h\nu(n + \frac{1}{2}), \quad n = 0, 1, 2, \dots \quad (20.8.1)$$

Since the probability of an atom's energy being E_n is proportional to $\exp[-E_n/k_B T]$, the partition function, Q_x , for vibration along the x axis is given by the expression:

$$Q_x = e^{-(\beta h\nu/2)} \sum_0^{\infty} e^{-\beta h\nu n} = e^{-(\beta h\nu/2)} \frac{1}{1 - e^{-\beta h\nu}}, \quad \beta = \frac{1}{k_B T} \quad (20.8.2)$$

The same expression holds for the partition functions Q_y and Q_z for vibrations along the y and z directions. The total partition function $Q = Q_x Q_y Q_z$. The average energy U of an atom, vibrating with a frequency ν can now be obtained using the general relation (20.5.4):

$$U = -\frac{\partial \ln(Q)}{\partial \beta} = \frac{3h\nu}{2} + \frac{3h\nu}{e^{h\nu\beta} - 1} \quad (20.8.3)$$

In a solid consisting of one mole of atoms, the total energy is $N_A U$. The molar heat capacity $C_{mV} = N_A (\partial U / \partial T)_V$ can now be calculated. The result is

$$C_{mV} = N_A \left(\frac{\partial U}{\partial T} \right)_V = N_A \frac{3h\nu(h\nu/k_B T^2)e^{h\nu\beta}}{(e^{h\nu\beta} - 1)^2} = \frac{3R(h\nu\beta)^2}{(e^{h\nu\beta/2} - e^{-h\nu\beta/2})^2}$$

in which we have used $N_A k_B = R$ and rewritten the denominator so that the final expression can be written in the form:

$$C_{mV}(T) = 3R \frac{(h\nu/2k_B T)^2}{[\sinh(h\nu/2k_B T)]^2} \quad (20.8.4)$$

It is easy to see that $C_{mV} \rightarrow 0$ as $T \rightarrow 0$, in agreement with experimental observations. For very large values of T , the value of C_{mV} approaches $3R$ in accord with the law of Dulong and Petit.

20.8.2 Debye's Theory of Solids

Though Einstein's theory shows that the quantization of the vibrational energy is behind the observed low-temperature behavior of the molar heat capacity, the assumption that all atoms vibrate with the same frequency is not physically realistic. In fact, the atoms vibrate with a range of frequencies given by the normal modes of the large vibrating solid. The normal vibrational modes in a solid are collective motion of atoms in which the atom positions have a wave form. When the volume of the solid is finite, standing vibrational modes are established such that the waves have zero amplitude at the boundaries. For simplicity we shall consider a rectangular solid of sides l_x , l_y and l_z .

The standing waves can be represented by a function W as

$$W(x,y,z) = A_x \sin\left(\frac{2\pi x}{\lambda_x}\right) A_y \sin\left(\frac{2\pi y}{\lambda_y}\right) A_z \sin\left(\frac{2\pi z}{\lambda_z}\right)$$

The boundary conditions that W must be zero at $x = 0$ and $x = l_x$, and similarly for y and z , implies that

$$l_x = n_x \frac{\lambda_x}{2}, \quad l_y = n_y \frac{\lambda_y}{2} \quad \text{and} \quad l_z = n_z \frac{\lambda_z}{2} \quad (20.8.5)$$

in which n_x , n_y and n_z , are positive integers. The product of the wavelength λ and the frequency v equals the velocity C of the sound wave in the solid in a particular direction. Vibrational motion in solids, however, has three independent modes: two transverse modes, in which the vibration is perpendicular to the direction of wave propagation, and one longitudinal mode, in which the vibration is parallel to the direction of propagation. In general, the transverse and longitudinal modes have differing velocities, which we shall denote as C_t and C_l respectively. Having made a note of this, let us calculate the number of states in the frequency range v and $v + dv$ for each mode.

From (20.8.5) it follows that the vibrational states are characterized by frequencies

$$v_x = n_x \frac{C}{2l_x}, \quad v_y = n_y \frac{C}{2l_y} \quad \text{and} \quad v_z = n_z \frac{C}{2l_z} \quad (20.8.6)$$

C being the velocity, C_t or C_l . Note that the frequencies representing each standing mode are positive numbers. We may visualize these frequencies as points in a three-dimensional lattice with one lattice point in a volume equal to $(C^3/8l_x l_y l_z) = (C^3/8V)$, in which V is the volume of the solid. We shall write the number of states in the frequency range v and $v + dv$ as $\rho(v)dv$, in which $\rho(v)$ is the density of states. The term $\rho(v)dv$ can be computed as the number of lattice points in the spherical shell of radius v and width dv :

$$\rho(v)dv = \frac{1}{8} \frac{4\pi}{(C^3/8V)} v^2 dv$$

The $1/8$ factor is included because v_x , v_y and v_z should be positive. For the two transverse and one longitudinal modes, the total density of states of the solid is

$$\rho(v)dv = 4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) v^2 dv \quad (20.8.7)$$

In a solid of N atoms, there is an upper bound to the frequency, which we shall denote by v_{\max} . For a solid with N atoms, there are a total of $3N$ independent modes of oscillations. Hence:

$$\int_0^{v_{\max}} \rho(v)dv = 4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \frac{v_{\max}^3}{3} = 3N$$

Using this relation, we can rewrite (20.8.7) in terms of v_{\max} :

$$\rho(v)dv = \frac{9N}{v_{\max}^3} v^2 dv \quad (20.8.8)$$

To calculate the total energy distributed in all the modes of vibration of the N atoms, we begin by noting that the average energy in each mode of frequency v is equal to one-third of the expression (20.8.3) (which is for three independent modes):

$$U(v) = \frac{hv}{2} + \frac{hv}{e^{hv\beta} - 1}$$

The total energy U_{tot} in all the available modes is therefore obtained by integrating this expression using the density of modes $\rho(v)$ given in Equation (20.8.8). Thus

$$U_{\text{tot}} = \frac{9N}{v_{\max}^3} \int_0^{v_{\max}} \left(\frac{hv}{2} + \frac{hv}{e^{hv\beta} - 1} \right) v^2 dv \quad (20.8.9)$$

As before, an expression for the molar heat capacity can be obtained by taking the derivative of U_{tot} with respect to T :

$$C_{mV} = \left(\frac{\partial U_{\text{tot}}}{\partial T} \right)_V = \frac{9N_A}{v_{\max}^3} \int_0^{v_{\max}} \left(\frac{(hv)^2 (e^{hv\beta}/k_B T^2)}{(e^{hv\beta} - 1)^2} \right) v^2 dv \quad (20.8.10)$$

It is easy to see that this expression can be rewritten as

$$C_{mV} = \frac{9N_A k_B}{(\beta h v_{\max})^3} \int_0^{\beta h v_{\max}} \frac{x^4 dx}{(e^{x/2} - e^{-x/2})^2} \quad (20.8.11)$$

It is not possible to express this integral in a closed form, but we can see that it is a function of $\beta h v_{\max}$. For solids, a characteristic temperature called the **Debye temperature** is defined as

$$\Theta_D \equiv \frac{h v_{\max}}{k_B} \quad (20.8.12)$$

By combining all terms in Equation (20.8.11) involving $\beta h v_{\max}$, the heat capacity is written in terms of Θ_D and a Debye function $D(\Theta_D/T)$:

$$C_{mV} = 3R D(\Theta_D/T) \quad (20.8.13)$$

In which

$$D(\Theta_D/T) = D(\beta h v_{\max}) = \frac{3}{(\beta h v_{\max})^3} \int_0^{\beta h v_{\max}} \frac{x^4 dx}{(e^{x/2} - e^{-x/2})^2}.$$

The properties of the Debye function have been studied and it can be shown that it has the following limiting behaviors:

$$\text{As } (\Theta_D/T) \rightarrow 0, \quad D(\Theta_D/T) \rightarrow 1$$

and

$$\text{As } (\Theta_D/T) \rightarrow \infty, \quad D(\Theta_D/T) \rightarrow \left(\frac{4\pi^4}{5} \right) \left(\frac{T}{\Theta_D} \right)^3 \quad (20.8.14)$$

This limiting behavior of the Debye function implies that, at high T , the heat capacity C_{mV} approaches the Dulong and Petit value of $3R$; for low T , however, it decreases as T^3 . It is this latter ' T^3 ' law' that was in close agreement with the experimentally observed values of heat capacities. It is sometimes called the **Debye T^3 law**.

20.9 Planck's Distribution Law for Thermal Radiation

In radiation in thermal equilibrium with matter, the energy is distributed among all the frequencies, which range from zero to infinity. According to classical electromagnetic theory, each of these modes must have some energy. An increase in the temperature T would imply an increase in the energy of all the modes. Since the frequencies range from zero to infinity, this implies that the energy density of radiation must be infinite, as must the heat capacity. It was to address this problem that Max Planck introduced the quantum hypothesis. In doing so, Planck used one of the most powerful aspects of thermodynamics: its universality regardless of the complexity or simplicity of the system. *Radiation in thermal equilibrium with matter at a temperature T will have the same properties regardless of the type of molecules it is interacting with.* Hence, any deductions made about thermal radiation interacting with idealized oscillators will also be valid for radiation reacting with complex molecules. Thus, Planck assumed that the oscillators absorbing and emitting radiation were simple harmonic and introduced the quantum hypothesis that the energy absorbed or emitted is in quanta of energy $E = hv$. It became clear from later development of quantum theory that electromagnetic radiation itself is quantized and that it had particle properties, the particles we call photons.

To calculate the energy density of thermal radiation, the well-known **Planck distribution**, we shall assume that the radiation is in a rectangular box as standing waves. Mathematically we may treat these standing waves just as we treated the vibrational modes in a solid. Thus, the number of frequencies in the range v and $v + dv$ for each independent mode is given by the expression

$$\rho(v) dv = \frac{V4\pi}{c^3} v^2 dv \quad (20.9.1)$$

in which V is the volume of the box and c is the velocity of light. Since electromagnetic waves are transverse waves, there are two independent modes corresponding to two independent states of polarization. Hence, for thermal radiation we must use

$$\rho(v) dv = \frac{V8\pi}{c^3} v^2 dv \quad (20.9.2)$$

Using energy levels of a simple harmonic oscillator, $hv(1/2 + n)$, for the energy of the each mode of radiation, we can write the partition function for the mode with frequency v :

$$Q = e^{-(\beta hv/2)} \sum_0^{\infty} e^{-\beta hvn} = e^{-(\beta hv/2)} \frac{1}{1 - e^{-\beta hv}}, \quad \beta = \frac{1}{k_B T} \quad (20.9.3)$$

As was done in the case of Einstein's theory of solids, we can calculate the average energy in each mode of frequency v , obtaining the expression:

$$U(v) = -\frac{\partial \ln(Q)}{\partial \beta} = \frac{hv}{2} + \frac{hv}{e^{\beta hv} - 1} \quad (20.9.4)$$

The first term is the zero point energy, which does not contribute to thermodynamic properties of radiation (though it is real and its presence can be seen in physical phenomena). We shall therefore drop it in the expression for the energy. Combining Equations (20.9.2) and (20.9.4), we can now write the energy density, $u(v) = U(v)/V$, as

$$u(v) dv = \frac{8\pi h}{c^3} \frac{v^3 dv}{e^{\beta hv} - 1} \quad (20.9.5)$$

This is the celebrated expression Planck derived for the energy density of thermal radiation. The quantum hypothesis makes the energy density finite because the modes of higher frequencies require higher energy quanta to increase their energy. Hence most of the very high frequency modes are in their ground state. This is in contrast to classical theory in which the energies of mode of all frequencies can be increased equally with heat.

The properties of thermal radiation that were discussed in Chapter 11, such as the Stefan–Boltzmann law and Wien’s displacement law can be derived from the Planck distribution. For example, the total energy density over the entire spectrum of frequencies is

$$u_{\text{tot}} = \int_0^\infty u(v) dv = \frac{8\pi h}{c^3} \int_0^\infty \frac{v^3}{e^{\beta hv} - 1} dv \quad (20.9.6)$$

The integral can be evaluated by defining $x = \beta hv$ and rewriting the integral in terms of x . The result is

$$u_{\text{tot}} = \int_0^\infty u(v) dv = \frac{8\pi h}{c^3(\beta h)^4} \int_0^\infty \frac{x^3}{e^x - 1} dx \quad (20.9.7)$$

The integral over x can be evaluated in closed form (using tables or *Mathematica*). It equals $(\pi^4/15)$. Thus, the above expression becomes

$$u_{\text{tot}} = \int_0^\infty u(v) dv = \frac{8\pi h}{c^3(\beta h)^4} \left(\frac{\pi^4}{15} \right) = \frac{8}{15} \frac{\pi^5 k_B^4}{c^3 h^3} T^4 \quad (20.9.8)$$

which shows that the total energy density of thermal radiation is proportional to T^4 , which is the Stefan–Boltzmann law.

To derive Wien’s displacement law from the Planck distribution, we first write the energy density in terms of the wavelength $\lambda = c/v$:

$$u(\lambda) d\lambda = 8\pi hc \frac{\lambda^{-5} d\lambda}{e^{hc/k_B T \lambda} - 1} \quad (20.9.9)$$

This expression can be written as a function of $T\lambda$ by defining $y = T\lambda$, writing the energy density as a function of y :

$$u(y) = 8\pi hc T^5 \frac{y^{-5}}{e^{hc/k_B y} - 1}$$

This function reaches its maximum value at a particular value of y , say y_{max} , independent of the value of T (though the value of the function at the maximum depends on T). That is the maximum is reached when

$$T\lambda_{\text{max}} = y_{\text{max}} \quad (20.9.10)$$

which is Wien's displacement law. The value of $y_{\max} = 2.8979 \times 10^{-3}$ m K. Similarly, other thermodynamic properties of thermal radiation can be derived from the partition function using the methods outlined in this chapter.

Appendix 20.1 Approximations and Integrals

A20.1.1 Stirling's Approximation

When N is a large number, $N!$ is a very large number. One can estimate the value of $N!$ using Stirling's approximation:

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \quad (\text{A20.1.1})$$

Using this approximation, we see that

$$\ln N! = N \ln N - N + (1/2) \ln(2\pi N) \quad (\text{A20.1.2})$$

For large N , the last term in Equation (A20.1.2) is small compared with the other two terms and it can be neglected. The resulting expression $\ln N! \approx N \ln N - N$ has been used in this chapter. One could also arrive at this result by using the approximation

$$\ln N! = \sum_{k=1}^N \ln k \approx \int_1^N \ln y \, dy = (y \ln y - y)|_1^N = N \ln N - N + 1 \quad (\text{A20.1.3})$$

in which the sum is approximated by an integral, an approximation valid for large N .

A20.1.2 Integrals used in Statistical thermodynamics

- (a) $\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2}$
- (b) $\int_0^\infty xe^{-ax^2} dx = \frac{1}{a}$
- (c) $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a}\right)^{1/2}$
- (d) $\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$

More generally:

- (e) $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \times 3 \times 5 \times \dots \times (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a}\right)^{1/2}$
- (f) $\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2} \left(\frac{1}{a^{n+1}}\right)$

Reference

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Example

Example 20.1 For the gas N₂ in a cube of side 10.0 cm, at T = 298 K, estimate the number of translational states that are below 3k_BT/2 and compare this with the number of molecules in this cube at p = 1.0 bar.

Solution The translational energies for a cube ($l_x = l_y = l_z = 1$) are given by (Box 20.1)

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2)$$

The value of $n^2 = n_x^2 + n_y^2 + n_z^2$ for which the energy is 3k_BT/2 is

$$n^2 = \frac{3k_B T}{h^2/8ml^2}$$

Substituting values $k_B = 1.38 \times 10^{-23}$ J K⁻¹, $T = 298$ K, $h = 6.626 \times 10^{-34}$ J s, $m = (28 \times 10^{-3}/N_A)$ kg and $l = 0.1$ m, we find $n^2 = 5.2 \times 10^{19}$. That means all quantum states in the sphere of radius n have energies less than 3k_BT/2. Since only positive values of n_x , n_y and n_z must be included:

$$\text{Total number of states with energy } E < \frac{3k_B T}{2} \text{ is } \frac{1}{8} \frac{4\pi}{3} n^3 = \frac{1}{8} \frac{4\pi}{3} (5.2 \times 10^{19})^{3/2} = 1.96 \times 10^{29}$$

$$\text{Number of molecules } \tilde{N} = \frac{N_A p V}{R T} = \frac{N_A \times 1.0 \times 10^5 \text{ Pa} \times 10^{-3} \text{ m}^3}{R \times 298 \text{ K}} = 2.4 \times 10^{22}$$

This calculation shows that the number of available translational states is much higher than the number of particles in a gas at ordinary pressures and temperatures.

Exercises

- Obtain Equation (20.4.5) using Stirling's approximation.
- Using an H–H bond length of 74 pm and an O=O bond length of 121 pm, calculate the characteristic rotational temperatures for H₂ and O₂.
- Using $q^{\text{vib}} = e^{-\beta \hbar \omega / 2} [1/(1 - e^{-\beta \hbar \omega})]$ show that

$$\langle E^{\text{vib}} \rangle = \hbar \omega \left(\frac{1}{2} + \frac{e^{-\hbar \omega / k_B T}}{1 - e^{-\hbar \omega / k_B T}} \right)$$

- 20.4** In earlier chapters we have expressed the chemical potential of an ideal gas $\mu = \mu^0(T) + RT \ln(p/p_0)$ (in which p_0 is the pressure of the standard state). In expression (20.7.4) the chemical potential is expressed in terms of the partition function and other molecular quantities. For a monatomic gas, rewrite (20.7.4) in the form $\mu = \mu^0(T) + RT \ln(p/p_0)$ and identify $\mu^0(T)$ as a function of T .
- 20.5** The bond length of H_2 is 74 pm. (a) Calculate the moment of inertia and express the rotational partition function as a function of T . (b) Obtain an expression for its molar energy as a function of T . (c) Calculate the molar heat capacity.
- 20.6** Calculate the equilibrium constant for the reaction $H_2 \rightleftharpoons H + H$.

21

Self-Organization and Dissipative Structures in Nature

21.1 Dissipative Structures in Diverse Disciplines

21.1.1 Limitations of the Local Equilibrium Assumption

Before presenting the diverse situations in which dissipative structures are known to appear, let us note the limitations of our method. The method based on local equilibrium that we followed is satisfactory in a large domain of experimentation and observation. Still there are situations where some extension and modification are necessary. Let us enumerate a few of them.

To begin with, we have rarefied media where the assumption of local equilibrium is not valid. The average energy at each point depends on the temperature at the boundaries. There are important situations in astrophysics that belong to this category.

We then have the case of strong gradients where we expect linear laws, such as the Fourier law for heat conduction, to fail. Experiments in these situations are difficult to perform and a general theoretical description, as in the case of the Fourier law, does not exist. Attempts to introduce such nonlinear outcomes into the thermodynamic description lead to the ‘extended thermodynamics’; [1] already mentioned in the text.

Finally, we have very interesting memory effects that appear for long times (as compared to characteristic relaxation times). This field started with important numerical simulations by Alder and Wainright [2], who showed that nonequilibrium processes may have ‘long-time tails’. In other words, the approach to equilibrium is not exponential as it was generally thought to be but polynomial (e.g. $t^{-3/2}$), which is much slower. To understand this effect, consider a molecule we set in motion with respect to the medium; its momentum is transmitted to the medium, which in turn reacts back on the molecule. This leads to memory effects, which are discussed in many papers [3, 4]. As a result nature has a much longer memory of irreversible processes than it was thought before. Again this shows that local equilibrium is an approximation, albeit a very good one.

However, already the formulation of nonequilibrium thermodynamics as used in this book has led to innumerable applications in most diverse fields. To whet the appetite of the readers, we shall quote a few of them, but the list is far from being extensive.

21.1.2 Material Science

Concepts such as fluctuations, dissipative structure and self-organization play an essential role in important advances in this field. A good introduction is given by Walgraef [5, 6]. Through new technologies (laser and particle irradiation, ion implantation, ultra fast quenches) it is now possible to produce materials in highly nonequilibrium conditions – and thus escape from the tyranny of the equilibrium phase diagram. Here are some examples studied in Walgraef's book:

- Materials such as quasi-crystals, high T superconductors, semiconductor heterostructures and superlattices are typical examples of nonequilibrium materials.
- It is now possible to produce complex structures or composites that simultaneously satisfy very diverse requirements. To do so, one has to control the material on length scales that vary from the atomic to the micrometer level. Self-organization is a precious ally for the design of such materials.
- Many materials are used in very hard conditions: they are submitted to deformations corrosion, irradiation and so on. In such conditions, their defect populations acquire complex behaviors described well by reaction–diffusion equations, and may therefore become organized in very regular structures that affect their physical properties. It is also clear now that instabilities and patterns occur all the time in materials science. They affect the properties of the materials and, hence, need to be understood and controlled.
- It is well known that defects play an important role in determining material properties. Point defects play a major role in all macroscopic material properties that are related to atomic diffusion mechanisms and to electronic properties in semiconductors. Line defects, or dislocations, are unquestionably recognized as the basic elements that lead to plasticity and fracture. While the study of individual solid-state defects has reached an advanced level, the study of collective behavior of defects, which arises in nonequilibrium conditions, is still in its infancy. Nonetheless, significant progress has been made in dislocation dynamics and plastic instabilities over the past several years, and the importance of nonlinear phenomena has also been assessed in this field. The dislocation structures have been observed experimentally.

Curiously, the instabilities and self-organization that occurs in far-from-equilibrium systems as a result of basic physical processes, such as chemical reactions and diffusion, also occur at a much more complex level of living systems. A mathematical modeling of these complex systems also consists of irreversible nonlinear equations. A basic feature in all these systems is the possibility of amplification of small fluctuations under certain conditions, which makes the system unstable. These systems undergo instabilities often due to autocatalytic processes and make a transition to states with distinctly different organization. Thus the paradigm of ‘order through fluctuations’ also holds here.

21.1.3 Multicellular Systems

One example of pattern formation in complex systems occurs in the life cycle of the *Dictyostelium discoideum*. Figure 21.1 describes the life cycle of this species. In (a), the amoebas are at the unicellular stage. They move in the surrounding medium; they feed on such nutrients as bacteria and proliferate by cell division. Globally speaking they constitute a uniform system, inasmuch as their density (number of cells per square centimeter) is essentially constant. Suppose now that the amoebas are subjected to starvation; in the laboratory this is induced deliberately, in Nature it may happen because of less favorable ambient conditions. This is the analog of applying a constraint in a physical or chemical experiment. Interestingly, the individual cells do not die. Rather, they respond to the constraint by aggregating (b) toward a center of attraction. The initial homogeneity is broken; space becomes structured. The resulting multicellular body, the plasmodium (c), is capable of moving, presumably to seek more favorable conditions of temperature and moisture. After this

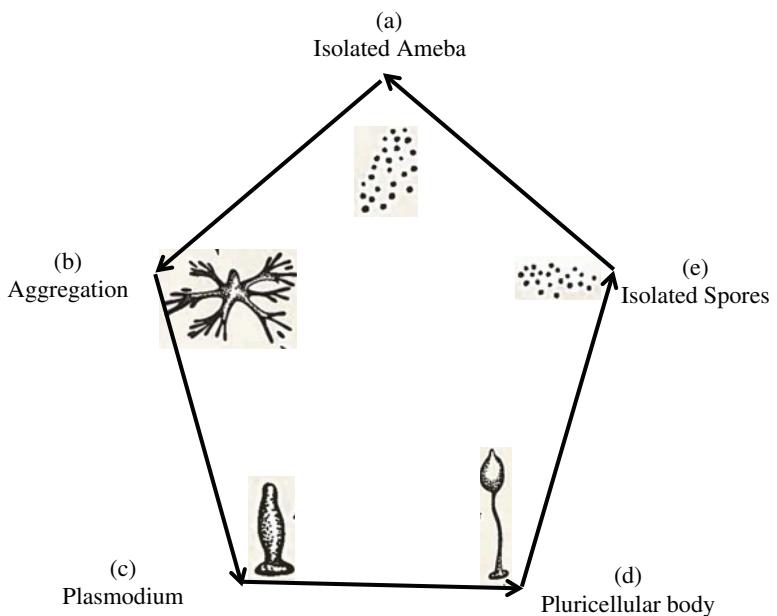


Figure 21.1 Life cycle of the slime mold (amoeba) *Dictyostelium discoideum*.

migration the body differentiates (d) and gives rise to two kinds of cells, one of which constitutes the stalk and the other a fruiting body within which spores are formed. Eventually the spores are disseminated (e) in the ambient medium, and if the conditions are favorable they germinate to become amoebas and the life cycle begins again.

Let us investigate the aggregation stage in more detail. The following phenomena are observed during this process. First, after starvation some of the cells begin to synthesize and release signals of a chemical substance known as cyclic adenosine monophosphate (cAMP) in the extracellular medium. The synthesis and release are periodic, just as in the chemical clock of the BZ system, with a well-defined period for given experimental conditions. The cAMP released by the ‘pioneer’ cells diffuses in the extracellular medium and reaches the surface of the neighboring cells. Two types of events are then switched on. First, these cells perform an oriented movement called chemotaxis toward the regions of higher concentration of cAMP, i.e. toward the pioneer cells. This motion gives rise to density patterns among the cells that look very much like the wave patterns in the BZ reagent (Figure 21.2). Second, the process of aggregation is accelerated by the ability of sensitized cells to amplify the signal and to relay it in the medium. This enables the organism to control a large territory and form a multicellular body comprising some 10⁵ cells.

Thus, the response to the starvation constraint gives rise to a new level of organization resulting from the concerted behavior of a large number of cells and enabling the organism to respond flexibly to a hostile environment. What are the mechanisms mediating this transition? Let us first observe that the process of chemotaxis leads to an amplification of the heterogeneity formed initially, when the pioneer cells begin to emit pulses of cAMP. Because it enhances the density of cells near the emission center, chemotaxis enhances movement of the other cells toward it. This constitutes what one usually calls a feedback loop, very similar to chemical autocatalysis.

As it turns out, a second feedback mechanism is present in *Dictyostelium discoideum* that operates at the subcellular level and is responsible for both the periodic emission of cAMP and the relay of the chemotactic

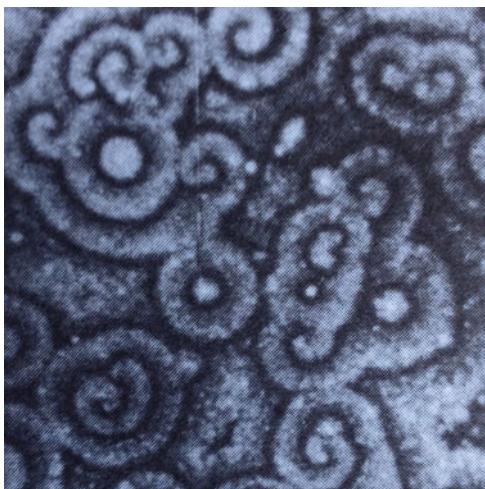


Figure 21.2 Concentric and spiral wave patterns of aggregating *Dictyostelium discoideum* cells. Periodic production of cAMP (shown in Figure 21.3) causes this pattern formation.

signal. This mechanism is related to the synthesis of cAMP by the cell. cAMP arises from the transformation of another important cellular constituent, adenosine triphosphate (ATP), which (through its phosphate bond) is one of the principal carriers of energy within living cells. The $\text{ATP} \rightarrow \text{cAMP}$ transformation is not spontaneous however; a catalyst is needed to accelerate it to a level compatible with vital requirements. In biological systems, the tasks of catalysis is assumed by enzymes. Some enzymes have a single active site that the reactants must reach in order to transform into products. However, in many cases there are cooperative enzymes, which have several sites; some of the sites are catalytic and others are regulatory. When special effector molecules bind to the latter sites, the catalytic function is considerably affected. In some cases the molecules reacting with or produced from the catalytic site may also act as effector molecules. This will switch on a feedback loop, which will be positive (activation) if the result is the enhancement of the rate of catalysis, or negative (inhibition) otherwise. The enzyme that catalyzes $\text{ATP} \rightarrow \text{cAMP}$ conversion is called adenylate cyclase and is fixed at the interior of the cell membrane. It interacts with a receptor fixed at the exterior phase of the membrane in a cooperative fashion. The cAMP produced diffuses in the extracellular medium through the cell membrane and can bind to the receptor and activate it, as shown in Figure 21.3. In this way it enhances its own production, thereby giving rise to a feedback loop capable of amplifying signals and of inducing oscillatory behavior.

21.1.4 Geological Systems

There have also been promising applications of ideas of self-organization to geology [7]. In numerous geological deposits spectacular regular mineralization structures are observed at a variety of space scales: metamorphic layers millimeters to meters thick, granites of centimeter-scale structure, agates with millimeter-to centimeter-wide bands, and others. Figure 21.4 shows an example of patterns in geological formulation. The traditional interpretation attributes these structures to sequential phenomena, tracing the effect of successive environmental or climatic changes. It appears, however, that a more satisfactory interpretation would be to attribute them to symmetry-breaking transitions induced by nonequilibrium constraints.

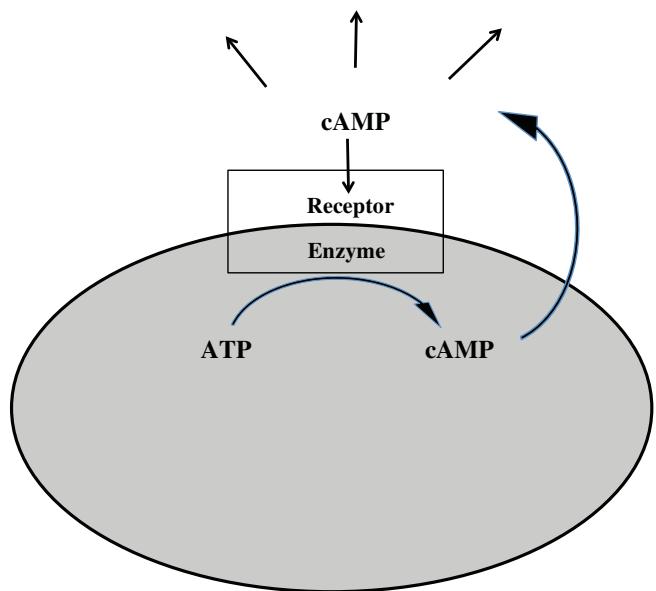


Figure 21.3 Oscillatory synthesis of cAMP in slime mold *Dictyostelium discoideum* and its diffusion out of the cell.

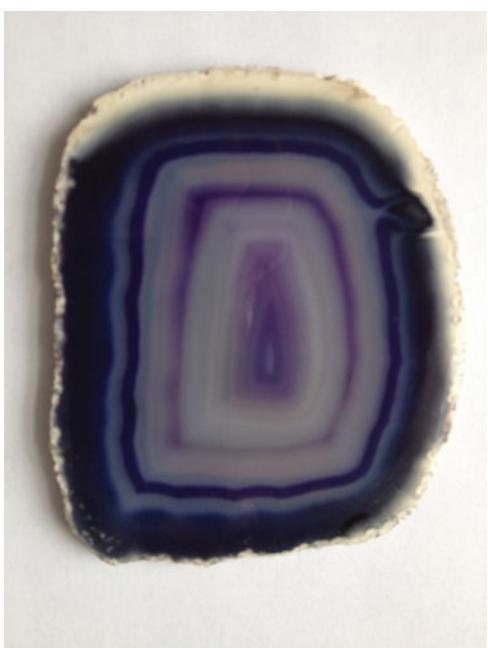


Figure 21.4 Geological pattern formation.

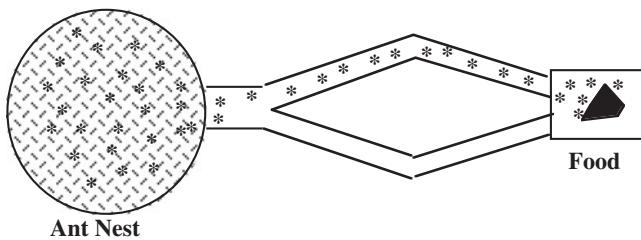


Figure 21.5 Bifurcation in the behavior of social insects such as ants can be seen in their choice of a path to the food source.

21.1.5 Social Insects

Many other examples may be found in the literature. Bifurcations can be found in the behavior of social insects as well [8–11]. Suppose we realize the following situation. There is a nest and food sources with two identical bridges of equal distances leading from the nest to the food source (Figure 21.5). At first, the same number of ants are traveling on the two bridges. After some time, practically all are found on the same bridge due to the chemical substance ‘pheromones’ and their catalytic effects. Note that which bridge will be used is unpredictable. This corresponds to a typical symmetry-breaking bifurcation.

21.1.6 Periodicity in Climate

The climatic conditions that prevailed in the last two or three hundred million years were extremely different from those of the present day. During this period, with the exception of the Quaternary era (our era, which began about two million years ago), there was practically no ice on the continents and the sea level was about 80 meters higher than at present. Climate was particularly mild and the temperature differences between equatorial ($25\text{--}30^{\circ}\text{C}$) and polar ($8\text{--}10^{\circ}\text{C}$) regions were relatively lower.

It was during the Tertiary era, some 40 million years ago, that a sharper contrast between equatorial and polar temperatures began to develop. In the relatively short time of 100 000 years, the sea temperature south of New Zealand dropped by several degrees. This was probably the beginning of the Antarctic current, which reduces the exchange of heat between high and low latitudes and contributes to a further cooling of the masses of water ‘trapped’ in this way near the polar regions. Once again, we see a feedback mechanism in action.

At the beginning of the Quaternary era this difference was sufficiently important to allow for the formation and maintenance of continental ice. In the northern hemisphere a series of glaciations took place in an intermittent fashion, sometimes pushing the glaciers as far as the middle latitudes. These climatic episodes present an average periodicity of about 100 000 years, though with considerable random-looking variations, as shown in Figure 21.6.

The last advance of continental ice in the northern hemisphere attained its maximum some 18 000 years ago, and its relics are still with us. While the amount of continental ice today is about 30 million cubic kilometers, confined essentially to Antarctica and Greenland, there was at that time about 70 to 80 million cubic kilometers covering, in addition, much of North America and Northern Europe. Because of the huge quantities of water trapped in the glaciers, the sea level was some 120 meters lower than today. Since then a large part of the ice has melted, thus defining the coastlines and most of the other features of the present-day landscape. The fact that our ecosystem is unstable makes it difficult to separate the ‘anthropic signal’ from the spontaneous evolution of the system.

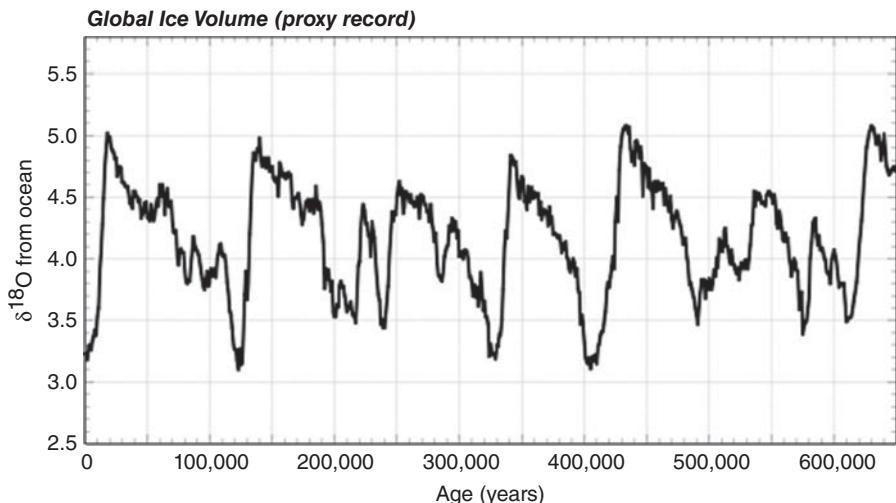


Figure 21.6 Variation of global ice volume during the last 1 million years, inferred from oxygen isotopes.

In conclusion, we cannot escape the feeling that we live in an age of transition, an age that demands a better understanding of our environment. We must find and explore new resources and achieve a less destructive coexistence with Nature. We cannot anticipate the outcome of this period of transition, but it is clear that science and especially nonequilibrium thermodynamics is bound to play an increasingly important role in our effort to meet the challenge of understanding and reshaping our global environment.

21.2 Towards a Thermodynamic Theory of Organisms

In the previous section, we have seen how wide spread structures created by dissipative processes are in Nature. However, we do not have a satisfactory thermodynamic understanding of the most spectacular dissipative structure of all: the biological organism. In Section 19.6, we have noted a few fundamental differences between dissipative structures and designed structures, the latter referring to machines or computers. Upon reflection, it is clear that Newtonian science, based on reversible laws, has put us on the path to the world of machines that we inhabit – a world that is very different from that of organisms. The difference, arguably, is the difference between reversible mechanics and irreversible thermodynamics. Let us explore this fundamental difference in some detail.

The organization of a machine, its structure and function, comes from processes external to it. So when we encounter a machine that we have never encountered before, taking it apart and analyzing how its components are made and arranged also gives us a way to build one – assuming we have the necessary external processes we call ‘technology’. Not so with organisms, as noted by the theoretical biologist Robert Rosen [12]. We have been analyzing the structure and organization of a living cell for well over a century, and although we have an immense knowledge of its makeup, all the way down to the molecular level, we do not know how to build a living cell or even one that vaguely resembles one. Why this difference between machines and organisms? It is because the processes that bring about an organism are not a part of our technology. Organisms are based on self-organization brought about by internal irreversible processes. The organization of machines comes from processes external to it, and ideal machines are reversible. We have not yet developed a technology based on irreversible processes and self-organization that can emerge from it. The study of dissipative structures that

Table 21.1 A comparison of designed structures and dissipative structures.

Designed structures (machines/computers)	Dissipative structures (nonequilibrium systems and organisms)
<ul style="list-style-type: none"> • Based on the reversible laws of mechanics • Structure designed and assembled through processes external to the system • Dissipative processes limit the efficiency of the system • Structure and function are clearly differentiated in the design • Structure designed to perform a certain function • Generally not self-healing 	<ul style="list-style-type: none"> • Based on irreversible processes and the law of thermodynamics • Structure arises spontaneously through entropy generating dissipative processes • Dissipative processes are essential to the system; without them the structure ceases to exist • Structure and function cannot always be clearly differentiated. • Context-dependent function arises because of structure • Self-healing

began over 50 years ago has yet to give us insight into processes that produce organisms. It is a challenge for the future. How might we meet this challenge?

To lay a conceptual framework, we may begin by looking deeper into the differences between dissipative structures and machines. Table 21.1 gives a list of differences, some of which we have already discussed in Section 19.6. In addition to these differences, in organisms we see both structure and function resulting in behavior that seems directed towards a particular end, such as seeking food or avoiding adverse conditions. Organisms interact with their environment and respond in ways that enable them to reach a particular end. From a thermodynamic point of view, we may interpret it as *end-directed evolution*, by which we mean that the system may take several different paths, but reach the same final state. End-directed evolution is a familiar concept in thermodynamics; after all, according to the Second Law, systems evolve to states of maximum entropy or minimum Gibbs or Helmholtz energy. We might not know the mechanism or the path a system will take to its final extremum state, but we can be sure that it will reach that state. In this case, the final state is an equilibrium state in which there is no entropy production. It is possible that end-directed evolution may also be a property of far-from-equilibrium systems. The studies of dissipative structures to date, however, have mostly been done on structures and the processes that produce and maintain the structure. End-directed evolution in dissipative structures have not been investigated much.

End-directed evolution has two aspects: the state to which it will evolve and the stability of that state. Regarding the former, it has been hypothesized that a nonequilibrium system will evolve to a state in which *the rate of entropy production is maximized* [13–19]. According to this hypothesis, the great diversity of behavior we see in organisms and the evolution of life is a result of nature evolving to states of an ever increasing rate of entropy production. In Section 19.7, we have commented on structural instability caused by the emergence of a new catalyst in a system. In general, whenever a catalyst enters a system, it will increase the rate of entropy production by increasing the velocity of reaction if the corresponding affinity is not significantly lowered. Such observations are in accord with this hypothesis. However, the maximum entropy production hypothesis is a subject of much debate: while many studies have indicated its validity, there are others that have indicated otherwise. Indeed, close to equilibrium, in the linear regime, we have seen in Section 17.2 that the rate of entropy production is minimized, not maximized. Yet, the hypothesis has been a useful tool to predict some far-from-equilibrium steady states [15–18]. Perhaps there is a set of conditions that need to be fulfilled for its validity that has not yet been identified; perhaps there is a different principle, or more than one principle depending on the system being studied. Future studies will shed light on this line of thought.

Let us turn to the second aspect, stability of the end state. This means that, when perturbed, the system will find a path to return to the end state. In other words, if the end state is perturbed due to a change in the environment, the system will find a means to restore the end state. The diversity of paths that the system is capable of taking to reach the end state may lead to interesting behavior, which resembles those we see in organisms.

As an example, let us consider a spatial dissipative structure that is maintained by the inflow of energy/matter at one location. Let us further assume that the structure maximizes a thermodynamics quantity Y (such as the rate of entropy production) and its form depends on the location at which the energy/matter flows into the system. Now if the location of the energy/matter source is moved, the system is no longer in a state that maximizes Y . In response to this perturbation, the system will evolve to a new state in which Y is maximized. This type of end-directed evolution resembles the response of an organism to a change in the location of the source of its ‘food’. To be sure, an organism is much more complex; nevertheless, studies of dissipative structures will give us thermodynamic principles on which the behavior of organisms are founded.

There are several other traits of organisms, such as collective behavior, in which we see that functional differentiation might also appear in much simpler dissipative structures that interact with each other. Here one may introduce the concept of *functional symmetry breaking*. Consider N identical elements in a nonequilibrium system that interact with each other. When the mutual interaction is weak – because N is small, for example – one might expect the behavior of the N elements to be identical or *functionally symmetric*, i.e., statistically their properties are identical. When the interaction strength increases – due to increasing N , for example – the system might reach a transition point above which the elements no longer have identical behavior; they might show cooperative behavior in which elements have a distinctly different behavior resulting in *breaking of functional symmetry*. Such transitions might also be in accord with a general extremization principle. Examples of functional symmetry breaking in interacting dissipative structures can already be found in recent studies [20]. More examples are likely to emerge due to a growing interest in such studies.

Clearly, the above concepts and examples are but the tip of the iceberg of a thermodynamic theory of organism. However, we can see in it the potential of concepts such as *end-directed evolution*, *thermodynamic stability* and *functional symmetry breaking* in formulating a thermodynamic theory of origin of the behavior we see in organisms.

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Epilogue

In the preface we remarked that science has no final formulation. So it is with thermodynamics. There are more laws to be discovered that involve non-equilibrium quantities such as thermodynamic forces, fluxes and the rates of entropy production. It has much to contribute to our understanding of living organisms, ecology and our place in the web of life. The primacy of irreversible processes in Nature is indisputable. Yet, we have been steeped in a world view of classical and quantum mechanics which posits that change, and the processes that bring about change, are reversible, that irreversibility is merely a property of large systems which we can only describe using probability, that it is a consequence of necessary approximations we must make, that it is essentially an illusion. But, we see everywhere in nature change that is irreversible, and organization, and life itself, born out of irreversible processes. It makes one wonder: is mechanics a convenient approximation of natural processes that are fundamentally irreversible and not the converse, as the current dogma holds? Why is it difficult to see that, because we ignore irreversible aspects of change in formulating the laws of classical and quantum mechanics, we are left with idealized reversible change, and a world without an arrow of time? Why is this idealized reversible world real and the arrow of time, manifest in irreversible processes that bring about life itself, an illusion? However we see the relationship between Nature and time-reversible mechanics, it is a fact that whenever we describe a natural process, we must always include some aspects of irreversibility and thermodynamics for a complete description of that process.

Nature has a history – for long time the ideal of physics was geometry, as implied in Einstein's general relativity. Relativity is certainly one of the great achievement of the human mind. But the geometrical view is incomplete. Now we see that narrative elements play also a basic role. This leads to a different concept of nature in which the arrow of time is essential. After all, this arrow appears as the feature which is common to all objects in the expanding bubble which is our universe. We all age in the same direction, all stars, all rocks age in the same direction even if the mechanism of aging is different in each case.

Time, better the direction of time, is the fundamental existential dimension of human life. We discover now that the flow of time is universal, it is not an illusion that separates us from nature.

Physical Constants and Data

Avogadro constant	$N_A = 6.022137 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	$k_B = 1.38066 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.082058 \text{ atm L mol}^{-1} \text{ K}^{-1}$ $= 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$
Faraday constant	$F = 9.6485 \times 10^4 \text{ C mol}^{-1}$
Stefan-Boltzmann constant	$\sigma = (c\beta/4) = 5.6705 \times 10^{-8} \text{ J m}^{-2} \text{ K}^{-4} \text{ s}^{-1}$
Triple point of water*	$T_{tp}(\text{H}_2\text{O}) = 273.16 \text{ K}$
Zero of Celsius scale*	$T(0^\circ\text{C}) = 273.15 \text{ K}$
Molar volume of ideal gas at 1 bar and 273.15 K	$V_0 = 22.711 \text{ L mol}^{-1}$
Permittivity of vacuum*	$\epsilon_0 = 8.854187816 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
Permeability of vacuum*	$\mu_0 = 4\pi \times 10^{-7} \text{ N A}^{-2}$
Speed of light in vacuum*	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$
Planck constant	$h = 6.62607 \times 10^{-34} \text{ J s}$
Elementary charge	$e = 1.60218 \times 10^{-19} \text{ C}$
Electron rest mass	$m_e = 9.10939 \times 10^{-31} \text{ kg} = 5.486 \times 10^{-4} \text{ u}$
Proton rest mass	$m_p = 1.67262 \times 10^{-27} \text{ kg} = 1.00728 \text{ u}$
Neutron rest mass	$m_n = 1.67493 \times 10^{-27} \text{ kg} = 1.00867 \text{ u}$
Gravitational constant	$G = 6.6726 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$
Standard gravitational acceleration*	$g = 9.80665 \text{ m s}^{-2} = 32.17 \text{ ft s}^{-2}$
Mass of the Earth	$5.98 \times 10^{24} \text{ kg}$
Average radius of the Earth	$6.37 \times 10^3 \text{ km}$
Average Earth-Sun distance	$1.495 \times 10^8 \text{ km}$
Radius of the Sun	$6.96 \times 10^5 \text{ km}$
Sun's energy incident at the top of the atmosphere	$1340 \text{ J m}^{-2} \text{ s}^{-1} = 0.032 \text{ cal cm}^{-2} \text{ s}^{-1}$
About 31% of this energy is reflected back into space.	

*Exact values by definition.

Conversion Factors

Bar	$1 \text{ bar} = 10^5 \text{ Pa}$
Standard atmosphere*	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$
Torr (mm Hg)	$1 \text{ Torr} = 133.322 \text{ Pa}$
Calorie*	$1 \text{ cal} = 4.184 \text{ J}$
Erg	$1 \text{ erg} = 10^{-7} \text{ J}$
Gauss	$1 \text{ G} = 10^{-4} \text{ T}$
Debye	$1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$
Atomic mass unit	$1 \text{ u} = 1.66054 \times 10^{-27} \text{ kg}$
Electron volt	$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J} = 96.4853 \text{ kJ mol}^{-1}$
Metric ton	$1 \text{ metric ton} = 1000 \text{ kg}$
Pound	$1 \text{ lb} = 16 \text{ oz} = 0.45359 \text{ kg}$
Gallon (U.S.)	$1 \text{ gal} = 4 \text{ quarts} = 3.78541 \text{ L}$
Gallon (British imperial)	$1 \text{ gal} = 4 \text{ quarts} = 4.545 \text{ L}$

*Exact values by definition.

Standard Thermodynamic Properties

The standard state pressure is 100 kPa (1 bar). An entry of 0.0 for $\Delta_f H^0$ for an element indicates the reference state of that element.

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
<i>Compounds not containing carbon</i>						
Ac	Actinium	gas	406.0	366.0	188.1	20.8
Ag	Silver	cry	0.0	0.0	42.6	25.4
AgBr	Silver bromide	cry	-100.4	-96.9	107.1	52.4
AgBrO ₃	Silver bromate	cry	-10.5	71.3	151.9	
AgCl	Silver chloride	cry	-127.0	-109.8	96.3	50.8
AgClO ₃	Silver chlorate	cry	-30.3	64.5	142.0	
Al	Aluminum	cry	0.0	0.0	28.3	24.4
		gas	330.0	289.4	164.6	21.4
AlB ₃ H ₁₂	Aluminum borohydride	liq	-16.3	145.0	289.1	194.6
AlBr	Aluminum bromide (AlBr)	gas	-4.0	-42.0	239.5	35.6
AlCl	Aluminum chloride (AlCl)	gas	-47.7	-74.1	228.1	35.0
AlCl ₃	Aluminum trichloride	cry	-704.2	-628.8	110.7	91.8
AlF	Aluminum fluoride (AlF)	gas	-258.2	-283.7	215.0	31.9
AlF ₃	Aluminum trifluoride	cry	-1510.4	-1431.1	66.5	75.1
AlI ₃	Aluminum triiodide	cry	-313.8	-300.8	159.0	98.7
AlO ₄ P	Aluminum phosphate (AlPO ₄)	cry	-1733.8	-1617.9	90.8	93.2
AlS	Aluminum sulfide (AlS)	gas	200.9	150.1	230.6	33.4
Al ₂ O	Aluminum oxide (Al ₂ O)	gas	-130.0	-159.0	259.4	45.7
Al ₂ O ₃	Aluminum oxide (Al ₂ O ₃)	cry	-1675.7	-1582.3	50.9	79.0
Ar	Argon	gas	0.0		154.8	20.8
As	Arsenic (gray)	cry	0.0		35.1	24.6
AsBr ₃	Arsenic tribromide	gas	-130.0	-159.0	363.9	79.2
AsCl ₃	Arsenic trichloride	gas	-261.5	-248.9	327.2	75.7
AsF ₃	Arsenic trifluoride	liq	-821.3	-774.2	181.2	126.6
As ₂	Arsenic (As ₂)	gas	222.2	171.9	239.4	35.0
Au	Gold	cry	0.0	0.0	47.4	25.4
AuH	Gold hydride (AuH)	gas	295.0	265.7	211.2	29.2
B	Boron	cry (rhombic)	0.0	0.0	5.9	11.1
BCl	Chloroborane (BCl)	gas	149.5	120.9	213.2	31.7

(continued)

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
BCl ₃	Boron trichloride	liq	-427.2	-387.4	206.3	106.7
BF	Fluoroborane (BF)	gas	-122.2	-149.8	200.5	29.6
BH ₃ O ₃	Boric acid (H ₃ BO ₃)	cry	-1094.3	-968.9	88.8	81.4
BH ₄ K	Potassium borohydride	cry	-227.4	-160.3	106.3	96.1
BH ₄ Li	Lithium borohydride	cry	-190.8	-125.0	75.9	82.6
BH ₄ Na	Sodium borohydride	cry	-188.6	-123.9	101.3	86.8
BN	Boron nitride (BN)	cry	-254.4	-228.4	14.8	19.7
B ₂	Boron (B ₂)	gas	830.5	774.0	201.9	30.5
Ba	Barium	cry	0.0	0.0	62.8	28.1
		gas	180.0	146.0	170.2	20.8
BaBr ₂	Barium bromide	cry	-757.3	-736.8	146.0	
BaCl ₂	Barium chloride	cry	-858.6	-810.4	123.7	75.1
BaF ₂	Barium fluoride	cry	-1207.1	-1156.8	96.4	71.2
BaO	Barium oxide	cry	-553.5	-525.1	70.4	47.8
BaO ₄ S	Barium sulfate	cry	-1473.2	-1362.2	132.2	101.8
Be	Beryllium	cry	0.0	0.0	9.5	16.4
BeCl ₂	Beryllium chloride	cry	-490.4	-445.6	82.7	64.8
BeF ₂	Beryllium fluoride	cry	-1026.8	-979.4	53.4	51.8
BeH ₂ O ₂	Beryllium hydroxide	cry	-902.5	-815.0	51.9	
BeO ₄ S	Beryllium sulfate	cry	-1205.2	-1093.8	77.9	85.7
Bi	Bismuth	cry	0.0	0.0	56.7	25.5
BiCl ₃	Bismuth trichloride	cry	-379.1	-315.0	177.0	105.0
Bi ₂ O ₃	Bismuth oxide (Bi ₂ O ₃)	cry	-573.9	-493.7	151.5	113.5
Bi ₂ S ₃	Bismuth sulfide (Bi ₂ S ₃)	cry	-143.1	-140.6	200.4	122.2
Br	Bromine	gas	111.9	82.4	175.0	20.8
BrF	Bromine fluoride	gas	-93.8	-109.2	229.0	33.0
BrH	Hydrogen bromide	gas	-36.3	-53.4	198.7	29.1
BrH ₄ N	Ammonium bromide	cry	-270.8	-175.2	113.0	96.0
BrK	Potassium bromide	cry	-393.8	-380.7	95.9	52.3
BrKO ₃	Potassium bromate	cry	-360.2	-217.2	149.2	105.2
BrLi	Lithium bromide	cry	-351.2	-342.0	74.3	
BrNa	Sodium bromide	cry	-361.1	-349.0	86.8	51.4
Br ₂ Ca	Calcium bromide	cry	-682.8	-663.6	130.0	
Br ₂ Hg	Mercury bromide (HgBr ₂)	cry	-170.7	-153.1	172.0	
Br ₂ Mg	Magnesium bromide	cry	-524.3	-503.8	117.2	
Br ₂ Zn	Zinc bromide	cry	-328.7	-312.1	138.5	
Br ₄ Ti	Titanium bromide (TiBr ₄)	cry	-616.7	-589.5	243.5	131.5
Ca	Calcium	cry	0.0	0.0	41.6	25.9
CaCl ₂	Calcium chloride	cry	-795.4	-748.8	108.4	72.9
CaF ₂	Calcium fluoride	cry	-1228.0	-1175.6	68.5	67.0
CaH ₂	Calcium hydride (CaH ₂)	cry	-181.5	-142.5	41.4	41.0
CaH ₂ O ₂	Calcium hydroxide	cry	-985.2	-897.5	83.4	87.5
CaN ₂ O ₆	Calcium nitrate	cry	-938.2	-742.8	193.2	149.4
CaO	Calcium oxide	cry	-634.9	-603.3	38.1	42.0
CaO ₄ S	Calcium sulfate	cry	-1434.5	-1322.0	106.5	99.7
CaS	Calcium sulfide	cry	-482.4	-477.4	56.5	47.4
Ca ₃ O ₈ P ₂	Calcium phosphate	cry	-4120.8	-3884.7	236.0	227.8

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
Cd	Cadmium	cry	0.0	0.0	51.8	26.0
CdO	Cadmium oxide	cry	-258.4	-228.7	54.8	43.4
CdO ₄ S	Cadmium sulfate	cry	-933.3	-822.7	123.0	99.6
Cl	Chlorine	gas	121.3	105.3	165.2	21.8
ClCu	Copper chloride (CuCl)	cry	-137.2	-119.9	86.2	48.5
ClF	Chlorine fluoride	gas	-50.3	-51.8	217.9	32.1
ClH	Hydrogen chloride	gas	-92.3	-95.3	186.9	29.1
ClHO	Hypochlorous acid (HOCl)	gas	-78.7	-66.1	236.7	37.2
ClH ₄ N	Ammonium chloride	cry	-314.4	-202.9	94.6	84.1
ClK	Potassium chloride (KCl)	cry	-436.5	-408.5	82.6	51.3
ClKO ₃	Potassium chlorate (KClO ₃)	cry	-397.7	-296.3	143.1	100.3
ClKO ₄	Potassium perchlorate (KClO ₄)	cry	-432.8	-303.1	151.0	112.4
ClLi	Lithium chloride (LiCl)	cry	-408.6	-384.4	59.3	48.0
ClNa	Sodium chloride (NaCl)	cry	-411.2	-384.1	72.1	50.5
ClNaO ₂	Sodium chloride (NaClO ₂)	cry	-307.0			
ClNaO ₃	Sodium chlorate (NaClO ₃)	cry	-365.8	-262.3	123.4	
Cl ₂	Chlorine (Cl ₂)	gas	0.0	0.0	223.1	33.9
Cl ₂ Cu	Copper chloride (CuCl ₂)	cry	-220.1	-175.7	108.1	71.9
Cl ₂ Mn	Manganese chloride (MnCl ₂)	cry	-481.3	-440.5	118.2	72.9
Cl ₃ U	Uranium chloride (UCl ₃)	cry	-866.5	-799.1	159.0	102.5
Cl ₄ Si	Silicon tetrachloride	liq	-687.0	-619.8	239.7	145.3
Co	Cobalt	cry	0.0	0.0	30.0	24.8
CoH ₂ O ₂	Cobalt hydroxide (Co(OH) ₂)	cry	-539.7	-454.3	79.0	
CoO	Cobalt oxide (CoO)	cry	-237.9	-214.2	53.0	55.2
Co ₃ O ₄	Cobalt oxide (Co ₃ O ₄)	cry	-891.0	-774.0	102.5	123.4
Cr	Chromium	cry	0.0	0.0	23.8	23.4
CrF ₃	Chromium fluoride (CrF ₃)	cry	-1159.0	-1088.0	93.9	78.7
Cr ₂ FeO ₄	Chromium iron oxide (FeCr ₂ O ₄)	cry	-1444.7	-1343.8	146.0	133.6
Cr ₂ O ₃	Chromium oxide (Cr ₂ O ₃)	cry	-1139.7	-1058.1	81.2	118.7
Cs	Cesium	cry	0.0	0.0	85.2	32.2
CsF	Cesium fluoride	cry	-553.5	-525.5	92.8	51.1
Cs ₂ O	Cesium oxide (Cs ₂ O)	cry	-345.8	-308.1	146.9	76.0
Cu	Copper	cry	0.0	0.0	33.2	24.4
CuO	Copper oxide (CuO)	cry	-157.3	-129.7	42.6	42.3
CuO ₄ S	Copper sulfate (CuSO ₄)	cry	-771.4	-662.2	109.2	
CuS	Copper sulfide (CuS)	cry	-53.1	-53.6	66.5	47.8
Cu ₂	Copper (Cu ₂)	gas	484.2	431.9	241.6	36.6
Cu ₂ O	Copper oxide (Cu ₂ O)	cry	-168.6	-146.0	93.1	63.6
Cu ₂ S	Copper sulfide (Cu ₂ S)	cry	-79.5	-86.2	120.9	76.3
F ₂	Fluorine (F ₂)	gas	0.0	0.0	202.8	31.3
F	Fluorine	gas	79.4	62.3	158.8	22.7
FH	Hydrogen fluoride	gas	-273.3	-275.4	173.8	
FK	Potassium fluoride (KF)	cry	-567.3	-537.8	66.6	49.0
FLi	Lithium fluoride (LiF)	cry	-616.0	-587.7	35.7	61.6

(continued)

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
FNa	Sodium fluoride (NaF)	cry	-576.6	-546.3	51.1	46.9
F ₂ HK	Potassium hydrogen fluoride (KHF ₂)	cry	-927.7	-859.7	104.3	76.9
F ₂ HNa	Sodium hydrogen fluoride (NaHF ₂)	cry	-920.3	-852.2	90.9	75.0
F ₂ Mg	Magnesium fluoride	cry	-1124.2	-1071.1	57.2	61.6
F ₂ O ₂ U	Uranyl fluoride	cry	-1648.1	-1551.8	135.6	103.2
F ₂ Si	Difluorosilylene (SiF ₂)	gas	-619.0	-628.0	252.7	43.9
F ₂ Zn	Zinc fluoride	cry	-764.4	-713.3	73.7	65.7
F ₃ OP	Phosphoryl fluoride	gas	-1254.3	-1205.8	285.4	68.8
F ₃ P	Phosphorus trifluoride	gas	-958.4	-936.9	273.1	58.7
F ₄ S	Sulfur fluoride (SF ₄)	gas	-763.2	-722.0	299.6	77.6
F ₆ S	Sulfur fluoride (SF ₆)	gas	-1220.5	-1116.5	291.5	97.0
F ₆ U	Uranium fluoride (UF ₆)	cry	-2197.0	-2068.5	227.6	166.8
Fe	Iron	cry	0.0	0.0	27.3	25.1
FeO ₄ S	Iron sulfate (FeSO ₄)	cry	-928.4	-820.8	107.5	100.6
FeS	Iron sulfide (FeS)	cry	-100.0	-100.4	60.3	50.5
FeS ₂	Iron sulfide (FeS ₂)	cry	-178.2	-166.9	52.9	62.2
Fe ₂ O ₃	Iron oxide (Fe ₂ O ₃)	cry	-824.2	-742.2	87.4	103.9
Fe ₃ O ₄	Iron oxide (Fe ₃ O ₄)	cry	-1118.4	-1015.4	146.4	143.4
H ₂	Hydrogen (H ₂)	gas	0.0	0.0	130.7	28.8
H	Hydrogen	gas	218.0	203.3	114.7	20.8
HI	Hydrogen iodide	gas	26.5	1.7	206.6	29.2
HKO	Potassium hydroxide (KOH)	cry	-424.8	-379.1	78.9	64.9
HLi	Lithium hydride (LiH)	cry	-90.5	-68.3	20.0	27.9
HNO ₂	Nitrous acid (HONO)	gas	-79.5	-46.0	254.1	45.6
HNO ₃	Nitric acid	liq	-174.1	-80.7	155.6	109.9
HNa	Sodium hydride	cry	-56.3	-33.5	40.0	36.4
HNaO	Sodium hydroxide (NaOH)	cry	-425.6	-379.5	64.5	59.5
HO	Hydroxyl (OH)	gas	39.0	34.2	183.7	29.9
HO ₂	Hydroperoxy (HOO)	gas	10.5	22.6	229.0	34.9
H ₂ Mg	Magnesium hydride	cry	-75.3	-35.9	31.1	35.4
H ₂ MgO ₂	Magnesium hydroxide	cry	-924.5	-833.5	63.2	77.0
H ₂ O	Water	liq	-285.8	-237.1	70.0	75.3
H ₂ O ₂	Hydrogen peroxide	liq	-187.8	-120.4	109.6	89.1
H ₂ O ₂ Sn	Tin hydroxide (Sn(OH) ₂)	cry	-561.1	-491.6	155.0	
H ₂ O ₂ Zn	Zinc hydroxide	cry	-641.9	-553.5	81.2	
H ₂ O ₄ S	Sulfuric acid	liq	-814.0	-690.0	156.9	138.9
H ₂ S	Hydrogen sulfide	gas	-20.6	-33.4	205.8	34.2
H ₃ O ₄ P	Phosphoric acid	cry	-1284.4	-1124.3	110.5	106.1
		liq	-1271.7	-1123.6	150.8	145.0
H ₃ P	Phosphine	gas	5.4	13.4	210.2	37.1
H ₄ IN	Ammonium iodide	cry	-201.4	-112.5	117.0	
H ₄ N ₂	Hydrazine	liq	50.6	149.3	121.2	98.9
H ₄ N ₂ O ₃	Ammonium nitrate	cry	-365.6	-183.9	151.1	139.3

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
H ₄ Si	Silane	gas	34.3	56.9	204.6	42.8
H ₈ N ₂ O ₄ S	Ammonium sulfate	cry	-1180.9	-901.7	220.1	187.5
He	Helium	gas	0.0		126.2	20.8
HgI ₂	Mercury iodide (HgI ₂) (red)	cry	-105.4	-101.7	180.0	
HgO	Mercury oxide (HgO) (red)	cry	-90.8	-58.5	70.3	44.1
HgS	Mercury sulfide (HgS)	cry	-58.2	-50.6	82.4	48.4
Hg ₂	Mercury (Hg ₂)	gas	108.8	68.2	288.1	37.4
Hg ₂ O ₄ S	Mercury sulfate (Hg ₂ SO ₄)	cry	-743.1	-625.8	200.7	132.0
I	Iodine	gas	106.8	70.2	180.8	20.8
IK	Potassium iodide	cry	-327.9	-324.9	106.3	52.9
IKO ₃	Potassium iodate	cry	-501.4	-418.4	151.5	106.5
ILi	Lithium iodide	cry	-270.4	-270.3	86.8	51.0
INa	Sodium iodide	cry	-287.8	-286.1	98.5	52.1
INaO ₃	Sodium iodate	cry	-481.8			92.0
K	Potassium	cry	0.0	0.0	64.7	29.6
KMnO ₄	Potassium permanganate	cry	-837.2	-737.6	171.7	117.6
KNO ₂	Potassium nitrite	cry	-369.8	-306.6	152.1	107.4
KNO ₃	Potassium nitrate	cry	-494.6	-394.9	133.1	96.4
K ₂ O ₄ S	Potassium sulfate	cry	-1437.8	-1321.4	175.6	131.5
K ₂ S	Potassium sulfide (K ₂ S)	cry	-380.7	-364.0	105.0	
Li	Lithium	cry	0.0	0.0	29.1	24.8
Li ₂	Lithium (Li ₂)	gas	215.9	174.4	197.0	36.1
Li ₂ O	Lithium oxide (Li ₂ O)	cry	-597.9	-561.2	37.6	54.1
Li ₂ O ₃ Si	Lithium metasilicate	cry	-1648.1	-1557.2	79.8	99.1
Li ₂ O ₄ S	Lithium sulfate	cry	-1436.5	-1321.7	115.1	117.6
Mg	Magnesium	cry	0.0	0.0	32.7	24.9
MgN ₂ O ₆	Magnesium nitrate	cry	-790.7	-589.4	164.0	141.9
MgO	Magnesium oxide	cry	-601.6	-569.3	27.0	37.2
MgO ₄ S	Magnesium sulfate	cry	-1284.9	-1170.6	91.6	96.5
MgS	Magnesium sulfide	cry	-346.0	-341.8	50.3	45.6
Mn	Manganese	cry	0.0	0.0	32.0	26.3
MgNa ₂ O ₄	Sodium permanganate	cry	-1156.0			
MnO	Manganese oxide (MnO)	cry	-385.2	-362.9	59.7	45.4
MnS	Manganese sulfide (MnS)	cry	-214.2	-218.4	78.2	50.0
Mn ₂ O ₃	Manganese oxide (Mn ₂ O ₃)	cry	-959.0	-881.1	110.5	107.7
Mn ₂ O ₄ Si	Manganese silicate (Mn ₂ SiO ₄)	cry	-1730.5	-1632.1	163.2	129.9
N ₂	Nitrogen (N ₂)	gas	0.0	0.0	191.6	29.1
N	Nitrogen	gas	472.7	455.5	153.3	20.8
NNaO ₂	Sodium nitrite	cry	-358.7	-284.6	103.8	
NNaO ₃	Sodium nitrate	cry	-467.9	-367.0	116.5	92.9
NO ₂	Nitrogen dioxide	gas	33.2	51.3	240.1	37.2
N ₂ O	Nitrous oxide	gas	82.1	104.2	219.9	38.5
N ₂ O ₃	Nitrogen trioxide	liq	50.3			

(continued)

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
N ₂ O ₅	Nitrogen pentoxide	cry	-43.1	113.9	178.2	143.1
Na	Sodium	cry	0.0	0.0	51.3	28.2
NaO ₂	Sodium superoxide (NaO ₂)	cry	-260.2	-218.4	115.9	72.1
Na ₂	Sodium (Na ₂)	gas	142.1	103.9	230.2	37.6
Na ₂ O	Sodium oxide (Na ₂ O)	cry	-414.2	-375.5	75.1	69.1
Na ₂ O ₂	Sodium peroxide (Na ₂ O ₂)	cry	-510.9	-447.7	95.0	89.2
Na ₂ O ₄ S	Sodium sulfate	cry	-1387.1	-1270.2	149.6	128.2
Ne	Neon	gas	0.0		146.3	20.8
Ni	Nickel	cry	0.0	0.0	29.9	26.1
NiO ₄ S	Nickel sulfate (NiSO ₄)	cry	-872.9	-759.7	92.0	138.0
NiS	Nickel sulfide (NiS)	cry	-82.0	-79.5	53.0	47.1
O	Oxygen	gas	249.2	231.7	161.1	21.9
OP	Phosphorus oxide (PO)	gas	-28.5	-51.9	222.8	31.8
O ₂ Pb	Lead oxide (PO ₂)	cry	-277.4	-217.3	68.6	64.6
O ₂ S	Sulfur dioxide	gas	-296.8	-300.1	248.2	39.9
O ₂ Si	Silicon dioxide (α -quartz)	cry	-910.7	-856.3	41.5	44.4
O ₂ U	Uranium oxide (UO ₂)	cry	-1085.0	-1031.8	77.0	63.6
O ₃	Ozone	gas	142.7	163.2	238.9	39.2
O ₃ PbSi	Lead metasilicate (PbSiO ₃)	cry	-1145.7	-1062.1	109.6	90.0
O ₃ S	Sulfur trioxide	gas	-395.7	-371.1	256.8	50.7
O ₄ SZn	Zinc sulfate	cry	-982.8	-871.5	110.5	99.2
P	Phosphorus (white)	cry	0.0	0.0	41.1	23.8
	Phosphorus (red)	cry	-17.6		22.8	21.2
Pb	Lead	cry	0.0	0.0	64.8	26.4
PbS	Lead sulfide (PbS)	cry	-100.4	-98.7	91.2	49.5
Pt	Platinum	cry	0.0	0.0	41.6	25.9
PtS	Platinum sulfide (PtS)	cry	-81.6	-76.1	55.1	43.4
PtS ₂	Platinum sulfide (PtS ₂)	cry	-108.8	-99.6	74.7	65.9
S	Sulfur	cry (rhombic)	0.0	0.0	32.1	22.6
	Sulfur	cry (monoclinic)	0.3			
S ₂	Sulfur (S ₂)	gas	128.6	79.7	228.2	32.5
Si	Silicon	cry	0.0	0.0	18.8	20.0
Sn	Tin (white)	cry	0.0		51.2	27.0
	Tin (gray)	cry	-2.1	0.1	44.1	25.8
Zn	Zinc	cry	0.0	0.0	41.6	25.4
		gas	130.4	94.8	161.0	20.8
<i>Compounds containing carbon</i>						
C	Carbon (graphite)	cry	0.0	0.0	5.7	8.5
	Carbon (diamond)	cry	1.9	2.9	2.4	6.1
CAgN	Silver cyanide (AgCN)	cry	146.0	156.9	107.2	66.7
CBaO ₃	Barium carbonate (BaCO ₃)	cry	-1216.3	-1137.6	112.1	85.3
CBrN	Cyanogen bromide	cry	140.5			
CCaO ₃	Calcium carbonate (calcite)	cry	-1207.6	-1129.1	91.7	83.5
	Calcium carbonate (aragonite)	cry	-1207.8	-1128.2	88.0	82.3
CCl ₂ F ₂	Dichlorodifluoromethane	gas	-477.4	-439.4	300.8	72.3

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
CCl ₃ F	Trichlorofluoromethane	liq	-301.3	-236.8	225.4	121.6
CCuN	Copper cyanide (CuCN)	cry	96.2	111.3	84.5	
CFe ₃	Iron carbide (Fe ₃ C)	cry	25.1	20.1	104.6	105.9
CFeO ₃	Iron carbonate (FeCO ₃)	cry	-740.6	-666.7	92.9	82.1
CKN	Potassium cyanide (KCN)	cry	-113.0	-101.9	128.5	66.3
CKNS	Potassium thiocyanate (KSCN)	cry	-200.2	-178.3	124.3	88.5
CK ₂ O ₃	Potassium carbonate (KCO ₃)	cry	-1151.0	-1063.5	155.5	114.4
CMgO ₃	Magnesium carbonate (MgCO ₃)	cry	-1095.8	-1012.1	65.7	75.5
CNNa	Sodium cyanide (NaCN)	cry	-87.5	-76.4	115.6	70.4
CNNaO	Sodium cyanate	cry	-405.4	-358.1	96.7	86.6
CNa ₂ O ₃	Sodium carbonate (NaCO ₃)	cry	-1130.7	-1044.2	135.0	112.3
CO	Carbon monoxide	gas	-110.5	-137.2	197.7	29.1
CO ₂	Carbon dioxide	gas	-393.5	-394.4	213.8	37.1
CO ₃ Zn	Zinc carbonate (ZnCO ₃)	cry	-812.8	-731.5	82.4	79.7
CS ₂	Carbon disulfide	liq	89.0	64.6	151.3	76.4
CSi	Silicon carbide (cubic)	cry	-65.3	-62.8	16.6	26.9
CHBr ₃	Tribromomethane	liq	-28.5	-5.0	220.9	130.7
CHClF ₂	Chlorodifluoromethane	gas	-482.6		280.9	55.9
CHCl ₃	Trichloromethane	liq	-134.5	-73.7	201.7	114.2
CHN	Hydrogen cyanide	liq	108.9	125.0	112.8	70.6
CH ₂	Methylene	gas	390.4	372.9	194.9	33.8
CH ₂ I ₂	Diiodomethane	liq	66.9	90.4	174.1	134.0
CH ₂ O	Formaldehyde	gas	-108.6	-102.5	218.8	35.4
CH ₂ O ₂	Formic acid	liq	-424.7	-361.4	129.0	99.0
CH ₃	Methyl	gas	145.7	147.9	194.2	38.7
CH ₃ Cl	Chloromethane	gas	-81.9		234.6	40.8
CH ₃ NO ₂	Nitromethane	liq	-113.1	-14.4	171.8	106.6
CH ₄	Methane	gas	-74.4	-50.3	186.3	35.3
CH ₄ N ₂ O	Urea	cry	-333.6			
CH ₄ O	Methanol	liq	-239.1	-166.6	126.8	81.1
C ₂	Carbon (C ₂)	gas	831.9	775.9	199.4	43.2
C ₂ Ca	Calcium carbide	cry	-59.8	-64.9	70.0	62.7
C ₂ ClF ₃	Chlorotrifluoroethylene	gas	-555.2	-523.8	322.1	83.9
C ₂ Cl ₄	Tetrachloroethylene	liq	-50.6	3.0	266.9	143.4
C ₂ Cl ₄ F ₂	1,1,1,2-Tetrachloro-2,2-difluoroethane	gas	-489.9	-407.0	382.9	123.4
C ₂ H ₂	Acetylene	gas	228.2	210.7	200.9	43.9
C ₂ H ₂ Cl ₂	1,1-Dichloroethylene	liq	-23.9	24.1	201.5	111.3
C ₂ H ₂ O	Ketene	gas	-47.5	-48.3	247.6	51.8
C ₂ H ₂ O ₄	Oxalic acid	cry	-821.7		109.8	91.0
C ₂ H ₃ Cl ₃	1,1,1-Trichloroethane	liq	-177.4		227.4	144.3
		gas	-144.6		323.1	93.3
C ₂ H ₃ N	Acetonitrile	liq	31.4	77.2	149.6	91.4

(continued)

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
C ₂ H ₃ NaO ₂	Sodium acetate	cry	-708.8	-607.2	123.0	79.9
C ₂ H ₄	Ethylene	gas	52.5	68.4	219.6	43.6
C ₂ H ₄ Cl ₂	1,1-Dichloroethane	liq	-158.4	-73.8	211.8	126.3
		gas	-127.7	-70.8	305.1	76.2
C ₂ H ₄ O ₂	Acetic acid	liq	-484.5	-389.9	159.8	123.3
		gas	-432.8	-374.5	282.5	66.5
C ₂ H ₅ I	Iodoethane	liq	-40.2	14.7	211.7	115.1
C ₂ H ₆	Ethane	gas	-83.8	-31.9	229.6	52.6
C ₂ H ₆ O	Dimethyl ether	gas	-184.1	-112.6	266.4	64.4
C ₂ H ₆ O	Ethanol	liq	-277.7	-174.8	160.7	112.3
C ₂ H ₆ S	Ethanethiol	liq	-73.6	-5.5	207.0	117.9
C ₂ H ₇ N	Dimethylamine	gas	-18.5	68.5	273.1	70.7
C ₃ H ₇ N	Cyclopropylamine	liq	45.8		187.7	147.1
C ₃ H ₈	Propane	gas	-104.7			
C ₃ H ₈ O	1-Propanol	liq	-302.6		193.6	143.9
C ₃ H ₈ O ₃	Glycerol	liq	-668.5		206.3	218.9
C ₄ H ₄ O	Furan	liq	-62.3		177.0	115.3
C ₄ H ₄ O ₄	Fumaric acid	cry	-811.7		168.0	142.0
C ₄ H ₆	1,3-Butadiene	liq	87.9		199.0	123.6
C ₄ H ₆ O ₂	Methyl acrylate	liq	-362.2		239.5	158.8
C ₄ H ₈	Isobutene	liq	-37.5			
C ₄ H ₈	Cyclobutane	liq	3.7			
C ₄ H ₈ O	Butanal	liq	-239.2		246.6	163.7
C ₄ H ₈ O	Isobutanal	liq	-247.4			
C ₄ H ₈ O ₂	1,4-Dioxane	liq	-353.9		270.2	152.1
C ₄ H ₈ O ₂	Ethyl acetate	liq	-479.3		257.7	170.7
C ₄ H ₁₀ O	1-Butanol	liq	-327.3		225.8	177.2
C ₄ H ₁₀ O	2-Butanol	liq	-342.6		214.9	196.9
C ₄ H ₁₂ Si	Tetramethylsilane	liq	-264.0	-100.0	277.3	204.1
C ₅ H ₈	Cyclopentene	liq	4.4		201.2	122.4
C ₅ H ₁₀	1-Pentene	liq	-46.9		262.6	154.0
C ₅ H ₁₀	Cyclopentane	liq	-105.1		204.5	128.8
C ₅ H ₁₂	Isopentane	liq	-178.5		260.4	164.8
C ₅ H ₁₂	Neopentane	gas	-168.1			
C ₅ H ₁₂ O	Butyl methyl ether	liq	-290.6		295.3	192.7
C ₆ H ₆	Benzene	liq	49.0			136.3
C ₆ H ₆ O	Phenol	cry	-165.1		144.0	127.4
C ₇ H ₈	Toluene	liq	12.4			157.3
C ₇ H ₈ O	Benzyl alcohol	liq	-160.7		216.7	217.9
C ₇ H ₁₄	Cycloheptane	liq	-156.6			
C ₇ H ₁₄	Ethylcyclopentane	liq	-163.4		279.9	
C ₇ H ₁₄	1-Heptene	liq	-97.9		327.6	211.8
C ₈ H ₁₆	Cyclooctane	liq	-167.7			
C ₈ H ₁₈	Octane	liq	-250.1			254.6
		gas	-208.6			
C ₉ H ₂₀	Nonane	liq	-274.7			284.4

Molecular formula	Name	State	$\Delta_f H^0$ kJ mol ⁻¹	$\Delta_f G^0$ kJ mol ⁻¹	S^0 J mol ⁻¹ K ⁻¹	C_p J mol ⁻¹ K ⁻¹
C ₉ H ₂₀ O	1-Nonanol	liq	-456.5			
C ₁₀ H ₈	Naphthalene	cry	77.9		167.4	165.7
C ₁₀ H ₂₂	Decane	liq	-300.9			314.4
C ₁₂ H ₁₀	Biphenyl	cry	99.4		209.4	198.4
C ₁₂ H ₂₆	Dodecane	liq	-350.9			375.8

Energy Units and Conversions

Metric units:

10^3 kilo (k)	10^6 mega (M) Million	10^9 giga (G) Billion	10^{12} tera (T) Trillion	10^{15} peta (P) Quadrillion	10^{18} exa (E) Quintillion
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Energy conversion table

Energy	kWh	Btu	Calorie (10^3 cal)	Joule (J)
kWh	1	3412	860	3.6×10^6
Btu	2.93×10^{-4}	1	0.252	1054
Calorie (10^3 cal)	1.16×10^{-3}	3.97	1	4.18×10^3
Joule (J)	2.78×10^{-7}	9.5×10^{-5}	0.24×10^{-3}	1
Therm	29.31	100 000	25 200	105.5×10^6
MeV				1.6×10^{-19} J
TOE (tonne of oil equivalent)	1.16×10^4	3.97×10^7	1.00×10^7	41.85×10^9 J

Quad = 10^{15} Btu

CCF = 100 cubic feet

Energy content of fuels

Coal	25 million BTU/ton (short ton = 907.18 kg, ton = 1016 kg, metric ton = 10^3 kg)
Crude oil	5.6 million BTU/barrel (a barrel = 42 gallons = 158.97 L)
Oil	5.78 million BTU/barrel = 1700 kWh/barrel
Gasoline	5.6 million BTU/barrel (a barrel = 42 gallons = 158.97 L) = 1.33 therms/gallon = 39 kWh/gal = 10.3 kWh/L
Natural gas liquids	4.2 million BTU/barrel
Natural gas	1030 BTU/cubic foot
Wood	20 million BTU/cord

Other unit conversions

1 HP = 0.746 kW

1 gallon = 3.785 L 1000 L = 1 m³ 1 barrel = 42 gallons = 158.97 L

Answers to Exercises

Chapter 1

Exercise 1.1 The pressure exerted by a gas depends on both the mass and the average speed of the molecules.

At a given temperature, the heavier molecules have a lower average speed in just such a way that the pressures of two gases are equal if (N/V) is the same!

Exercise 1.3 (a) 40.9 mol, (b) About 7×10^{16} mol, (c) 4.3×10^{19} mol, (d) 9100 years

Exercise 1.4 150 atm and 180 atm

Exercise 1.5 (a) 0.08%

Exercise 1.6 $U(\text{ideal}) - U(\text{vw}) = 263 \text{ J} = 4.2\% \text{ of } U(\text{ideal})$

Exercise 1.7 (a) 24.5 L, (b) 1.174 L, (c) The Avogadro volume using the VW equation is 1.178 L.

Exercise 1.8 $2.5 \times 10^{-10} \text{ m}$

Exercise 1.12	Gas	T_c (K)	p_c (atm)	V_{mc} (L)
	CO_2	303.4	72.9	0.128
	H_2	33.1	12.7	0.0798
	CH_4	189.7	45.5	0.128

Exercise 1.13 The *Mathematica* code is in Appendix 1.2, Code C.

Chapter 2

Exercise 2.2 Energy turned to heat = 23.05 kcal; change of T of 1.0 L of water = 23.0 K

Exercise 2.3 (a) 4.54 amp, (b) 11.6 min

Exercise 2.4 (a) See Box 2.2, (b) 2.02 kJ

Exercise 2.5 Sound velocity for argon = 320 m s^{-1} ; for nitrogen = 352 m s^{-1}

Exercise 2.6 He: $\gamma = 1.667$, $M = 4.00 \times 10^{-3} \text{ kg}$, $C = 972 \text{ m s}^{-1}$ (965 m s^{-1})

CO₂: $\gamma = 1.304$, $M = 44.01 \times 10^{-3} \text{ kg}$, $C = 259 \text{ m/s}$ (259 m/s)

N₂: $\gamma = 1.404$, $M = 28.01 \times 10^{-3} \text{ kg}$, $C = 337 \text{ m s}^{-1}$ (334 m/s)

Exercise 2.8 Final $T = 334 \text{ K}$

Exercise 2.9 Enthalpy change = 4.22 kJ

Exercise 2.10 (a) -542.2 kJ, (b) -4817.2 kJ, (c) -1030 kJ

Exercise 2.11 Note that these values are only estimates and are not very accurate. Combustion enthalpy of C₇H₁₆ = -3672 kJ mol⁻¹; of C₈H₁₈ = -4168 kJ mol⁻¹; of C₉H₂₀ = -4664 kJ mol⁻¹. Divide these values by the molecular weight of the corresponding compound to obtain the enthalpy per gram.

Exercise 2.12 Combustion energy of 1.0 g of sucrose = 16.8 kJ. Energy needed to lift 100 kg wt through 1 m is 980 J. With 16.8 kJ, the 100 kg mass can be lifted $(16.8 \text{ kJ}/0.98 \text{ kJ m}^{-1}) = 17.1 \text{ m!}$

Exercise 2.13 When $\xi = 0.25$ mol, the amount of $\text{CH}_4 = 2.75$ mol, $\text{O}_2 = 1.5$ mol, $\text{CO}_2 = 0.25$ mol, $\text{H}_2\text{O} = 0.5$ mol. The amount of heat released = 222 kJ. When all the 2.0 mol of O_2 (which is the limiting reactant) has reacted $\xi = 1.0$ mol.

Exercise 2.14 Change in the mass of the Sun in 1 million years = 1.37×10^{23} kg (for comparison: mass of the Earth 5.98×10^{24} kg. Present mass of the Sun = 1.99×10^{30} kg)

Exercise 2.15 2.72×10^{12} J

Chapter 3

Exercise 3.2 201 K

Exercise 3.3 242 J

Exercise 3.4 (a) Maximum efficiency = 0.952, (b) Maximum energy available = 97 J

Exercise 3.5 30 m

Exercise 3.6 1.6 J/K

Exercise 3.7 Change in entropy = 2.2×10^{-4} J/K. Rate of change = 9.6×10^{-4} J K $^{-1}$ s $^{-1}$

Exercise 3.8 Entropy = 13.1 J K^{-1}

Exercise 3.9 Maximum power = 1.2 kW m^{-2} . Solar cells that cost about $\$540 \text{ m}^{-2}$ produce power at a cost of about \$0.15 per kW h.

Chapter 4

Exercise 4.1 In a living cell, which is an open system, $dS = d_iS + d_eS$. The entropy d_eS due to the exchange of matter and energy can be negative, but according to the Second Law $d_iS > 0$. Thus, though $d_iS > 0$, since $d_eS < 0$, the total $dS < 0$; this does not violate the Second Law.

Exercise 4.2	Quantity	Units
	Entropy, S	J K $^{-1}$
	Chemical potential, μ	J mol $^{-1}$
	Affinity, A	J mol $^{-1}$

Exercise 4.3 S_1 and S_3 are not extensive.

Exercise 4.4 (c) S at any time t is given by

$$S(t) = (N_{A0} - \xi) \left[S_{0A} + C_{VA} \ln T + R \ln \left(\frac{V}{N_{A0} - \xi} \right) \right] + 2\xi(t) \left[S_{0B} + C_{VB} \ln T + R \ln \left(\frac{V}{2\xi} \right) \right]$$

Chapter 5

Exercise 5.2 $F_f - F_i = -NRT \ln \left(\frac{V_f}{V_i} \right)$

Exercise 5.8 $\frac{\Delta G_f}{T_f} = \frac{\Delta G_i}{T_i} + \Delta H \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$

Exercise 5.9 For an ideal gas $F = N(u_0 + C_V T) - TN[s_0 + C_V \ln T + R \ln(V/N)]$

Exercise 5.10 $S = \frac{c}{T^2} - a$ and $H = b + \frac{2c}{T}$

Exercise 5.12 (b) $h = 3.1$ cm

Exercise 5.13 (b) 1.5 atm

Chapter 6

Exercise 6.1

- (a) $F(V, T, N) = N(u_0 + C_V T) - TN[s_0 + C_V \ln T + R \ln(V/N)]$
 (b) $G(p, T, N) = N(u_0 + C_V T + RT) - NT[s_0 + C_V \ln T + R \ln(RT)] + NRT \ln p$
 (c) Thus $\mu(T, n) = (u_0 + C_V T) - T[s_0 + C_V \ln T - R] + RT \ln(n)$,

where $n = (N/V)$

- Exercise 6.2** van der Waals: $a = 0.816 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 30.0 \times 10^{-3} \text{ L mol}^{-1}$,
 Berthelot: $a = 80.0 \text{ atm L}^2 \text{ K mol}^{-2}$, $b = 30.0 \times 10^{-3} \text{ L mol}^{-1}$,
 Dieterici: $a = 2.00 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 45.0 \times 10^{-3} \text{ L mol}^{-1}$,

- Exercise 6.6** (a) $U(\text{ideal}) = 8.54 \text{ kJ}$, $U(\text{ideal}) - U(\text{vw}) = 0.728 \text{ kJ}$

Exercise 6.8

- (a) $Z = \left[\frac{V_m}{V_m - b} - \frac{a}{RT} \frac{1}{V_m} \right]$
 (b) $F_{\text{vw}} - F_{\text{ideal}} = -\frac{3.59 \times 101.3}{V} \text{ J} - (8.314 \text{ J K}^{-1}) T \ln \left(\frac{V - 0.0427 \text{ L}}{V} \right)$

Chapter 7

- Exercise 7.1** BP of hexane at 0.5 atm = 48.3 °C

- Exercise 7.2** At an altitude of 2 miles water boils at about 87 °C

- Exercise 7.4** Number of phases = 4

Chapter 8

Exercise 8.2

- (a) Mole fractions: NaOH: 0.07, H₂O: 0.93
 (b) Molality = 4.17 mol kg⁻¹
 (c) Molarity = 4.0 M

Exercise 8.3

- (a) PO₂ = 0.21 atm, PN₂ = 0.78 atm, etc.
 (b) Concentration of O₂ in lakes = $2.7 \times 10^{-4} \text{ M}$

Exercise 8.4

- (a) Concentration of N₂ in blood = $5.1 \times 10^{-4} \text{ M}$
 (b) At a depth of 100 m N₂ concentration in blood = $5.5 \times 10^{-4} \text{ M}$

Exercise 8.5

- (a) [N₂] = $5.1 \times 10^{-4} \text{ M}$
 (b) [N₂] = $5.5 \times 10^{-3} \text{ M}$

Exercise 8.6 Boiling point of sugar solution = 373.28 K

Boiling point of NaCl solution = 373.46 K

Exercise 8.7

- (a) $T_f = [273 - (0.032V)]$ K in which V is in mL per liter of water
- (b) $V = 312$ mL per liter of water for a decrease of 10 °C in freezing point
- (c) $T_b = 102.67$ °C

Exercise 8.8 T_b of nitrobenzene = 212.68 K**Exercise 8.9** X = 128.7 g/mol**Exercise 8.10**

- (a) Molecular weightt of hemoglobin is about 70 000
- (b) $\pi = 31$ atm

Exercise 8.11 Osmotic pressure of sea water = 27 atm**Exercise 8.12**

- (a) Pressure needed for reverse osmosis = 24 atm. Work = 2.4 kJ L⁻¹
- (b) Energy cost for 100 L is about \$0.02
- (c) Evaporation using sunlight

Exercise 8.13 1.66×10^8 N = 1.7×10^7 kg wt**Exercise 8.14** $\gamma_{\text{Ca}^{2+}} = 0.317$, $\gamma_{\text{Cl}^-} = 0.750$ **Exercise 8.15** $m_{\text{Ag}^+} = 1.33 \times 10^{-5}$ m**Chapter 9****Exercise 9.1**

- (a) At about $T = 33\,000$ the C–H bond will break due to collisions.
- (b) At about 5.6×10^{10} K, avg KE equals nucleon binding energy. So we may expect nuclear reactions to take place at this temperature.

Exercise 9.2 At $T = 300$ K, $k = 7.81 \times 10^6$ M⁻¹ s⁻¹.At $T = 350$ K, $R_f = 4.38 \times 10^{-2}$ M s⁻¹.**Exercise 9.3** $E_a = 1.33 \times 10^{13}$ s⁻¹, $\Delta H^\ddagger = 125.6$ kJ mol⁻¹ and $\Delta S^\ddagger = -2.89$ J K⁻¹ mol⁻¹.**Exercise 9.4**

- (a) Reaction velocity = -0.069 M/s
- (b) $[A]_{\text{eq}} = [A]_0 - \xi_{\text{eq}}$, $[B]_{\text{eq}} = [B]_0 + 2\xi_{\text{eq}}$
- (c) $[A]_{\text{eq}} = 0.045$ M, $[B]_{\text{eq}} = 0.007$ M

Exercise 9.6 $k = 3.83 \times 10^{-12}$ s⁻¹

Radioactive decay is unaffected by temperature.

Exercise 9.7 Chirping depends on a rate-limiting step that obeys the Arrhenius law.**Exercise 9.9** At 25 °C, pH = 5.77 and at 35 °C, pH = 5.75

Exercise 9.10

- (a) $K = 6.74$
 (b) $K = 1.32 \times 10^{90}$
 (c) $K = 4.53 \times 10^{-31}$

Exercise 9.12

- (a) $K = 5.80 \times 10^5$ at $T = 25^\circ\text{C}$
 (b) $K = 6.3 \times 10^{-4}$ at $T = 400^\circ\text{C}$ and $\Delta G_{rxn} = 41.24 \text{ kJ/mol}$

Exercise 9.13 $K = 2.6$, At equilibrium $N_{\text{trans}} = 1.8 \text{ mol}$; $N_{\text{cis}} = 0.7 \text{ mol}$

Chapter 10

Exercise 10.1 Using the molar mass of N_2 the pressure at 2.5 km is 0.73 atm

Boiling point of water = 91.1°C

Exercise 10.2 $0.46 \text{ J K}^{-1} \text{ s}^{-1}$

Exercise 10.3

- (a) $K = 8.31 \times 10^{148}$
 (b) $K = 1.12 \times 10^{25}$
 (c) $K = 9.24 \times 10^{18}$
 (d) $K = 5.36 \times 10^{137}$

Exercise 10.4

- (a) 0.70 V
 (b) 0.79 V
 (c) 0.78 V

Exercise 10.5 $\frac{m_{k+}^{\text{in}}}{m_{k+}^{\text{out}}} = 33.2$

Exercise 10.7 $J_N = \frac{Dn(0)gM}{RT} e^{-gMx/RT}$

Exercise 10.8 $F(T) = e^{C - \mu_0(T)/RT}$

Exercise 10.9 Fraction of dipoles between 10° and $20^\circ = 2.26 \times 10^{-2}$

Chapter 11

Exercise 11.2 $\beta = \int_0^\infty \frac{8\pi h}{c^3} \left(\frac{k_B}{h}\right)^4 \frac{x^3 dx}{(e^x - 1)}$

Exercise 11.4 $\frac{V_{2.8\text{ K}}}{V_{10^{10}\text{ K}}} = 4.5 \times 10^{28}$

Exercise 11.5 $\lambda_{\text{max}}^{10000} = 290 \text{ nm}$

Exercise 11.6 $u(\lambda, T)d\lambda = 8\pi hc \frac{1}{(e^{hc/\lambda k_B T} - 1)} \frac{d\lambda}{\lambda^5}$

Exercise 11.7 $\frac{dS}{dt} = 6.58 \times 10^{14} \text{ J K}^{-1} \text{s}^{-1}$

Chapter 12

Exercise 12.1 $-c 3.7 \times 10^{-23} \text{ atm L K}^{-1} = -c 3.7 \times 10^{-21} \text{ J K}^{-1}$

Chapter 13

No numerical answers

Chapter 14

No numerical answers

Chapter 15

No numerical answers

Chapter 16

Exercise 16.3 For this system, we see that the cross-diffusional current could be of the order of $2 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$

Chapter 17

No numerical answers

Chapter 18

Exercise 18.1

- (a) $\frac{A}{RT} = \ln \frac{x_L}{x_D} \ll 1$ in which x_L and x_D are mole fractions. This will be true when x_L nearly equals x_D , i.e. when the two concentrations are nearly equal.

- (b) For notational simplicity we use $x = \text{N}_2\text{O}_4$ and $y = \text{NO}_2$.

$$\frac{A}{RT} = \frac{-4.71 \text{ kJ mol}^{-1}}{RT} + \ln \frac{p_x}{p_y^2}$$

When $T = 298 \text{ K}$, $\frac{A}{RT} = -1.9 + \ln \frac{p_x}{p_y^2}$

In the linear regime, near equilibrium $(A/RT) \ll 1$ implies $\ln \left(\frac{p_x}{p_y^2} e^{-1.9} \right) \ll 1$ in which p is measured in bars. At equilibrium, if $p_x = 1.0 \text{ bar}$, $p_y = 0.38 \text{ bar}$.

Chapter 19

No numerical answers

Chapter 20

Exercise 20.2 Rotational temperature for H₂ is 88 K, for O₂ it is 2.06 K

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