

THE PRINCIPLES OF CHEMICAL EQUILIBRIUM

WITH APPLICATIONS IN CHEMISTRY
AND CHEMICAL ENGINEERING

BY
KENNETH DENBIGH, F.R.S.,

FOURTH EDITION



CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge CB2 1RP, United Kingdom

CAMBRIDGE UNIVERSITY PRESS

The Edinburgh Building, Cambridge CB2 2RU, United Kingdom
40 West 20th Street, New York, NY 10011-4211, USA
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1966, 1971, 1981

This book is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without
the written permission of Cambridge University Press.

First published 1955

Reprinted 1957, 1961, 1964

Second edition 1966

Third edition 1971

Reprinted 1973, 1978

Fourth edition 1981

Reprinted 1986, 1987, 1989, 1992, 1993, 1997

British Library cataloguing in publication data

Denbigh, Kenneth George

The principles of chemical equilibrium – 4th edition

1. Thermodynamics

2. Chemical reactions

I. Title

541'.369 QD504 80-40925

ISBN 0 521 23682 7 hardback

ISBN 0 521 28150 4 paperback

Transferred to digital printing 2002

CONTENTS

<i>Preface to the First Edition</i>	page iii
<i>Preface to the Fourth Edition</i>	iv
<i>List of Symbols</i>	xvii
<i>Values of Physical Constants</i>	xxi

PART I: THE PRINCIPLES OF THERMODYNAMICS

Chapter 1: First and Second Laws

1·1 Introduction	3
1·2 Thermodynamic systems	5
1·3 Thermodynamic variables	6
1·4 Temperature and the zeroth law	9
1·5 Work	14
1·6 Internal energy and the first law	15
1·7 Heat	18
1·8 Expression of the first law for an infinitesimal process	19
1·9 Adiabatically impossible processes	21
1·10 Natural and reversible processes	23
1·11 Systematic treatment of the second law	25
1·12 Final statement of the second law	39
1·13 A criterion of equilibrium. Reversible processes	40
1·14 Maximum work	43
1·15 The fundamental equation for a closed system	45
1·16 Summary of the basic laws	46
1·17 Natural processes as mixing processes	48
1·18 The molecular interpretation of the second law	56
<i>Problems</i>	60

Chapter 2: Auxiliary Functions and Conditions of Equilibrium

2·1	The functions H , A and G	page 63
2·2	Properties of the enthalpy	63
2·3	Properties of the Helmholtz free energy	66
2·4	Properties of the Gibbs function	67
2·5a	Availability	70
2·5b	Digression on the useful work of chemical reaction	72
2·6	The fundamental equations for a closed system in terms of H , A and G	76
2·7	The chemical potential	76
2·8	Criteria of equilibrium in terms of extensive properties	82
2·9	Criteria of equilibrium in terms of intensive properties	85
2·10	Mathematical relations between the various functions of state	89
2·11	Measurable quantities in thermodynamics	94
2·12	Calculation of changes in the thermodynamic functions over ranges of temperature and pressure	98
2·13	Molar and partial molar quantities	99
2·14	Calculation of partial molar quantities from experimental data	104
	<i>Problems</i>	106

**PART II: REACTION AND PHASE
EQUILIBRIA**

Chapter 3: Thermodynamics of Gases

3·1	Models	111
3·2	The single perfect gas	111
3·3	The perfect gas mixture	114
3·4	Imperfect gases	119
3·5	The Joule–Thomson effect	120

Contents

ix

3·6	The fugacity of a single imperfect gas	<i>page</i> 122
3·7	Fugacities in an imperfect gas mixture	125
3·8	Temperature coefficient of the fugacity and standard chemical potential	127
3·9	Ideal gaseous solutions and the Lewis and Randall rule	128
	<i>Problems</i>	130

Chapter 4: Equilibria of Reactions Involving Gases

4·1	Introduction	133
4·2	The stoichiometry of chemical reaction	133
4·3	Preliminary discussion on reaction equilibrium	135
4·4	Concise discussion on reaction equilibrium	139
4·5	The equilibrium constant for a gas reaction	140
4·6	The temperature dependence of the equilibrium constant	143
4·7	Other forms of equilibrium constant for perfect gas mixtures	146
4·8	Free energies and enthalpies of formation from the elements	148
4·9	Some examples	149
4·10	Free energies of formation of non-gaseous substances or from non-gaseous elements	153
4·11	Preliminary discussion on reaction equilibria involving gases together with immiscible liquids and solids	156
4·12	Concise discussion on reaction equilibria involving gases together with immiscible liquids and solids	159
4·13	Example on the roasting of galena	161
4·14	Measurement of the free energy of reaction by use of galvanic cells	163
4·15	Alternative discussion of the galvanic cell	167
4·16	Number of independent reactions	169
4·17	Conditions of equilibrium for several independent reactions	172

4·18	General remarks on simultaneous reactions	<i>page</i> 173
4·19	General remarks on maximum attainable yield	175
	<i>Problems</i>	177
 <i>Chapter 5: Phase Rule</i>		
5·1	Introduction	182
5·2	The phase rule for non-reactive components	184
5·3	The phase rule for reactive components	187
5·4	Additional restrictions	188
5·5	Example of the application of the phase rule	188
5·6	Alternative approach	191
5·7	Two examples from the zinc smelting industry	191
	<i>Problems</i>	194
 <i>Chapter 6: Phase Equilibria in Single Component Systems</i>		
6·1	Introduction	196
6·2	The Clausius–Clapeyron equation	197
6·3	The enthalpy of vaporization and its temperature coefficient	200
6·4	Integration of the Clausius–Clapeyron equation	202
6·5	The effect of a second gas on the vapour pressure of a liquid or solid	203
6·6	Lambda transitions	207
	<i>Problems</i>	213
 <i>Chapter 7: General Properties of Solutions and the Gibbs–Duhem Equation</i>		
7·1	The Gibbs–Duhem equation	215
7·2	Pressure-temperature relations	216
7·3	Partial pressure-composition relations	221
7·4	The empirical partial pressure curves of binary solutions	222
7·5	Application of the Gibbs–Duhem equation to the partial pressure curves	232

Contents

xi

7·6	Application of the Gibbs–Duhem equation to the total pressure curve	<i>page</i> 235
7·7	The Gibbs–Duhem equation in relation to Raoult’s and Henry’s laws	236
7·8	The Gibbs–Duhem equation in relation to the Margules and van Laar equations	240
	<i>Problems</i>	242

Chapter 8: Ideal Solutions

8·1	Molecular aspects of solutions	244
8·2	Definition of the ideal solution	249
8·3	Raoult’s and Henry’s laws	249
8·4	Imperfect vapour phase	252
8·5	The mixing properties of ideal solutions	252
8·6	The dependence of vapour-solution equilibria on temperature and pressure	255
8·7	Nernst’s law	256
8·8	Equilibrium between an ideal solution and a pure crystalline component	257
8·9	Depression of the freezing-point	260
8·10	Elevation of the boiling-point	261
8·11	The osmotic pressure of an ideal solution	262
8·12	The ideal solubility of gases in liquids	264
8·13	The ideal solubility of solids in liquids	266
	<i>Problems</i>	267

Chapter 9: Non-Ideal Solutions

9·1	Conventions for the activity coefficient on the mole fraction scale	270
9·2	The activity coefficient in relation to Raoult’s and Henry’s laws	271
9·3	The use of molality and concentration scales	274
9·4	Convention for the activity-coefficient on the molality scale	276
9·5	The effect of temperature and pressure	278

9-6	The determination of activity coefficients	<i>page</i> 281
9-7	The Gibbs–Duhem equation applied to activity coefficients	284
9-8	The calculation of the activity coefficient of the solute	284
9-9	Excess functions of non-ideal solutions	285
9-10	The activity	287
9-11	The osmotic coefficient	288
	<i>Problems</i>	288
 <i>Chapter 10: Reaction Equilibrium in Solution. Electrolytes</i>		
10-1	Reaction equilibrium in solution	292
10-2	Free energy of formation in solution. Convention concerning hydrates	295
10-3	Equilibrium constants expressed on the molality and volume concentration scales	298
10-4	Temperature and pressure dependence of the equilibrium constant	299
10-5	Ratio of an equilibrium constant in the gas phase and in solution	301
10-6	Notation for electrolytes	302
10-7	Lack of significance of certain quantities	303
10-8	Dissociation equilibrium and the chemical potential of the electrolyte	304
10-9	Activity coefficients	305
10-10	Phase equilibrium of an electrolyte. Solubility product	307
10-11	Equilibrium constant for ionic reactions	309
10-12	Magnitude of activity coefficients of charged and uncharged species	310
10-13	Free energy of dissociation	312
10-14	The hydrogen ion convention and the free energies and enthalpies of formation of individual ions	314
10-15	Activity coefficients and free energies as measured by the use of the galvanic cell	316
10-16	Activity coefficients by use of the Gibbs–Duhem equation	322
10-17	Partial pressure of a volatile electrolyte	324
10-18	Limiting behaviour at high dilution	325
	<i>Problems</i>	327

PART III: THERMODYNAMICS IN RELATION
TO THE EXISTENCE OF MOLECULES

<i>Chapter 11: Statistical Analogues of Entropy and Free Energy</i>		
11-1	Thermodynamics and molecular reality	<i>page</i> 333
11-2	The quantum states of macroscopic systems	333
11-3	Quantum states, energy states and thermodynamic states	334
11-4	Fluctuations	335
11-5	Averaging and the statistical postulate	336
11-6	Accessibility	337
11-7	The equilibrium state	338
11-8	Statistical methods	339
11-9	The ensemble and the averaging process	340
11-10	Statistical analogues of the entropy and Helmholtz free energy	345
11-11	Comparison of statistical analogues with thermodynamic functions	350
11-12	Thermal and configurational entropy	353
11-13	Appendix I. Origin of the canonical distribution	356
11-14	Appendix II. Entropy analogues	359
<i>Problem</i>		360
 <i>Chapter 12: Partition Function of a Perfect Gas</i>		
12-1	Distinguishable states of a gas and the molecular partition function	361
12-2	Schrödinger's equation	365
12-3	Separability of the wave equation	367
12-4	Factorization of the molecular partition function	371
12-5	The translational partition function	372
12-6	The internal partition function	376
12-7	Thermodynamic properties of the perfect gas	377
12-8	The Maxwell-Boltzmann distribution	383

12·9	Distribution over translational and internal states	<i>page</i> 386
12·10	Number of translational states of a given energy	387
12·11	The Maxwell velocity distribution	390
12·12	Principle of equipartition	392
12·13	Appendix. Some definite integrals	394
	<i>Problems</i>	396

Chapter 13: Perfect Crystals and the Third Law

13·1	Normal co-ordinates	397
13·2	The Schrödinger equation for the crystal	400
13·3	The energy levels of the harmonic oscillator	401
13·4	The partition function	402
13·5	The Maxwell-Boltzmann distribution	405
13·6	The high temperature approximation	406
13·7	The Einstein approximation	408
13·8	The Debye approximation	409
13·9	Comparison with experiment	411
13·10	Vapour pressure at high temperature	414
13·11	The third law—preliminary	416
13·12	Statement of the third law	421
13·13	Tests and applications of the third law	424
	<i>Problems</i>	427

Chapter 14: Configurational Energy and Entropy

14·1	Introduction	429
14·2	Example 1: the lattice model of mixtures	432
14·3	Example 2: the Langmuir isotherm	436

Chapter 15: Chemical Equilibrium in Relation to Chemical Kinetics

15·1	Introduction	439
15·2	Kinetic species	440

Contents

xv

15-3	Variables determining reaction rate	<i>page</i> 441
15-4	Forward and backward processes	442
15-5	Thermodynamic restrictions on the form of the kinetic equations	444
15-6	The temperature coefficient in relation to thermodynamic quantities	449
15-7	Transition-state theory	450
15-8	The equilibrium assumption	453
15-9	The reaction rate	455
	<i>Appendix.</i> Answers to Problems and Comments	460
	<i>Index</i>	487

CHAPTER 1

FIRST AND SECOND LAWS

1.1. Introduction

One reason why the study of thermodynamics is so valuable to students of chemistry and chemical engineering is that it is a theory which can be developed in its entirety, without gaps in the argument, on the basis of only a moderate knowledge of mathematics. It is therefore a self-contained logical structure, and much benefit—and incidentally much pleasure—may be obtained from its study. Another reason is that it is one of the few branches of physics or chemistry which is largely independent of any assumptions concerning the nature of the fundamental particles. It does not depend on ‘mechanisms’, such as are used in theories of molecular structure and kinetics, and therefore it can often be used as a check on such theories.

Thermodynamics is also a subject of immense practical value. The kind of results which may be obtained may perhaps be summarized very briefly as follows:

(a) On the basis of the first law, relations may be established between quantities of heat and work, and these relations are not restricted to systems at equilibrium.

(b) On the basis of the first and second laws together, predictions may be made concerning the effect of changes of pressure, temperature and composition on a great variety of physico-chemical systems. These applications are limited to systems at equilibrium. Let χ be a quantity characteristic of an equilibrium, such as the vapour pressure of a liquid, the solubility of a solid, or the equilibrium constant of a reaction. Then some of the most useful results of thermodynamics are of the form

$$\left(\frac{\partial \ln \chi}{\partial T}\right)_p = \frac{(\text{A characteristic energy})}{RT^2},$$
$$\left(\frac{\partial \ln \chi}{\partial p}\right)_t = \frac{(\text{A characteristic volume})}{RT}.$$

The present volume is mainly concerned with the type of results of (b) above. However, in any actual problem of chemistry, or the chemical industry, it must always be decided, in the first place, whether the essential features of the problem are concerned with *equilibria* or with *rates*. This point may be illustrated by reference to two well-known chemical reactions.

In the synthesis of ammonia, under industrial conditions, the reaction normally comes sufficiently close to equilibrium for the applications of thermodynamics to prove of immense value.† Thus it will predict the influence of changes of pressure, temperature and composition on the maximum attainable yield. By contrast in the catalytic oxidation of ammonia the yield of nitric oxide is determined, not by the opposition of forward and backward reactions, as in ammonia synthesis, but by the relative speeds of two independent processes which compete with each other for the available ammonia. These are the reactions producing nitric oxide and nitrogen respectively, the latter being an undesired and wasteful product. The useful yield of nitric oxide is thus determined by the *relative speeds* of these two reactions on the surface of the catalyst. It is therefore a problem of rates and not of equilibria.

The theory of equilibria, based on thermodynamics, is much simpler, and also more precise, than any theory of rates which has yet been devised. For example, the equilibrium constant of a reaction in a perfect gas can be calculated exactly from a knowledge only of certain macroscopic properties of the pure reactants and products. The rate cannot be so predicted with any degree of accuracy for it depends on the details of molecular structure and can only be calculated, in any precise sense, by the immensely laborious process of solving the Schrödinger wave equation. Thermodynamics, on the other hand, is independent of the fine structure of matter,‡ and its peculiar simplicity arises from a certain condition which must be satisfied in any state of equilibrium, according to the second law.

The foundations of thermodynamics are three facts of ordinary experience. These may be expressed very roughly as follows:

- (1) bodies are at equilibrium with each other only when they have the same degree of 'hotness';
- (2) the impossibility of perpetual motion;
- (3) the impossibility of reversing any natural process in its entirety.

In the present chapter we shall be concerned with expressing these facts more precisely, both in words and in the language of mathematics. It will be shown that (1), (2) and (3) above each gives rise to the definition of a certain function, namely, temperature, internal energy and entropy respectively. These have the property of being entirely determined by the state of a body and therefore they form exact differentials. This leads to the following equations which contain the *whole* of the fundamental theory:

† The error in using thermodynamic predictions, as a function of the extent to which the particular process falls short of equilibrium, is discussed by Rastogi and Denbigh, *Chem. Eng. Science*, 7 (1958), 261.

‡ In making this statement we are regarding thermodynamics as having its own secure empirical basis. On the other hand, the laws of thermodynamics may themselves be interpreted in terms of the fine structure of matter, by the methods of statistical mechanics (Part III).

$$dU = dq + dw,$$

$$dS = dq/T, \quad \text{for a reversible change,}$$

$$dS \geq 0, \quad \text{for a change in an isolated system,}$$

$$dU = TdS - pdV + \sum \mu_i dn_i \quad \text{for each homogeneous part of a system.}$$

Subsequent chapters of Parts I and II will be concerned with the elaboration and application of these results. The student is advised that there is no need to commit any equations to memory; the four above, together with a few definitions of auxiliary quantities such as free energy, soon become familiar, and almost any problem can be solved by using them.

In conclusion to this introduction it may be remarked that a new branch of thermodynamics has developed during the past few decades which is not limited in its applications to systems at equilibrium. This is based on the use of the principle of microscopic reversibility as an auxiliary to the information contained in the laws of classical thermodynamics. It gives useful and interesting results when applied to non-equilibrium systems in which there are coupled transport processes, as in the thermo-electric effect and in thermal diffusion. It does not have significant applications in the study of chemical reaction or phase change and for this reason is not included in the present volume.†

1.2. Thermodynamic systems

These may be classified as follows:

Isolated systems are those which are entirely uninfluenced by changes in their environment. In particular, there is no possibility of the transfer either of energy or of matter across the boundaries of the system.

Closed systems are those in which there is the possibility of energy exchange with the environment, but there is no transfer of matter across the boundaries. This does not exclude the possibility of a change of internal composition due to chemical reaction.

Open systems are those which can exchange both energy and matter with their environment. An open system is thus not defined in terms

† For an elementary account of the theory see the author's *Thermodynamics of the Steady State* (London, Methuen, 1951). Also Prigogine's *Introduction to the Thermodynamics of Irreversible Processes* (Wiley, 1962), Callens' *Thermodynamics* (Wiley, 1960), Fitt's *Non-Equilibrium Thermodynamics* (McGraw-Hill, 1962), van Rysselberghe's *Thermodynamics of Irreversible Processes* (Hermann, 1963) and de Groot and Mazur's *Non-Equilibrium Thermodynamics* (North Holland Publishing Co., 1962). For criticism see Truesdell's *Rational Thermodynamics* (McGraw-Hill, 1969).

of a given piece of material but rather as a region of space with geometrically defined boundaries across which there is the possibility of transfer of energy and matter.

Where the word *body* is used below it refers either to the isolated or the closed system. The preliminary theorems of thermodynamics all refer to bodies, and many of the results which are valid for them are not directly applicable to open systems.

The application of thermodynamics is simplest when the system under discussion consists of one or more parts, each of which is spatially uniform in its properties and is called a *phase*. For example, a system composed of a liquid and its vapour consists almost entirely of two homogeneous phases. It is true that between the liquid and the vapour there is a layer, two or three molecules thick, in which there is a gradation of density, and other properties, in the direction normal to the interface. However, the effect of this layer on the thermodynamic properties of the overall system can usually be neglected. This is because the work involved in changes of interfacial area, of the magnitudes which occur in practice, is small compared to the work of volume change of the bulk phases. On the other hand, if it were desired to make a thermodynamic analysis of the phenomena of surface tension it would be necessary to concentrate attention on the properties of this layer.

Thermodynamic discussion of real systems usually involves certain approximations which are made for the sake of convenience and are not always stated explicitly. For example, in dealing with vapour-liquid equilibrium, in addition to neglecting the interfacial layer, it is customary to assume that each phase is uniform throughout its depth, despite the incipient separation of the components due to the gravitational field. However, the latter effect can itself be treated thermodynamically, whenever it is of interest.

Approximations such as the above are to be distinguished from certain *idealizations* which affect the validity of the fundamental theory. The notion of isolation is an idealization, since it is never possible to separate a system completely from its environment. All insulating materials have a non-zero thermal conductivity and allow also the passage of cosmic rays and the influence of external fields. If a system were completely isolated it would be unobservable.

1·3. Thermodynamic variables

Thermodynamics is concerned only with the macroscopic properties of a body and not with its atomic properties, such as the distance between the atoms in a particular crystal. These macroscopic properties form a large class and include the volume, pressure, surface

tension, viscosity, etc., and also the 'hotness'. They may be divided into two groups as follows:

The *extensive* properties, such as volume and mass, are those which are additive, in the sense that the value of the property for the whole of a body is the sum of the values for all of its constituent parts.

The *intensive* properties, such as pressure, density, etc., are those whose values can be specified at each point in a system and which may vary from point to point, when there is an absence of equilibrium. Such properties are not additive and do not require any specification of the quantity of the sample to which they refer.

Consider the latter class and let it be supposed that the system under discussion is closed and consists of a single phase which is in a state of equilibrium, and is not significantly affected by external fields. For such a system it is usually found that the specification of any two of the intensive variables will determine the values of the rest. For example, if $I_1, I_2, \dots, I_j, \dots, I_n$, are the intensive properties then the fixing of, say, I_1 and I_2 will give the values of all the others. Thus†

$$I_j = f(I_1, I_2) \quad (j = 3, 4, \dots, n). \quad (1.1)$$

For example, if the viscosity of a sample of water is chosen as $0.506 \times 10^{-3} \text{ N s m}^{-2}$ and its refractive index as 1.328 9, then its density is $0.988 \text{ l g cm}^{-3}$, its 'hotness' is 50°C , etc. In the next section, instead of choosing viscosity and refractive index, we shall take as our reference variables the pressure and density, which are a more convenient choice. On this basis we shall discuss what is meant by 'hotness' or 'temperature' (which it is part of the business of thermodynamics to define), and thereafter we shall take pressure and temperature as the independent intensive variables, as is always done in practice.

What has just been said, to the effect that two intensive properties of a phase usually determine the values of the rest, applies to mixtures as well as to pure substances. Thus a given mixture of alcohol and water has definite properties at a chosen pressure and density. On the other hand, in order to specify which particular mixture is under discussion it is necessary to choose an extra set of variables, namely, those describing the *chemical composition* of the system. These variables depend on the notion of the *pure substance*, namely, a substance which cannot be separated into fractions of different properties by means of the *same processes* as those to which we intend to apply our

† The equation means that I_3, I_4 , etc., are all functions of I_1 and I_2 . Thus $I_3 = f(I_1, I_2)$ might stand for $I_3 = I_1^2 I_2^4$, $I_3 = I_1 / I_2^3$, etc. A simple relation of this kind is $T = \text{constant } p/\rho$ for the temperature of a gas as a function of its pressure and density. However, for most substances and properties the precise form of the functional relationship is unknown.

thermodynamic discussion; for example, the simple physical processes such as vaporization, passage through a semi-permeable membrane, etc. If there are q pure substances present, the composition may be expressed by means of $q - 1$ of the mole fractions, denoted x_1, x_2, \dots, x_{q-1} . Thus in place of the previous relation we have

$$I_j = f(I_1, I_2, x_1, x_2, \dots, x_{q-1}). \quad (1\cdot2)$$

These considerations apply to each phase of the system.

Turning now to the *extensive* properties it is evident that the choice of only two of these is insufficient to determine the state of a system, even if it is a pure substance. Thus if we fix both the volume and mass of a quantity of hydrogen, it is still possible to make simultaneous changes of pressure and of 'hotness'. An extensive property of a pure phase is usually determined by the choice of *three* of its properties, one of which may be conveniently chosen as the mass (thereby determining the quantity of the pure phase in question) and the other two as intensive properties. For example, if E_1, E_2, \dots, E_r are extensive properties, then any one of them will usually be determined by the same two intensive variables, I_1 and I_2 , as chosen previously, together with the total mass m . Thus

$$E_i = m \times f(I_1, I_2) \quad (i = 1, 2, \dots, r). \quad (1\cdot3)$$

This equation expresses also that E_i is proportional to m , since E_i is additive. It will be recognized that the quotient E_i/m , of which specific volume is an example, is a member of the group of intensive variables. Such quotients are called *specific properties*. In the case of a phase which is a mixture it is also necessary, of course, to specify the composition:

$$E_i = m \times f(I_1, I_2, x_1, x_2, \dots, x_{q-1}). \quad (1\cdot4)$$

It may be remarked that thermodynamics provides no criterion with regard to the minimum number of variables required to fix the state of a system. There are a number of instances in which the remarks above with regard to two intensive variables fixing the remainder are inapplicable. For example, we can find pairs of states of liquid water, one member of each pair being on one side of the point of maximum density and the other member on the other side, each of which have the same density and the same pressure (chosen as greater than the vapour pressure) and yet do not have identical values of other properties, such as viscosity. This is because the density does not vary monotonically with the other variables, but passes through a maximum.

In other instances it is necessary to introduce an extra variable of state. For example, in the case of a magnetic substance it will be necessary to specify, say, the field intensity together with pressure

and 'hotness'. Similarly, in the case of colloids, emulsions and fine powders the properties are greatly affected both by the total interfacial area and by the distribution of the particles over the size range.

The minimum number of variables of state, whose values determine the magnitudes of all other macroscopic variables, is thus an empirical fact to be determined by experience. In any particular application, if it is found that the system does not appear to obey the laws of thermodynamics, it may be suspected that an insufficient number of variables of state have been included in the equations.

1.4. Temperature and the zeroth law†

In the last section only passing reference was made to the property of 'hotness'. It is part of thermodynamics to define what is meant by this, whereas the mechanical and geometrical concepts, such as pressure and volume, are taken as being understood.

Now it is a fact of experience that a set of bodies can be arranged in a *unique* series according to their hotness, as judged by the sense of touch. That is to say, if A is hotter than B , and B is hotter than C , then A is also hotter than C . The same property is shown also by the real numbers; thus if n_a, n_b and n_c are three numbers such that $n_a > n_b$ and $n_b > n_c$, then we have also $n_a > n_c$. This suggests that the various bodies arranged in their order of hotness, can each be assigned a number such that larger numbers correspond to greater degrees of hotness. The number assigned to a body may then be called its temperature, but there are obviously an infinite variety of ways in which this numbering can be carried out.

The notion of temperature must clearly be placed on a more exact basis than is provided by the sense of touch. Furthermore, in order to avoid any circularity in the argument, this must be done without any appeal to the notion of heat, which follows logically at a later stage.

The definition of temperature now to be obtained depends on what happens when two bodies are placed in contact under conditions where their pressures and volumes can be varied independently. For this purpose each body must be enclosed by an impermeable wall which can be moved inwards or outwards.

It is useful to think of two kinds of impermeable wall. The first, which will be called *diathermal* or *non-adiabatic*, is such that two bodies separated by a wall of this kind are nevertheless capable of exerting an influence on each other's thermodynamic state through the wall. The existence of diathermal materials is, of course, a matter of common experience and shortly they will be identified as materials

† The discussion of temperature and the first law is based on that of Born, *Phys. Z.* **22** (1921), 218, 249, 282; also his *Natural Philosophy of Cause and Chance* (Oxford, 1949).

capable of transmitting what will then be called *heat*. The second type of wall will be called *adiabatic*. A body completely surrounded by a wall of this kind cannot be influenced (apart from the possible effects of force fields) from outside, except by compressing or expanding the wall, or otherwise causing internal motion.

As remarked by Pippard† the adiabatic wall may be thought of as the end stage of a process of extrapolation. A metal wall is clearly diathermal in the above sense; on the other hand the type of double, and internally highly evacuated, wall used in a vacuum flask is almost completely adiabatic. The concept of the ideal adiabatic wall is thus a legitimate extrapolation from the conditions existing in the vacuum flask.

The definition which has been made does not depend on any previous knowledge of heat. Similarly, we shall speak of any change taking place inside an adiabatic wall as being an *adiabatic process*. Bodies will also be said to be in *thermal contact* when they are either in direct contact (e.g. two pieces of copper) or in contact through a non-adiabatic wall (e.g. two samples of gas). Their final state, when all observable change has come to an end, is called *thermal equilibrium*.

Now it is a fact of experience that if bodies *A* and *B* are each in thermal equilibrium‡ with a third body, they are also in thermal equilibrium with each other. This result is so familiar that it is regarded almost as a truism. However, there is no self-apparent reason why it should be so, and it must be regarded as an empirical fact of nature and has become known as the *zeroth law of thermodynamics*. It is the basis of the scientific concept of temperature, which may now be outlined as follows.

We consider two bodies, each of them a homogeneous phase in a state of internal equilibrium, which are in contact through a non-adiabatic wall. The thermodynamic state of each body may be completely specified by means of two variables only, and these may conveniently be chosen as the volume per unit mass and the pressure. These variables will determine the property called 'hotness', together with all other properties. Let the variables be p and v for the one body and P and V for the other. When they are brought into contact in this way, at initially different degrees of hotness, there is a slow change in the values of the pressures and volumes until the state of thermal

† Pippard. *Elements of Classical Thermodynamics*, Cambridge, 1961.

‡ It has been pointed out by I. P. Bazarov (*Thermodynamics*, p. 4, Pergamon, 1964) that the fact that isolated systems do reach a state of equilibrium, and do not depart from it spontaneously, is essentially a basic postulate of thermodynamics. Hatsopoulos and Keenan (*Principles of General Thermodynamics*, Wiley, 1965) have further explored the meaning of the equilibrium concept, and have put forward a *law of stable equilibrium* from which the first and second laws may be derived.

equilibrium is attained. Let p' , v' , P' and V' be the values of the variables at the state of equilibrium. If the first body is momentarily removed it will be found that its pressure and volume can be adjusted to a second pair of values, p'' and v'' , which will again give rise to a state of equilibrium with the other body, which is still at P' and V' . In fact, there are a whole sequence of states (p', v') , (p'', v'') , (p''', v''') , etc., of the first body, all of which are in equilibrium with the state (P', V') of the other.

We can thus draw a curve (Fig. 1 *a*), with co-ordinates p and v , which is the locus of all points which represent states of the first body which are in equilibrium with the state (P', V') of the second. According to the zeroth law all states along such a curve are also in equilibrium with each other; that is to say, two replicas of the first body would be in equilibrium with each other if their pressures and volumes correspond to any two points along this curve.

A similar curve (Fig. 1 *b*) can be drawn for the second body in its own P , V co-ordinates—that is, there is a curve which is the locus of all states which are in equilibrium with a given state of the first body, and therefore in equilibrium with each other. There are thus two

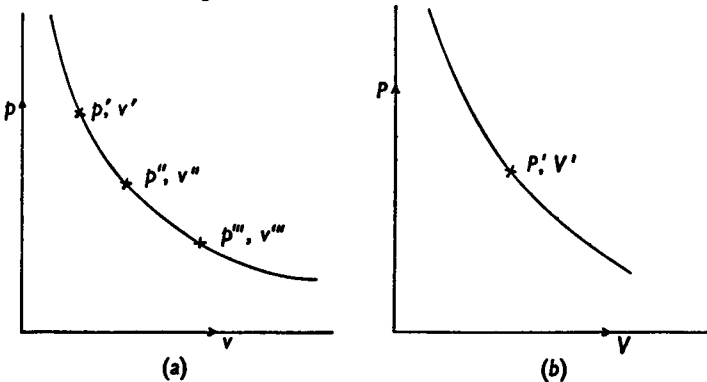


Fig. 1. The curves are not drawn to the equation $pv = \text{constant}$ because the discussion is not limited to perfect gases.

curves, one for each body, and every state on the one curve can be put into equilibrium with every other state on this curve, and also with every state on the other curve. Such states thus have a property in common and this will be called their *temperature*. It is consistent with our more intuitive ideas that such states are found also to have the same degree of hotness, as judged by the sense of touch. However, from the present point of view, this may now be regarded as being of physiological rather than of thermodynamic interest.

The existence of the common property along the two curves—which may now be called *isothermals*—can be seen more clearly as

follows. The equation to a curve concerning the variables p and v can be expressed in the form†

$$f(p, v) = \theta,$$

where θ is a constant for all points along the curve of Fig. 1a. Similarly for the other body we have $F(P, V) = \text{constant}$, along the curve of Fig. 1b. By inclusion of a suitable pure number in one or other of these functions the two constants can be made numerically equal.

Therefore

$$f(p, v) = F(P, V) = \theta. \quad (1.5)$$

There is thus a certain function, θ , of the pressure and volume of a phase which has the same value for all states of the phase which are in thermal equilibrium with each other and it is equal also to a function (not necessarily of the same form) of the pressure and volume of a second phase which is in thermal equilibrium with the first. It is this function which is called the temperature.

For example, if the first phase is a perfect gas the equation to the curve of Fig. 1a is simply $pv = \text{constant}$, and if the second phase is a gas which departs slightly from perfection, the curve of Fig. 1b can be represented by the equation $P(V - b) = \text{constant}$, where b is also a constant. Thus (1.5) may be expressed

$$\frac{pv}{\text{constant}} = \frac{P(V - b)}{\text{constant}} = \theta.$$

and such equations are called *equations of state*.

Returning to the earlier discussion, there are, of course, states of the first phase which are not in thermal equilibrium with the second one in its state (P', V') . Let equation (1.5) be rewritten

$$f(p_1, v_1) = F(P_1, V_1) = \theta_1,$$

then there are a whole sequence of new states (p'_2, v'_2) , (p''_2, v''_2) , etc., each of which gives rise to a state of thermal equilibrium with the second body in the states (P'_2, V'_2) , (P''_2, V''_2) , etc. These states define two new curves, one for each body, which satisfy the relation‡

$$f(p_2, v_2) = F(P_2, V_2) = \theta_2,$$

and thus define a different value of the temperature θ_2 .§ In fact, there is an infinite family of isothermals, some of which are shown in Fig. 2, such that all states on corresponding curves are in equilibrium with each other and thus define a particular temperature.

† For example, the equation to a straight line is $y - ax = \text{constant}$; the equation to a circle whose centre is at the origin is $x^2 + y^2 = \text{constant}$.

‡ It is tacitly assumed that the form of the function $f(p, v)$ is the same at the two temperatures θ_1 and θ_2 . (The same is assumed of $F(P, V)$.) Fortunately there exist substances—perfect or near perfect gases—for which this is true and one of these, such as nitrogen may be taken as the thermometric reference substance.

§ $f(p_2, v_2)$ is not necessarily quite the same function of p_2 and v_2 as $f(p_1, v_1)$ is of p_1 and v_1 . The functional relationship may change over the temperature interval, and similarly with regard to $F(P, V)$. However this does not affect the argument.