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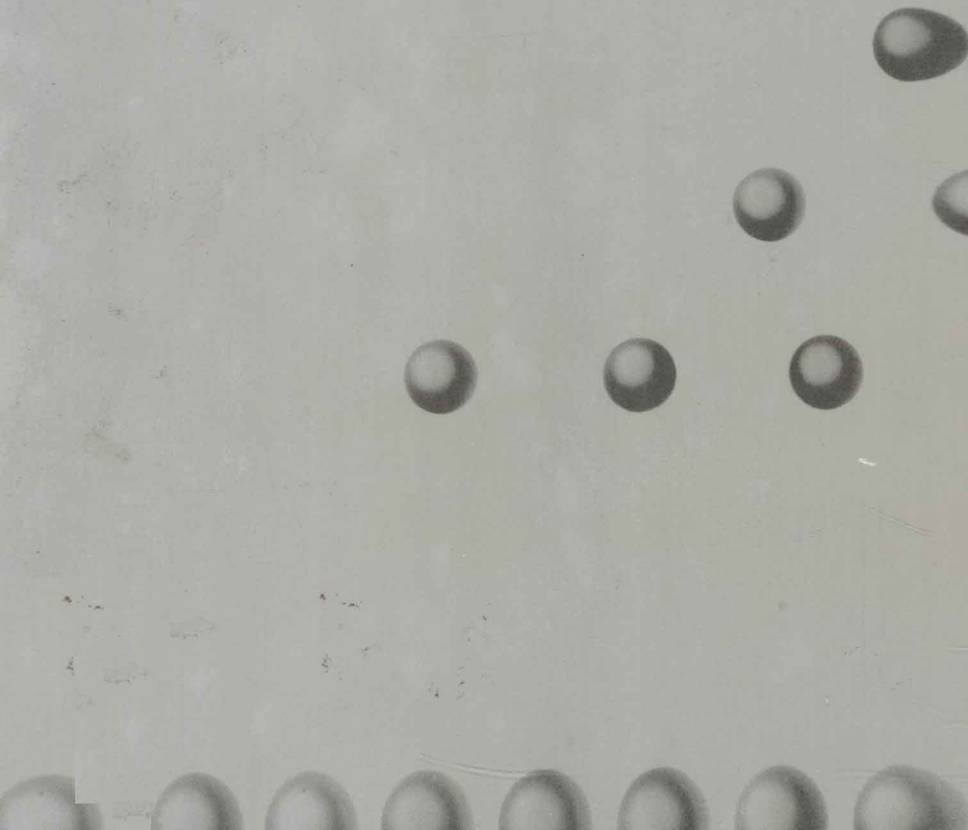
entropy and energy levels

R. P. H. Gasser
and W. G. Richards



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Entropy and energy levels

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Editor's Foreword

IT is of little use having a theory of the microscopic behaviour of atoms and molecules if from it cannot be extracted a theory of the behaviour of matter in bulk. The connexion is made through statistical mechanics, which computes from their microscopic properties the behaviour of statistically large assemblies of molecules. Both theories and models have two functions: apart from leading to the calculation and prediction of the properties of matter, they furnish a set of concepts in terms of which other concepts can be understood. In the present case the concepts of thermodynamics are enriched. Although thermodynamics can stand alone, and deal with manifestations without appealing to the microscopic behaviour of the components of the system, there is no doubt that its concepts can be delineated more sharply if their microscopic structure can be understood. This book is thus a linking book; it joins quantum theory (and its characteristic feature of discrete energy levels) to thermodynamics (and its most powerful and characteristic function, entropy). Through this connexion are joined spectroscopy and chemical reactions.

The concepts which in this volume are outlined in a simple, uncluttered way, are developed in the other volumes of this series. The concepts relating to energy levels in quantized systems are explained in my *Quanta: a handbook of concepts* (OCS 21), and the other wing, the wing of thermodynamics, is described by Smith in his *Basic chemical thermodynamics* (OCS 8). Application to reaction rates are introduced in this volume and are developed into a state useful for elementary applications in Pilling's *Chemical kinetics* (OCS 22). A specialized application to reaction rates is described by Albery in his *Electrode kinetics* (OCS 14).

P.W.A.

Preface

As College Tutors we find that a major difficulty in teaching statistical thermodynamics to chemistry students is that (somewhat surprisingly) when they first encounter this subject they often find the underlying physical principles more difficult to grasp than the mathematical formalism. Thus the question 'What is a partition function?' is usually met with blank incomprehension, even though the equation defining this function is well-known and its derivation can be reproduced on request. A number of existing textbooks provide excellent coverage of the more formal aspects of the subject and examine the philosophical foundations on which it rests. In this book, however, one of our principal aims is to make clear to the beginner the physical basis of the relation between the observable behaviour of systems of atoms or molecules and the properties of the individual particles. Some acquaintance with elementary calculus and quantum theory is assumed, as is a familiarity with the basic ideas of classical thermodynamics.

In pursuing our aim we have occasionally sacrificed rigour for the sake of clarity and we have thought it especially important to introduce at the earliest possible moment the world of experiment. This we regard as the best way to an understanding of the subject. We have chosen therefore to illustrate the principles by including reference to some modern experimental subjects such as lasers, spectroscopy, and superconductivity. It is our hope that, with this approach, even the student new to the subject will be enabled to see the immediate relevance of statistical thermodynamics to a number of subjects, which he will quickly recognize as being of general scientific interest and importance. We also hope that this attempt to provide a more widely scientifically cultured approach than is usual in elementary books will offer some insight into the powerful and exciting pervasiveness of the ideas of entropy and energy levels in atomic and molecular systems. The book does not attempt to provide a comprehensive coverage of the subject and, in particular, we have thought it wise to exclude any account of the statistical mechanics of solutions and of polymers. Solutions are treated in other works in this series; any worthwhile discussion of polymers would have required a considerable expansion to do justice to their importance. In our view this would have been undesirable. Our preference for a compact book is also reflected in the choice and number of problems. Those we have put in are intended more to illustrate and extend the discussion in the text, and thereby to increase the student's 'feeling' for the subject, than to test his ability to do numerical calculations.

The first chapters provide a basic outline of the subject and illustrate the influence of quantum effects. These ideas are then applied to a number of subjects, in which we hope that the reader will share our interest. Finally, we have allowed ourselves to range outside the more conventional bounds of the subject into areas of human endeavour where the applicability of statistical ideas is not yet fully established—and perhaps never will be. This may be thought a trifle over-ambitious in an elementary book, but it is part of our second important aim in writing this book, which has been to stimulate interest; even where, in so doing, the discussion may offend the purist.

We wish to express our thanks to our colleagues in the Physical Chemistry Laboratory with whom we have had many discussions about the contents of this book. These discussions have always been stimulating, often controversial, and usually enlightening.

ROBERT GASSER
Oxford 1973 GRAHAM RICHARDS

Acknowledgements

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FIG. 5.3(a): H. Wise, *J. phys. Chem.*, **58**, 389 (1954). FIG. 5.3(b): R. N. Doescher, *J. chem. Physics*, **20**, 331 (1952). FIG. 5.4: R. F. Barrow and J. G. Stamper, *Trans. Faraday Soc.*, **54**, 1592 (1958). Appendices 1, 2, and 3: J. E. Mayer and M. G. Mayer, *Statistical mechanics*, Wiley, New York, 1940.

1A	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	O
$_{1}$H 1·008																	$_{2}$He 4·003
$_{3}$Li 6·941	$_{4}$Be 9·012											$_{5}$B 10·81	$_{6}$C 12·01	$_{7}$N 14·01	$_{8}$O 16·00	$_{9}$F 19·00	$_{10}$Ne 20·18
$_{11}$Na 22·99	$_{12}$Mg 24·31											$_{13}$Al 26·98	$_{14}$Si 28·09	$_{15}$P 30·97	$_{16}$S 32·06	$_{17}$Cl 35·45	$_{18}$Ar 39·95
$_{19}$K 39·10	$_{20}$Ca 40·08	$_{21}$Sc 44·96	$_{22}$Ti 47·90	$_{23}$V 50·94	$_{24}$Cr 52·00	$_{25}$Mn 54·94	$_{26}$Fe 55·85	$_{27}$Co 58·93	$_{28}$Ni 58·71	$_{29}$Cu 63·55	$_{30}$Zn 65·37	$_{31}$Ga 69·72	$_{32}$Ge 72·59	$_{33}$As 74·92	$_{34}$Se 78·96	$_{35}$Br 79·90	$_{36}$Kr 83·80
$_{37}$Rb 85·47	$_{38}$Sr 87·62	$_{39}$Y 88·91	$_{40}$Zr 91·22	$_{41}$Nb 92·91	$_{42}$Mo 95·94	$_{43}$Tc 98·91	$_{44}$Ru 101·1	$_{45}$Rh 102·9	$_{46}$Pd 106·4	$_{47}$Ag 107·9	$_{48}$Cd 112·4	$_{49}$In 114·8	$_{50}$Sn 118·7	$_{51}$Sb 121·8	$_{52}$Te 127·6	$_{53}$I 126·9	$_{54}$Xe 131·3
$_{55}$Cs 132·9	$_{56}$Ba 137·3	$_{57}$La 138·9	$_{72}$Hf 178·5	$_{73}$Ta 180·9	$_{74}$W 183·9	$_{75}$Re 186·2	$_{76}$Os 190·2	$_{77}$Ir 192·2	$_{78}$Pt 195·1	$_{79}$Au 197·0	$_{80}$Hg 200·6	$_{81}$Tl 204·4	$_{82}$Pb 207·2	$_{83}$Bi 209·0	$_{84}$Po (210)	$_{85}$At (210)	$_{86}$Rn (222)
$_{87}$Fr (223)	$_{88}$Ra 226·0	$_{89}$Ac (227)															

Lanthanides	$_{57}$La 138·9	$_{58}$Ce 140·1	$_{59}$Pr 140·9	$_{60}$Nd 144·2	$_{61}$Pm (147)	$_{62}$Sm 150·4	$_{63}$Eu 152·0	$_{64}$Gd 157·3	$_{65}$Tb 158·9	$_{66}$Dy 162·5	$_{67}$Ho 164·9	$_{68}$Er 167·3	$_{69}$Tm 168·9	$_{70}$Yb 173·0	$_{71}$Lu 175·0
Actinides	$_{89}$Ac (227)	$_{90}$Th 232·0	$_{91}$Pa 231·0	$_{92}$U 238·0	$_{93}$Np 237·0	$_{94}$Pu (242)	$_{95}$Am (243)	$_{96}$Cm (248)	$_{97}$Bk (247)	$_{98}$Cf (251)	$_{99}$Es (254)	$_{100}$Fm (253)	$_{101}$Md (256)	$_{102}$No (254)	$_{103}$Lw (257)

SI units

Physical quantity	*Old unit*	*Value in SI units*
energy	calorie (thermochemical)	4·184 J (joule)
	*electronvolt—eV	$1{\cdot}602 \times 10^{-19}$ J
	*electronvolt per molecule	96·48 kJ mol^{-1}
	erg	10^{-7} J
	*wave number—cm^{-1}	$1{\cdot}986 \times 10^{-23}$ J
entropy (S)	eu = cal g^{-1} $°\mathrm{C}^{-1}$	4184 J kg^{-1} K^{-1}
force	dyne	10^{-5} N (newton)
pressure (P)	atmosphere	$1{\cdot}013 \times 10^{5}$ Pa (pascal), or N m^{-2}
	torr = mmHg	133·3 Pa
dipole moment (μ)	debye—D	$3{\cdot}334 \times 10^{-30}$ C m
magnetic flux density (H)	*gauss—G	10^{-4} T (tesla)
frequency (ν)	cycle per second	1 Hz (hertz)
relative permittivity (ε)	dielectric constant	1
temperature (T)	*°C and °K	1 K (kelvin); 0 °C = 273·2 K

(* indicates permitted non-SI unit)

Multiples of the base units are illustrated by length

fraction	10^{9}	10^{6}	10^{3}	1	(10^{-2})	10^{-3}	10^{-6}	10^{-9}	(10^{-10})	10^{-12}
prefix	giga-	mega-	kilo-	metre	(centi-)	milli-	micro-	nano-	(*ångstrom)	pico-
unit	Gm	Mm	km	m	(cm)	mm	μm	nm	(*Å)	pm

The fundamental constants

Avogadro constant	L or N_A	$6{\cdot}022 \times 10^{23}$ mol^{-1}
Bohr magneton	μ_B	$9{\cdot}274 \times 10^{-24}$ J T^{-1}
Bohr radius	a_0	$5{\cdot}292 \times 10^{-11}$ m
Boltzmann constant	k	$1{\cdot}381 \times 10^{-23}$ J K^{-1}
charge of a proton (charge of an electron = $-e$)	e	$1{\cdot}602 \times 10^{-19}$ C
Faraday constant	F	$9{\cdot}649 \times 10^{4}$ C mol^{-1}
gas constant	R	8·314 J K^{-1} mol^{-1}
nuclear magneton	μ_N	$5{\cdot}051 \times 10^{-27}$ J T^{-1}
permeability of a vacuum	μ_0	$4\pi \times 10^{-7}$ H m^{-1} or N A^{-2}
permittivity of a vacuum	ε_0	$8{\cdot}854 \times 10^{-12}$ F m^{-1}
Planck constant	h	$6{\cdot}626 \times 10^{-34}$ J s
(Planck constant)/2π	$\hbar$	$1{\cdot}055 \times 10^{-34}$ J s
rest mass of electron	m_e	$9{\cdot}110 \times 10^{-31}$ kg
rest mass of proton	m_p	$1{\cdot}673 \times 10^{-27}$ kg
speed of light in a vacuum	c	$2{\cdot}998 \times 10^{8}$ m s^{-1}

$\ln 10 = 2{\cdot}303$ $\ln x = 2{\cdot}303 \lg x$ $\lg e = 0{\cdot}4343$ $\pi = 3{\cdot}142$

$R \ln 10 = 19{\cdot}14$ J K^{-1} mol^{-1} $RTF^{-1} \ln 10 = 59{\cdot}16$ mV at 298·2 K

Contents

1. The laws of thermodynamics

THERMODYNAMICS is a subject that seeks to interpret the properties of chemical systems. It is particularly concerned with systems at equilibrium and no attention is paid to the rate at which equilibrium is achieved: this latter subject is the province of reaction kinetics. So far it has been found that three laws of thermodynamics are necessary and sufficient. An understanding of the first two laws does not need an atomic theory of the nature of matter though the laws can be appreciated much better with such a theory. The third law can be comprehended properly only from a microscopic molecular viewpoint. Of these three laws, it is with the third that we shall be principally concerned. But, because of the close inter-relation of all three, we start with a brief consideration of each.

The first law of thermodynamics

The First Law† is the well known energy-equivalence law. 'Energy cannot be created nor destroyed, only converted from one form to another'. The most useful algebraic formulation of this law for the chemist is

$$q = \Delta U - w,$$

where q is a quantity of heat supplied to the system, ΔU is the change in internal energy and w is any work done on the system by external forces.

Classical thermodynamicists felt no need of statistical pictures to explain this law nor to interpret the thermodynamic functions, q, U, and w. Nonetheless statistical concepts do aid our understanding. Particularly we think of the internal energy U as the sum of the energies of the components. To take the familiar case of a monatomic ideal gas: the internal energy is simply the sum of the kinetic energies of the component atoms. When an infinitesimal quantity of heat δq is supplied to an ideal gas there may be an increase in internal energy δU and work may be done by the gas if it is allowed to expand by a volume δV. Under normal laboratory conditions, where the external pressure is kept constant, the work done by the gas $(= -\delta w)$ is $P\delta V$. Thus

$$\delta q = \delta U + P\delta V$$

or, for a finite change from an initial state A to a final state B,

$$q_{\mathrm{B}} - q_{\mathrm{A}} = U_{\mathrm{B}} - U_{\mathrm{A}} + P(V_{\mathrm{B}} - V_{\mathrm{A}}) = (U_{\mathrm{B}} + PV_{\mathrm{B}}) - (U_{\mathrm{A}} + PV_{\mathrm{A}}).$$

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† For an introduction to the chemical consequences of the first law, see Smith, *Basic chemical thermodynamics* (OCS 8).

It is convenient to have a new thermodynamic function for $(U+PV)$, which is called the *enthalpy*, H. This function is appropriate when we are considering changes at constant pressure.

The second law of thermodynamics†

A traditional way of expressing the second law is in terms of heat engines. This seems a long way from the behaviour of molecules although mathematically the connection can be made quite readily. From a consideration of the properties of heat engines operating reversibly, it is possible to define a new thermodynamic function, the entropy, S, which is governed by the equation

$$\Delta S = \frac{q_{\text{reversible}}}{T}.$$

A readily measurable entropy change occurs when a pure substance changes phase. In this case $q_{\text{reversible}}$ and T are respectively the molar latent heat, L (e.g. of melting or boiling) and the temperature of the phase change. It has been observed that the entropy change on boiling (b) many non-associated organic liquids is approximately constant:

$$\Delta S_{\mathrm{b}} = \frac{L}{T_{\mathrm{b}}} \approx 86\ \mathrm{J\ K^{-1}\ mol^{-1}}.$$

This value of ΔS_{b} is often called Trouton's constant.

Hereafter we shall omit the subscript 'reversible'; all changes are assumed to be carried out reversibly. For molecular problems the clearest statement of the second law is *When left to themselves systems tend to alter in such a way that the entropy of the system increases.* The understanding of this statement is helped by an understanding of the concept of entropy. Statistically, entropy is thought of as a measure of the chaos or disorder of the system or even, less exactly, as the 'ignorance' about a situation. This latter rather qualitative statement will be returned to at the very end of this book, whilst in Chapter 3 a firm analytical definition of 'disorder' will be given. Even in an undefined way the idea that entropy, as measured by disorder, tends to increase spontaneously is in accord with everyday experience and enables us to rationalize directions of change.

The position of a chemical equilibrium is governed by two factors. While the energy tends to reach a minimum the entropy tends to reach a maximum. The balance between these two, often opposing, factors is described by another thermodynamic function, free energy. Depending on whether the system is

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† See Smith (1973) for a discussion of entropy and its role in chemistry.

at constant volume or at constant pressure the free energies are defined as follows:

$A = U - TS$ Helmholtz free energy (constant volume)

$G = H - TS$ Gibbs free energy (constant pressure)

The second law, however, gives us no information about the absolute values of S, A, and G but only about *changes* in these quantities.

The third law of thermodynamics

The third law of thermodynamics is concerned with the behaviour of the absolute value of entropy as the absolute zero of temperature is approached. Although the first and second laws do not rely on statistical interpretations of the thermodynamic functions, a proper understanding of the third law is possible only if we provide a microscope molecular interpretation. Various formulations of this law have been used and we shall use the phraseology of Simon:

> 'The contribution to the entropy of a system by each aspect which is in internal thermodynamic equilibrium tends to zero at the absolute zero.'

Familiar examples of 'aspects' include the rotational and vibrational motions of molecules, the process of mixing, and the spatial disposition of the magnetic moments of unpaired electrons in paramagnetic compounds. The consequence of the third law is that the total entropy of a substance tends to zero at the lowest temperatures and thus that all these properties should achieve an ordered state as the absolute zero is approached. However, the third law gives no guidance about the mechanism by which the ordering is to be achieved. It is worthwhile comparing our definition of the third law with another familiar formulation:

> 'The entropy of a perfect crystalline solid tends to zero as the temperature tends to the absolute zero.'

A 'perfect crystalline solid' is thus the analogue of 'an aspect in internal thermodynamic equilibrium'.

In making an experimental confirmation of the third law one often measures the heat capacity and calculates the entropy of a substance from as low a temperature as possible up to room temperature, and then compares the result with the entropy calculated from the formulae of statistical thermodynamics. In many cases there is excellent agreement between theory and experiment and there are good grounds for believing that the third law is as valid as the first and second laws. Also interesting are those few cases in which there are discrepancies between theory and experiment. These discrepancies are always in the direction of the system having more entropy than measurements based on the third law appear to indicate. Such discrepancies suggest that even at the lowest temperatures the sample retains some disorder; i.e., for at least one aspect of the system the entropy has not vanished. The reason for a non-vanishing entropy is that the aspect with which the entropy is associated has not maintained its true internal thermodynamic equilibrium. This failure to maintain equilibrium need not surprise us, since it is commonplace in everyday life; mixtures of reactive chemicals whose equilibrium composition overwhelmingly favours products which are produced in a strongly exothermic reaction frequently fail to react (fortunately for the motorist) in the absence of an external agent. Similarly when an aspect of a system has reached a low enough temperature for its entropy to tend to zero there may be no kinetic pathway of sufficiently low energy available. For example, the two isotopes of chlorine that go to make up sodium chloride crystal have an entropy of mixing that should disappear at low temperatures. However, this ordering process would require the movement of chloride ions through the lattice, which is impossibly slow at low temperatures, and so the entropy remains. Anomalies in absolute entropies are often associated with the difficulty a constituent of a solid may have in undertaking molecular motion at low temperatures. However it is necessary to consider each particular example of an anomaly separately in order to identify in detail the origin of the residual entropy. We shall discuss this subject in more detail in Chapter 9.

Some useful results from classical thermodynamics

Having summarized the laws of thermodynamics we now give an even briefer résumé of the results of classical thermodynamics. These are quite simply obtained starting with the first two laws and the definitions of U, H, S, A, and G. Full details may be found in Smith (1973).

Two *heat capacities* are commonly defined. These are the heat capacity at constant volume (C_V) and the heat capacity at constant pressure (C_P):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \text{ and } C_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

For closed systems the following set of equations expresses the changes in the thermodynamic functions when the only work that can be done is PV work:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$$