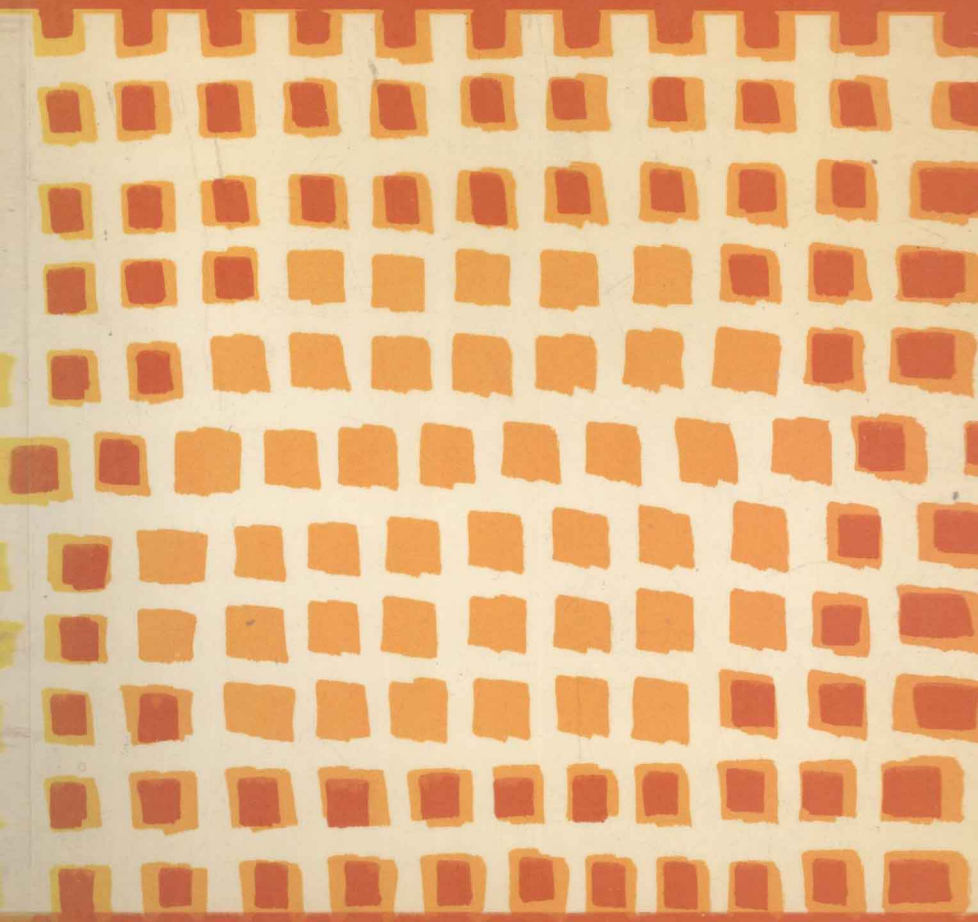


KENNETH DENBIGH

The Principles of Chemical Equilibrium

THIRD EDITION



CAMBRIDGE UNIVERSITY PRESS

THE PRINCIPLES OF CHEMICAL EQUILIBRIUM

WITH APPLICATIONS IN CHEMISTRY
AND CHEMICAL ENGINEERING

BY

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PREFACE TO THE FIRST EDITION

My aim has been to write a book on the general theory of chemical equilibrium, including its statistical development, and displaying its numerous practical applications, in the laboratory and industry, by means of problems. It is hoped that the book may be equally useful to students in their final years of either a chemistry or a chemical engineering degree.

Thermodynamics is a subject which needs to be studied not once but several times over at advancing levels. In the first round, usually taken in the first or second year of the degree, a good deal of attention is given to calorimetry, before going forward to the second law. In the second or third rounds—such as I am concerned with in this book—it is assumed that the student is already very familiar with the concepts of temperature and heat, but it is useful once again to go over the basis of the first and second laws, this time in a more logical sequence.

The student's confidence, and his ability to apply thermodynamics in novel situations, can be greatly developed if he works a considerable number of problems which are both theoretical and numerical in character. Thermodynamics is a quantitative subject and it can be mastered, not by the memorizing of proofs, but only by detailed and quantitative application to specific problems. The student is therefore advised not to aim at committing anything to memory. The *three or four* basic equations which embody the 'laws', together with a few defining relations, soon become familiar, and all the remainder can be obtained from these as required.

The problems at the end of each chapter have been graded from the very easy to those to which the student may need to return several times before the method of solution occurs to him. At the end of the book some notes are given on the more difficult problems, together with numerical answers.

Questions marked C.U.C.E. are from the qualifying and final examinations for the Cambridge University Chemical Engineering degree, and publication is by permission. The symbols which occur in these questions are not always quite the same as in the text, but their meaning is made clear.

In order to keep the size of the book within bounds, the thermodynamics of interfaces has not been included. The discussion of galvanic cells and the activity coefficients of electrolytes is also rather brief.

Part I contains the basis of thermodynamics developed on traditional lines, involving the Carnot cycle. Part II contains the main development in the field of chemical equilibria, and the methods adopted here have been much influenced by Guggenheim's books, to which I am greatly indebted. Part III contains a short introduction to statistical mechanics along the lines of the Gibbs ensemble and the methods used by R. C. Tolman in his *Principles of Statistical Mechanics*.

It is a great pleasure to acknowledge my gratitude to a number of friends. In particular, my best thanks are due to Dr Peter Gray, Professor N. R. Amundson, Dr J. F. Davidson and Dr R. G. H. Watson, for helpful criticism and suggestions, and to Professor T. R. C. Fox, for stimulating and friendly discussions on thermodynamics over several years. Finally I wish to express my appreciation of the good work of the Cambridge University Press, and my thanks to Messrs Jonathan and Philip Denbigh, for help with the proof correcting, and to my wife for help in many other ways.

K. G. D.

CAMBRIDGE

October 1954

PREFACE TO THE THIRD EDITION

Since this book first appeared a number of correspondents have sent very helpful comments. I am particularly indebted to Professor Peter Gray, Professor E. A. Guggenheim and Professor J. S. Rowlinson, most of whose suggested improvements have been incorporated in the text.

The revision for the third edition has included the following:

- (1) Complete adoption of the notation recommended in the 1969 I.U.P.A.C. publication *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (Butterworths, 1970). This has involved thousands of small changes in the text; if readers find symbols which have escaped alteration, or any other sorts of error, I should be most grateful if they would kindly let me know.
- (2) Adoption of the I.U.P.A.C. recommendation that work should be counted as positive when done *on* the system of interest. This is a rational proposal in so far as it gives work the same sign as an increment of internal energy, but it does have the unfortunate effect of making the important notion of *maximum work* rather less easy to explain. This will be seen from equations such as (2.16) of the new edition where I have felt obliged to use a double negative in order to make the meaning clear.

- (3) Partial adoption of the SI units†. Most of the examples concerning physical processes have been converted to kg, m, J, Pa, etc., but not the examples of Chapters 4 and 10. In these I have retained the use of the calorie ($= 4.184 \text{ J}$) for enthalpies and free energies of reaction and C_p power series, because this is the unit in which the only extensive compilations of these quantities are at present available. For the same reason I have continued in places using the atmosphere as a unit of pressure ($1 \text{ atm} = 101.325 \text{ kPa} = 101\,325 \text{ Nm}^{-2}$). Indeed the atmosphere will be difficult to displace for as long as 1 atm pressure continues to be used as a standard state. Otherwise a tiresome numerical factor must be introduced into the equation $\Delta G_T^0 = -RT \ln K_p$.

The present edition is thus not a 'completely SI edition'. I hope nevertheless that it will provide students of chemistry and chemical engineering with many exercises in the use of SI and that they will thereby be in a better position to adopt the system fully as soon as the necessary compilations of basic data become available.

Additional changes to the text are the inclusion of ξ , the extent of reaction, certain improvements in the presentation of reaction equilibrium and the correction of a false impression concerning ergodicity in Chapter 11.

September 1970

K. G. D.

NOTE ON THE 1978 REPRINTING

I am greatly indebted to various correspondents who have so kindly taken the trouble to inform me about errors and misprints. Professor Thomas W. Weber gave me a list of forty items and several other correspondents have also contributed very helpfully to the improved accuracy of this reprinting.

December 1977

K. G. D.

† SI units are briefly described on p. xxi.

LIST OF SYMBOLS

		Definition	
		Equation	Page
a_i	Activity of i th species	—	287
A	Helmholtz free energy of a system	2·1	63
c_i	Molarity of i th species	9·11	275
C	Compressibility factor of a gas	3·51	124
C	Number of independent components of a system	—	171, 184, 187
c_p	Molar heat capacity at constant pressure	2·87	96
C_p	Heat capacity of system at constant pressure	2·86	95
c_V	Molar heat capacity at constant volume	2·87	96
C	Heat capacity of system at constant volume	2·86	95
e	Symbol for an electron	—	—
E	Any extensive property of a system	—	8
E	Electromotive force	—	75, 164
E	Total energy of a system	—	17
E_i	Energy of the i th quantum state of a macroscopic system	—	342
f	Fugacity	3·45 and 3·56	122, 125
f	Molecular partition function	12·9	364
F	The Faraday	—	75
F	Degrees of freedom of system	—	185
G	Gibbs free energy of system	2·3	63
$\Delta_f G_T^0$	Standard free energy of formation from the elements at temperature T	—	148
ΔG_T^0	Standard free energy change in reaction at temperature T	4·17	142
G^E	Excess free energy	—	285
h	Planck constant	—	—
h	Enthalpy per mole of a pure substance	—	100
H	Enthalpy of system	2·1	63

		Definition	
		Equation	Page
H_i	Partial molar enthalpy of i th species	2.104	101
$\Delta_f H_T$	Standard enthalpy of formation at temperature T	—	149
ΔH^0	Enthalpy change in reaction under conditions where the species obey the perfect gas laws or the ideal solution laws	4.22	144, 300
ΔH_0	An integration constant having the dimensions of an enthalpy change	4.26	145
k	Velocity constant of reaction	—	441
k	Boltzmann constant	—	345, 378
K	An equilibrium constant	4.12, 10.4 and 10.7	141, 293
K_f	Equilibrium constant expressed in fugacities	4.16	142
K_p	Equilibrium constant expressed in partial pressures	4.12	141
K'_p	Partial equilibrium constant	4.50	157, 159
K_i	Henry's law coefficient for i th species	8.17 and 9.5	250, 271
L	Enthalpy ('latent heat') of phase change	2.94 and 6.7	98, 198
m_i	Molality of i th species	9.7	274
M_i	Chemical symbol of i th species	—	—
n_i	Amount (mols) of i th species in system	—	—
N_i	Number of molecules of i th species in system	—	—
L	The Avogadro constant	—	378
N	Number of species in system	—	187
p_i	Partial pressure of i th species	3.20	115
p_i^*	Vapour pressure of pure i th species	—	223
p	Total pressure on system	—	—
P	Number of phases in system	—	184
P_i	A probability	—	340
q	Heat taken in by system	—	18
Q	Partition function of closed system at constant temperature and volume	11.12	345
R	Number of independent reactions in system	—	169
R	Gas constant	—	111

		Definition	
		Equation	Page
s	Entropy per mole of pure substance	2.99	98
S	Entropy of system	1.13	32
S_i	Partial molar entropy of i th species	2.104	99
S'	$S' \equiv -k \sum P_i \ln P_i$	11.14	343
S''	$S'' \equiv k \ln \Omega$	11.15	343
T	Temperature on thermodynamic scale	1.12	31
u	Internal energy per mole of pure substance	2.99	98
U	Internal energy of system	—	17
U_i	Partial molar internal energy of i th species	2.104	99
v	Volume per mole of pure substance	2.99	98
V	Volume of system	—	—
V_i	Partial molar volume of i th species	2.104	99
w	Work done on system	—	14
w'	Work done on system, not including that part which is due to volume change	—	66
w_{ij}	Potential energy of a pair of molecules of types i and j	—	243, 430
x_i	Mole fraction of i th species in condensed phase	—	—
y_i	Mole fraction of i th species in vapour phase	—	—
z_+, z_-	Charges of positive and negative ions respectively in units of the proton charge	—	73, 163, 300
α	Coefficient of thermal expansivity	2.88	94
β	A statistical parameter	11.10	342
γ_i	Activity coefficient of i th species	9.2, 9.3 and 9.16	269, 274
γ	Surface tension	—	—
Δ	Sign indicating excess of final over initial value	—	—
ϵ_i	Energy of the i th quantum state of a molecule	—	—
θ	Temperature on any scale	—	11
κ	Compressibility coefficient	2.89	94
μ_i	Chemical potential of i th species	2.39 and 2.41	76, 77
μ_i^0	Gibbs free energy per mole of pure substance at unit pressure and at the same temperature as that of the mixture under discussion	—	Ch. 3

		Definition	
		Equation	Page
μ_i^*	Gibbs free energy per mole of pure substance at the same temperature and pressure as that of mixture under discussion	—	Chs. 8 and 9
μ_i^\square	Chemical potential of i th species in a hypothetical ideal solution of unit molality at the same temperature and pressure as solution under discussion	—	276
μ	Joule-Thomson coefficient	3.42	120
ν_i	Stoichiometric coefficient for i th species in a reaction	—	134
ν_+, ν_-	Numbers of positive and negative ions respectively formed on dissociation of one molecule of electrolyte	—	302
ν	$\nu \equiv \nu_+ + \nu_-$	10.34	305
ξ	Extent of reaction	4.2	135
Π	Continued product operator sign	—	141
Π	Osmotic pressure	8.54	263
ρ	Density	—	—
σ	Created entropy	1.15	39
Σ	Summation operator sign	—	—
ϕ	Potential energy	—	17, 87
χ_i	Fugacity coefficient of i th species	3.54	125
ω_i	Degeneracy of the i th molecular energy level	—	361, 367
Ω	Number of accessible quantum states of a macroscopic system of constant energy and volume	—	335, 338
Ω_i	Ditto as applied to the particular energy state E_i	—	353, 367
\approx	Denotes an approximate equality	—	—
\doteq	Denotes a very close approximation	—	—
\equiv	Used where it is desired to emphasize that the relation is an identity, or a definition.	—	—

VALUES OF PHYSICAL CONSTANTS

Ice-point temperature	$T_{ice} = 273.15 \text{ K}$
Boltzmann constant	$k = 1.380\,54 \times 10^{-23} \text{ J K}^{-1}$
Planck constant	$h = 6.625\,6 \times 10^{-34} \text{ J s}$
Avogadro constant	$L = 6.022\,52 \times 10^{23} \text{ mol}^{-1}$
Faraday constant	$F = 96\,487 \text{ C mol}^{-1}$
Charge of proton	$e = 1.602\,10 \times 10^{-19} \text{ C}$
Gas constant	$R = 8.314\,3 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 1.987\,2 \text{ cal K}^{-1} \text{ mol}^{-1}$ $= 82.06 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

THE SI UNITS

The basic SI units are the metre (m), kilogramme (kg), second (s), kelvin (K; *not* °K), mole (mol), ampere (A) and candela (cd). The mole is the unit of 'amount of substance' and is defined as that amount of substance which contains as many elementary entities as there are atoms in 0.012 kg of carbon-12. It is thus precisely the same amount of substance as, in the c.g.s. system, had been called the 'gramme-molecule'. Some of the SI derived units which are important in the present volume, together with their symbols, are as follows:

for energy . . . the joule (J);	$\text{kg m}^2 \text{ s}^{-2}$
for force . . . the newton (N);	$\text{kg m s}^{-2} = \text{J m}^{-1}$
for pressure . . . the pascal (Pa);	$\text{kg m}^{-1} \text{ s}^{-2} = \text{N m}^{-2}$
for electric charge . . . the coulomb (C);	A s
for electric potential difference . . . the volt (V);	$\text{kg m}^2 \text{ s}^{-3} \text{ A}^{-1} = \text{J A}^{-1} \text{ s}^{-1}$

In terms of SI units two 'old-style' units which are also used in this book are:

the thermochemical calorie (cal)	$= 4.184 \text{ J}$
the atmosphere (atm)	$= 101.325 \text{ kPa} = 101\,325 \text{ N m}^{-2}$

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