APPLIED PHYSICAL CHEMISTRY

A Macmillan Chemistry Text

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APPLIED PHYSICAL CHEMISTRY

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PREFACE

This is a textbook of physical chemistry theory and the application of that theory to everyday industrial situations. Thus, although much of the content is of an essentially conventional character, it is presented in a manner that is more relevant to the requirements of a chemist employed in the manufacturing industries. Detailed treatment is included of such topics as phase-separation processes and instrumental methods of analysis, which receive only superficial treatment in most physical chemistry texts, while some of the more academic topics, such as the theory of molecular structure, have been omitted. Thus the student of chemistry will become acquainted with the fundamentals of physical chemistry while also recognising its relevance in a practical situation, and the student of chemical engineering will be familiarised with the essential relationships between physical chemistry and unit processes in the chemical and allied industries. Accordingly, the text has been liberally illustrated with worked (mainly industrial) numerical examples. Lack of space has prohibited the inclusion of further problems, but many similar examples will be found in *Applied Physical Chemistry Problems*, McGraw-Hill, London, 1968 by A. C. K. Smith

The SI system of units has been adhered to as far as possible, but in order to achieve realism it has been found necessary to make use of such quantities as parts per million (p.p.m.), weight/weight per cent (w/w%) and the hour, which although not recommended in SI are nevertheless essential components of the language of the industrial chemist.

This book is designed to meet the needs of students of chemistry, applied chemistry and chemical engineering in universities, polytechnics and technical colleges, who are studying for qualifications ranging from H.N.C., H.N.D. and L.R.I.C. to C.N.A.A. and also B.Sc. degrees. In addition, chemistry graduates who are about to enter or are already in industry, will find this text an extremely useful reference book for many of the situations they may encounter.

The authors would like to thank their colleagues for the many lively and illuminating discussions that have helped in the preparation of this book.

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Middlesbrough,
1974

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GLOSSARY OF SYMBOLS

As far as possible, internationally recommended symbols have been used throughout¹. Given below is a list of the more important symbols used in this book, together with the name of the quantity to which each symbol refers. The number in parentheses denotes the chapter in which a symbol represents a given quantity; where no number is quoted, the symbol applies generally throughout the book. In a few cases the use of a symbol to represent two or more quite distinct quantities cannot be avoided, and where this occurs the exact meaning of a symbol is made clear in the associated text.

Symbol	Quantity
A	surface area absorbance (8) frequency factor in the Arrhenius equation (10)
a_B	activity of substance B
B	rotational constant of a molecule (8)
C	number of components (4)
C_V	heat capacity at constant volume
C_P	heat capacity at constant pressure
$C_{P,B}^*$	molar heat capacity of pure B at constant pressure
$C_{V,B}^*$	molar heat capacity of pure B at constant volume
ΔC_P	change in the value of C_P accompanying a reaction
CU	deviation from centre zero in a differential thermal analysis (D.T.A.) (4)
c_B	concentration of a substance B
c	order of reaction (10)
ca	complete arrest in a thermal analysis cooling curve (4)
c_0	velocity of light
$c^\ddagger$	concentration of activated complex (10)
d	total cake thickness in a filter unit (12)
E	total energy of a system emptying time for a filter unit (12) electromotive force (11)
E_i	energy of the i th energy state
E_p	potential energy
$E^\ominus$	standard e.m.f. (11)
E_x	electrode potential of electrode x (11)
$E_x^\ominus$	standard electrode potential of electrode x (11)
E_{rest}	rest potential (11)
E_{corr}	corrosion potential (11)
$E_{\frac{1}{2}}$	halfwave potential (11)
$E^\ddagger$	activation energy

F	Faraday constant (11)
	moles of feed to a distillation column (5)
	number of degrees of freedom
F'	number of degrees of freedom in a limited phase system (4)
f	frequency of rotation of a drum filter (12)
f_B	fugacity or activity coefficient of substance B
f_B^*	fugacity of pure substance B
G	free energy
	conductance (11)
G_B^*	molar free energy of pure substance B
G^s	surface free energy
ΔG	change in free energy
$\Delta G^\ominus$	standard change in free energy
$\Delta_f G^\ominus$	standard free energy of formation
ΔG^s	change in free energy associated with the formation of a crystal nucleus (7)
ΔG_v	free-energy change associated with the appearance of a new phase (7)
$\Delta G^\ddagger$	free energy of activation
g	acceleration due to gravity
g_i	statistical weight of the i th energy state
H	enthalpy
	magnetic field strength (8)
H_B^*	molar enthalpy of pure substance B
H_B	partial molar enthalpy of substance B
ΔH	change in enthalpy
ΔH_v	molar enthalpy of vaporisation
$\Delta H^\ominus$	standard enthalpy change
$\Delta_f H^\ominus$	standard enthalpy of formation
h	Planck constant
I	transmitted or emitted radiant intensity (8)
	moment of inertia of a molecule (8)
	nuclear spin quantum number (8)
	ionic strength of a solution (11)
	current (11)
I_0	incident radiant intensity (8)
I_l	limiting current (11)
J	rotational quantum number (8)
	rate of formation of free radicals (10)
j	crystal shape factor (7)
	current density (11)
j_0	exchange current density (11)
j_l	limiting current density (11)
j_{corr}	corrosion current density (11)
K	equilibrium constant
	distribution coefficient (4)
	permeability coefficient (12)
K_c	concentration equilibrium constant
K_p	pressure equilibrium constant
K_x	mole fraction equilibrium constant
K_f	fugacity equilibrium constant

K_w	ionisation constant for water
K_a	ionisation constant of an acid
K_b	ionisation constant of a base
K_h	hydrolysis constant (11)
K_{In}	indicator ionisation constant (11)
K_s	stability constant for a complex ion
$K^\ddagger$	equilibrium constant for the formation of activated complex
k	Boltzmann constant
	rate constant for crystallisation (7)
	specific absorption coefficient (8)
	force constant of a molecule (8)
k_r	rate constant of a chemical reaction (10)
k_{-1}	rate constant of a reverse reaction (10)
L	Avogadro constant
l	mean free path (1)
	cell path length (8)
M	molar mass or relative molecular mass
m	mass of a particle
	particle size range function (12)
m_B	molality of substance B
m_N	nuclear magneton (8)
N	number of particles
	number of equilibrium stages in an extraction (6)
	number of substances (9)
n	number of moles
	principal quantum number (8)
	overall order of reaction (10)
nc	normal cooling in a thermal analysis cooling curve (4)
n_B	number of moles of substance B
O	moles of condensate returned to a distillation column (5)
P	pressure of a system
	number of phases
	moles of product from a distillation column (5)
	number of theoretical plates in column chromatography (12)
P'	number of phases in a condensed system (4)
P_R	reduced pressure of a gas
P_c	critical pressure of a gas
p	momentum (8)
p_B^*	vapour pressure of pure substance B
p_B	partial pressure of component B
pa	partial arrest in a thermal-analysis cooling curve (4)
$p^\ominus$	standard atmospheric pressure
$p.p.m.$	parts per million
Q	the relative heat-content condition of a distillation feed ($= Q_f/\Delta H_v$) (5)
	solvent-to-solid control parameter in an extraction (6)
	electrostatic charge (1)
Q_f	heat required to convert one mole of distillation feed to vapour at its boiling point (5)
Q_v	rate of evaporation in a molecular distillation (5)
q	heat absorbed

	volume of solid per unit volume of filtrate (12)
q_V	heat absorbed at constant volume
q_P	heat absorbed at constant pressure
q_{rev}	heat absorbed in a reversible process
q_{irrev}	heat absorbed in an irreversible process
q_B	partition function of substance B (9)
q_t	translational partition function (9)
q_v	vibrational partition function (9)
q_r	rotational partition function (9)
R	gas constant
	reflux ratio (5)
	distribution constant in a leaching process (6)
	number of independent reactions (9)
	electrical resistance (11)
	filter medium resistance (12)
R_f	ratio of the distance moved by a species to that moved by the mobile phase in chromatographic separation (12)
R_M	a polarity parameter in chromatography (12)
R_X	ratio of the distance moved by a species to that moved by a reference species in chromatographic separation (12)
r	particle radius (12)
r_{cr}	critical nucleus size (7)
S	entropy
	mass of pure solvent in an extraction (6)
	output rate from a filter unit (12)
S_B^*	molar entropy of pure substance B
S_B	partial molar entropy of substance B
ΔS	change in entropy
$\Delta S^\ominus$	standard entropy change
ST	start of a straight line portion in a D.T.A. curve (4)
s	filter cake compressibility function (12)
s_B	solubility of substance B
T	temperature
T_R	reduced temperature of a gas
T_c	critical temperature of a gas
T_b	normal boiling point of a liquid (4)
t	time
$t_{\frac{1}{2}}$	half-period of a reaction (10)
U	thermodynamic energy
U_B^*	molar thermodynamic energy of pure substance B
U_B	partial molar thermodynamic energy of substance B
u	effective flow rate through a reactor (10)
$\langle u \rangle$	mean velocity of a particle
$\langle u^2 \rangle$	mean square velocity of a particle
V	volume
	moles of vapour leaving a distillation column (5)
V_r	effective volume of a reactor (10)
V_c	critical volume of a gas
V_R	reduced volume of a gas
V_B^*	molar volume of pure substance B

V_B	partial molar volume of substance B
v	vibrational quantum number (8)
v^I	volume of solvent I (4)
W	probability (3) moles of waste from a distillation boiler (5) mass of pure dry inert solid in an extraction (6)
w	work done on a system
X_B	composition parameter of substance B
x	distance (12) mass of adsorbate adsorbed by unit mass of adsorbent (12)
x_B	mole fraction of substance B in liquid phase
x_i	liquid coordinate of the point of intersection of the operating line in a McCabe and Thiele diagram (5)
x_m	mass of adsorbate required to form a complete monolayer on the surface of unit mass of adsorbent (12)
y_B	mole fraction of substance B in the vapour phase activity coefficient of substance B
y_i	vapour coordinate of the point of intersection of the operating line in a McCabe and Thiele diagram (5)
$y_{\pm}$	mean activity coefficient of an electrolyte
Z	collision number
z	compressibility of a gas (1) number of faradays passed during an electrochemical reaction (11)
z_i	charge number of the i th ion (11)
α	exponential function in the Margules equation (4.7) efficiency factor in a molecular distillation (5) absolute degree of supersaturation (7) degree of ionisation (11) transfer coefficient (11) specific cake resistance (12)
β	relative supersaturation (7)
Γ_B	surface excess of substance B (12)
γ	surface or interfacial tension coefficient of supersaturation (7) kinetic chain length of a polymer (10)
γ_B	activity coefficient of substance B fugacity coefficient of substance B
δ	chemical shift with respect to that of the tetramethyl silane protons, which is given the value 0
δ	filter-cake thickness (12)
ϵ	molar absorption coefficient
ξ	electrokinetic potential (12)
η	viscosity overpotential (11)
θ	angle (12) fraction of adsorbent surface covered by adsorbate (12)
κ	conductivity (11)
Λ	molar conductivity (11)
Λ_0	molar conductivity at zero concentration (11)
Λ_i	molar ion conductivity of the i th ion (11)

XX GLOSSARY OF SYMBOLS

λ	wavelength
μ	dipole moment (1)
	reduced mass of a molecule (8)
μ_B	chemical potential of a substance B
$\mu_B^\ominus$	standard chemical potential of substance B
μ_B^s	chemical potential of a finely divided solid B (7)
ν_B	stoichiometric coefficient for substance B taking part in a chemical reaction
ν	frequency
$\bar{\nu}$	wavenumber
ξ	extent of reaction
π	surface pressure (12)
ρ	density
σ	collision diameter
σ_B	area occupied by one molecule of substance B in a surface (12)
τ	chemical shift with respect to that of the tetramethyl silane proton, which is given the value of 10
ψ	wave function (8)
	electrostatic potential (11)
ω	frequency of a molecular vibration (8)
$\bar{\omega}$	wavenumber of a molecular vibration (8)