PHYSICAL CHEMISTRY

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ИЗДАТЕЛЬСТВО МИР

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КУРС ФИЗИЧЕСКОЙ ХИМИИ

ТОМ I

ИЗДАТЕЛЬСТВО
«ХИМИЯ»
МОСКВА

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PHYSICAL CHEMISTRY

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VOLUME 1

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This book is the first volume of a university course in *physical chemistry*, and deals with the fundamentals of chemical thermodynamics, thermodynamics of solutions, chemical and heterogeneous equilibria, and surface phenomena and adsorption.

It is intended for students of chemical faculties of universities, and will also be found useful by postgraduate students and teachers of physical chemistry.

На английском языке

CONTENTS

LIST OF TABLES

SYMBOLS[1]

A	atomic mass; Helmholtz energy
A (A_s)[2]	area
a	activity; amount of adsorbate
B	second virial coefficient; volume effect
b	constant
C	heat value of calorimeter; molar heat capacity; third virial coefficient
c	concentration; heat capacity; number of microstates; velocity of light
D	coefficient of molecular diffusion; Debye function; diameter; fourth virial coefficient; quantity reflecting energy of interaction of solution components
d	density; diameter
E	ebullioscopic constant; electromotive force (emf); electrostatic field intensity; energy; modulus of elasticity
e	base of natural logarithms; charge of electron
F	Faraday constant
f	activity coefficient, molar-volume concentration basis; correction factor; degree of freedom; force of interaction; fugacity
G	Gibbs energy; weight
g	entropy factor; statistical weight of an energy level
H	enthalpy; height equivalent to one theoretical plate; modulus of hardness
h	heat of isothermal pressure increase; Planck constant
I	current intensity; intramolecular energy; moment of inertia
i	conventional chemical constant

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[1] In the English translation of this book the recommendations contained in the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* adopted by the IUPAC Council at Cortina d'Ampezzo, Italy, on July 7, 1969 (see *Pure and Applied Chemistry*, Vol. 21, No. 1, 1970) have been used wherever possible.—*Translator's note.*

[2] The symbol A_s is used when necessary to avoid confusion with the symbol A for Helmholtz energy.

J	mechanical equivalent of heat; quantum number of rotation
j	true chemical constant
K	cryoscopic constant; dissociation constant; equilibrium constant; hydrolysis constant; partition coefficient; quantum number
k	Boltzmann constant; Henry's coefficient; principal curvature; number of phases; separation factor
L	heat of transformation
l	heat of isothermal expansion; length
M	molecular mass
m	mass of adsorbent; mass of electron; molality
N	number of kilomoles; number of molecules
N_A	Avogadro constant
n	number of components; number of moles
P	degree of polymerization; mass per cent; probability
PE	Planck-Einstein function
p	momentum; pressure
Q	electric charge; heat; partition function
q	electric charge; solubility
R	gas constant; relative rate of movement of a component
r	mole ratio; radius
S	entropy
T	absolute temperature
t	temperature, °C; thickness; time
U	internal energy
u	velocity
V	volume
v	specific volume
W	mass function; work
w	mass of component; volume of part of adsorption space in pores of adsorbent; volume rate of flow
x	mole fraction
y	mole fraction of component in saturated vapour; relative unit of concentration
z	coordination number of lattice; distance; number of gramme-equivalents; number of particles per cubic centimetre; valence of an ion
α (alpha)	amount of adsorbate; cubic expansion coefficient; degree of dissociation; gas solubility coefficient; polarizability of a particle, temperature coefficient of electric resistance; volume correction for real gas
β (beta)	affinity coefficient; degree of transformation; gas absorption coefficient; pressure coefficient; refrigerating factor; relative unit of gas volume
Γ (gamma)	Gibbs adsorption

γ	activity coefficient; coefficient of volume expansion; ratio between heat capacities at constant pressure and constant volume
Δ (delta)	change in a function; distance; half-width of chromatographic zone
δ	increment; proportionality factor
ε (epsilon)	adsorption potential; constant; energy of interaction of molecules; surface energy; thermoelectromotive force
η (eta)	efficiency; viscosity
Θ (theta)	characteristic quantity of vibration; Debye's characteristic temperature
θ	angle; fractional coverage (fraction of surface covered by adsorbed molecules); temperature
ϰ (kappa)	conductivity; isothermal compressibility
λ (lambda)	heat of transformation; proportionality factor; thermal conductivity
μ (mu)	chemical potential; Joule-Thomson coefficient; number of primary elementary reactions; permanent dipole moment; reduced mass of molecule
ν (nu)	frequency; stoichiometric coefficient
ξ (xi)	extent of reaction
Π (pi)	osmotic pressure; product
π	ratio of circumference to diameter of circle, 3.14159; reduced pressure; surface pressure
ρ (rho)	density; main radius of curvature; mass concentration of substance; resistivity (also ρ_e)
Σ (sigma)	sum
σ	electric conductivity; ratio; surface tension; symmetry number of molecule
τ (tau)	reduced temperature; time
Φ (phi)	adsorption potential; potential energy; reduced isobaric potential; thermal flux
φ	osmotic coefficient; electric potential; volume fraction
χ (chi)	caloric coefficient; magnetic susceptibility
ω (omega)	area occupied by molecule of adsorbate; wave number

The superscript °(for example $S°$) on a thermodynamic function means that the substance is in its standard state.

The Greek letter Δ in front of a thermodynamic function (for example ΔG) means that the change (final minus initial) is referred to.

PREFACE

The present textbook is the first volume of a two-volume course prepared by a group of lecturers from the physical chemistry department of the chemical faculty of the Lomonosov State University (Moscow).

The first volume includes thermodynamics and its applications. The chapters devoted to the fundamentals of thermodynamics, thermodynamics of solutions and chemical thermodynamics have been written by Ya. I. Gerasimov, the part *Heterogeneous Phase Equilibria* by V. P. Dreving, the part *Surface Phenomena and Adsorption* and the chapter on *Gas Chromatography* by A. V. Kiselev.

The second volume covers chemical kinetics, catalysis and electrochemistry.

The course does not consider the structure of matter, since chemical faculties have separate courses in the *Structure of Molecules* and *Crystallochemistry*.

The authors acknowledge the fact that the complete volume of the proposed course exceeds the syllabus of a university general course in physical chemistry, but they presume that their work can be of assistance to university students in studying this subject.

The size of the book is due mainly to the fact that the authors did everything possible to set out the fundamentals and their mutual relationship as understandable as possible. The mathematical deductions are given in sufficient detail, and in a simple manner. The authors presume that the book will be understood by readers who are studying physical chemistry for the first time and have a knowledge of mathematics and physics within the scope of the usual courses in these subjects adhered to by chemical faculties.

The sections of the book designated by asterisks may be omitted when studying physical chemistry according to a required syllabus. This additional material, which is set out in the same comprehensible manner as the main part of the course, can be used for a more detailed study of the subject.

The chapter on *Gas Chromatography* has been written with account taken of the requests of students specializing in gas chromatography at chemical faculties of the Moscow State University and certain other universities. The text of this part is closely related to the contents of the preceding parts of the book devoted to solutions and adsorption, and as regards the nature of its exposition is an introduction into the given field understandable for those readers who have acquainted themselves with a number of chapters of this volume. This is why only the thermodynamic aspects of gas chromatography are mainly set out here. This part contains a quite considerable volume of material, but the authors, taking into account the great and growing significance of gas chromatography for many problems of chemistry and chemical technology, have included this part as a supplement to their course in *Physical Chemistry*.

Great assistance was rendered to the authors in preparing this course by many fellow workers and specialists from other educational and scientific institutions. The authors are grateful for the help rendered by V. Baibuz, I. Gibalo, Prof. M. Karapetyants, the late Prof. K. Khomyakov, Prof. V. Kireev, Prof. P. Kozlov, V. Medvedev, R. Petrova, Prof. O. Poltorak, Prof. V. Semenchenko, Prof. M. Shakhparonov, Prof. K. Shcherbakova, the late Prof. S. Skuratov, who read separate parts or chapters of the manuscript of the first volume and made valuable remarks that helped to improve the book.

The authors are greatly obliged to the reviewers of the book—the collective of the chair of physical chemistry of the Leningrad State University headed by member of the USSR Academy of Sciences Prof. B. P. Nikolsky, and to the late Prof. V. A. Shushunov for their attentive critical analysis.

The authors will be grateful to all their readers who inform them of any discovered shortcomings and omissions.