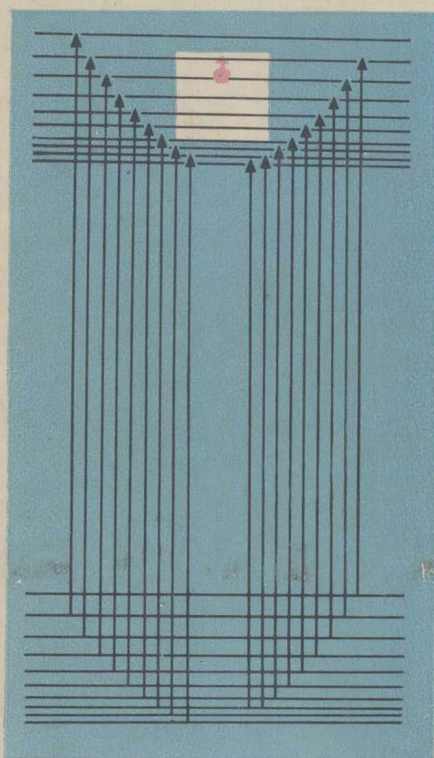


Problems  
and Exercises in  
**Physical  
Chemistry**

E.V. Kiselyova, G.S. Karetnikov,  
and I.V. Kudryashov



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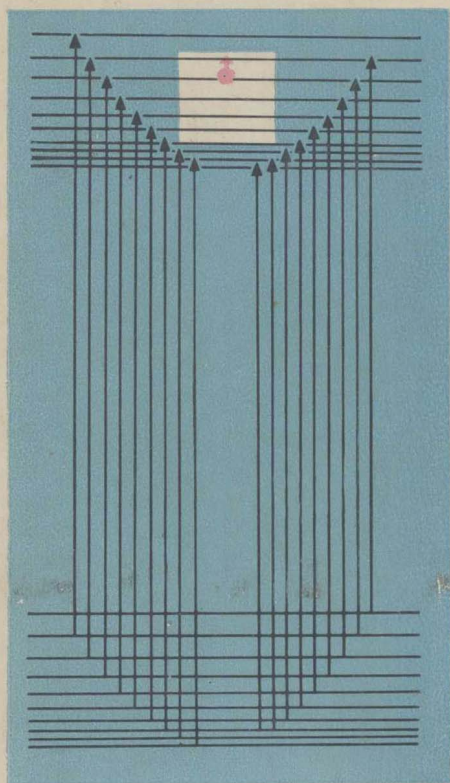
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E.V. Kiselyova, G.S. Karetnikov,  
and I.V. Kudryashov

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Mir Publishers  
Moscow

Translated from the Russian  
by  
V. G. VOPYAN

First published 1987  
Revised from the 1983 Russian edition

~~На~~ *английском языке*

Printed in the Union of Soviet Socialist Republics

© Издательство «Высшая школа», 1983  
© English translation, Mir Publishers, 1987

## Foreword

Chemical engineers and technologists (process engineers) must not only know the laws of physical chemistry, but also be able to use them judiciously in solving the problems in a particular field of their work. Solution of problems helps better assimilate the theory and contributes to its deeper understanding. The authors have tried to select problems covering virtually every aspect of the course in physical chemistry and pertaining to different chemical specialties.

To make sure that the student learns how to use reference books, the authors have excluded the values that can be found in readily available handbooks from most problems presented here. This book is divided into three parts: "Basic Theory of Physical-Chemistry Calculations", "Equilibrium State of Systems", and "Kinetics and Catalysis". Each chapter begins with the fundamental equations and symbols which are followed by problems with solutions, problems to be solved independently, and multivariant problems. Answers to the problems in the second category are provided at the end of the book. The multivariant problems have been written so as to allow the teacher to give an individual assignment to every student in the group. They are recommended for unassisted work. Multivariant problems may also be approached as single-variant ones with the teacher selecting out of the 15 to 25 choices available the one that suits best an individual student from the standpoint of his or her specialization.

In preparing the present edition, the authors took into account the main changes in the physical chemistry course and the recent trends that have established themselves in this field. They also acted in line with the general desire to reinforce the overall theoretical training of chemical and process engineers, which has recently been voiced by many a representative of the higher education establishment. This has prompted the authors to include a number of new chapters. The sequence in which the chapters are presented follows more closely the rigorous logic of the course: the geometrical parameters and energetic properties of molecules come first (Chapters 1 through 5), these are followed by analysis of the properties of substances in the ideal gaseous state, the next logical step being the real gaseous and condensed states of individual substances (Chapters 10 through 12).

Once the properties of individual substances have been covered, multiple-component systems in one or more phases are dealt with in Chapters 13 through 17. The more complex systems involved in chemical reactions are considered at equilibrium (Chapters 19 through 21) and in dynamics (from Chapter 23 on). The newly introduced chapters are representative of recent advances in physical chemistry.

In view of the general tendency to curtail supervised studies in the classroom in favour of independent work, emphases have been shifted accordingly. The theoretical introductions have been significantly cut down. In this respect, the authors' intent was to offer something different from a mere textbook. Primary emphasis has been placed on problems with solutions, which must serve as reference in cases where the student finds it difficult to use the right solution in his or her independent work.

This edition includes problems whose solution calls for the use of calculators. These problems are marked by asterisks. Presented at the end of some chapters are complex problems. Their solution requires knowledge of several topics from the course in physical chemistry. They may be recommended for term assignments.

The multivariant problems can be divided into two major categories: (1) problems covering the entire topic of the chapter to which they belong, whose solution requires the use of plots and handbooks and which are recommended for home assignments after the student has gone through the theoretical part and problems with solutions, and (2) problems dealing with a particular part of the chapter, which can be solved without involved calculations and plots and are recommended for testing. Multivariant problems typically include 25 assignments. In cases where no experimental data are available, an assignment may be presented under two or three variant numbers.

All values encountered throughout the book are in SI units with a few exceptions when they are given in other units still in common use.

This edition has been prepared with due account for the remarks and critical comments from the teachers of the Physical Chemistry Department of the D.I. Mendelev Institute of Chemical Engineering in Moscow and other institutes.

### International System of Units

The metric system of units of length, mass, force, and other physical quantities was developed during the French Revolution of 1789-94. Its simplicity and convenience have brought it into universal use. In scientific research, metric units have been substituted for the previously used units of measurement. The most extensive and



improved form of the metric system, known as the International System (or sometimes simply SI after the French name "système international"), was adopted officially by the General Conference on Weights and Measures in 1960.

The SI unit of mass is the kilogram (kg) defined as the mass of the international standard made of a platinum-iridium alloy and kept at the International Bureau of Weights and Measures in Paris. At present, there is one inconsistency in the SI system, which lies in the fact that the name of the unit of mass has the prefix "kilo". This inconsistency will persist until consensus is reached on the new name and symbol of the unit of mass. In the meantime, it should be remembered that one milligram, written as 1 mg, rather than one microkilogram, equals one millionth of the unit of mass, and not one thousandth as would be inferred from the prefix "milli".

The unit of length in the SI system is the metre (m). Previously, the metre was defined as the distance between two notches on the platinum-iridium standard also kept at the International Bureau of Weights and Measures in Paris. In 1960, an international agreement was reached to define the metre as the length equal to 1 650 763.73 wavelengths of the radiation corresponding to the orange-red line in the spectrum of krypton-86.

The SI unit of time is the second (s) which is defined as the duration of 9 192 631 770 periods of the radiation corresponding to the transition between two hyperfine levels of the ground state of the cesium-133 atom at a wavelength approximately equal to 3.26 cm. In the past, the second was defined as 1/86 400 the mean solar day.

The unit of volume in the SI system is the cubic metre (m<sup>3</sup>). In chemistry, wide use is made of the litre (l) as the unit of volume, which equals 1/10<sup>3</sup> m<sup>3</sup>. A millilitre, 1 × 10<sup>-3</sup> litre, is equal to one cubic centimetre: 1 ml = 1 cm<sup>3</sup>.

The SI unit of force, the newton (N), is defined as the force imparting an acceleration of 1 m s<sup>-2</sup> to a mass of 1 kg in the direction of the force. A newton equals 10<sup>5</sup> dynes (a dyne being the unit of force in the CGS system, equal to the force which imparts an acceleration of 1 cm s<sup>-2</sup> to a 1 g mass).

The unit of energy in the SI system is the joule (J) which is the work done by a force of magnitude of 1 N when the body to which it is applied is displaced 1 m in the direction of the force: 1 J = 1 N × 1 m = 10<sup>7</sup> erg = 10<sup>7</sup> dyne cm.

Formerly, the calorie was widely used as the unit of energy. The thermochemical calorie defined as 4.184 J is approximately equal to the amount of energy required to heat 1 g of water by 1 °C. The large calorie (kcal) equals 10<sup>3</sup> cal. The following conversion factors are good to remember: 1 cal = 4.184 J; 1 kcal = 4.184 kJ.

Symbols and Units of Measurement in the SI System and Factors of Conversion from the Systems Most Widely Used Before 1963 into the SI System

8

Foreword

Sym- bol	Name of quantity	SI unit	Units widely used before 1963	Factor of conversion into SI
<i>W</i>	Work done by the system	J/mole	litre atm/mole kcal/mole	$1.0133 \times 10^3$ $4.187 \times 10^3$
<i>a</i>	Activity	—	—	—
<i>a</i>	Van der Waals constant	$(\text{m}^3)^2 \text{ kmole}^{-2} \text{ N/m}^2$	litre <sup>2</sup> atm/mole <sup>2</sup>	$1.0133 \times 10^{-1}$
<i>b</i>	Van der Waals constant	$\text{m}^4 \text{ N/kmole}^2$	—	—
<i>C</i>	Heat capacity	$\text{m}^3/\text{kmole}$	litre/mole	1
<i>D</i>	Permittivity	$\text{J mole}^{-1} \text{ deg}^{-1}$	cal mole <sup>-1</sup> deg <sup>-1</sup>	4.187
<i>d</i>	Density	—	—	—
<i>E</i>	Energy	$\text{kg/m}^3$	g/cm <sup>3</sup>	$10^3$
<i>F</i>	Electromotive force	J	erg	$10^{-7}$
$\phi$	Electrode potential	V	V	1
<i>A</i>	Helmholtz energy (isochoric-isothermal potential)	V	V	1
<i>F</i>	Force	J/mole	kcal/mole	$4.187 \times 10^3$
<i>G</i>	Gibbs' energy (isobaric isothermal potential)	N	dyne	$10^{-5}$
<i>m</i>	Mass	J/mole	kcal/mole	$4.187 \times 10^3$
<i>H</i>	Enthalpy	kg	g	$10^{-3}$
<i>I</i>	Rotational moment of inertia	J/mole	kcal/mole	$4.187 \times 10^3$
<i>I</i>	Ionization potential	$\text{kg m}^2$	g cm <sup>2</sup>	$10^{-7}$
<i>j</i>	Rotational quantum number	J/mole	eV/mole	$9.6505 \times 10^4$
<i>K<sub>a</sub></i>	Chemical equilibrium constant	—	—	—
<i>K<sub>cr</sub></i>	Cryoscopic constant	—	—	—
		deg $10^3$ kg/kmole	deg g mole	1



(Table concluded)

Sym- bol	Name of quantity	SI unit	Units widely used before 1963	Factor of conversion into SI
$L$	Partial quantity	—	—	—
$\alpha$	Degree of dissociation	—	—	1
$\alpha$	Polarizability	$\text{m}^3$	$\text{cm}^3$	$10^{-3}$
$\gamma$	Activity coefficient	—	—	1
$\Delta$	Final change in a property	—	—	—
$\varepsilon$	Binding energy	J/kmole	kcal/mole	$4.187 \times 10^6$
$\eta$	Viscosity	$\text{Pa s (N s/m}^2)$	cP	$10^{-3}$
$\chi$	Electrical conductivity	$\text{mho m}^{-1}$	$\text{mho cm}^{-1}$	$10^{-2}$
$\lambda$	Equivalent conductivity	$\text{mho m}^2/\text{kg-eq}$	$\text{mho cm}^2/\text{g-eq}$	$10^{-1}$
$\lambda$	Wavelength	m	$\text{\AA}$	$10^{-10}$
$\mu$	Electric dipole moment	C m (m s A)	$10^{-18}$ e.s.u.	$0.333 \times 10^{-11}$
$\mu$	Chemical potential	—	—	1
$\nu$	Frequency	$\text{s}^{-1}$	$\text{s}^{-1}$	1
$\pi$	Osmotic pressure	Pa (N/m $^2$ )	atm	$1.0133 \times 10^5$
$\pi$	Reduced pressure	—	—	1
$\sigma$	Surface tension	N/m	dyne/cm	$10^{-3}$
$\sigma$	Gas-kinetic diameter	m	$\text{\AA}$	$10^{-10}$
$t$	Time	s	s	1
$\tau$	Reduced temperature	—	—	1
$\sim$	Wave number	$\text{m}^{-1}$	$\text{cm}^{-1}$	$10^2$

# Contents

Foreword	5
International System of Units	6
<b>Chapter 1. Fundamentals of Quantum Chemistry. The Chemical Bonding Theory and the LCAO-MO Method</b>	<b>15</b>
Exercises	18
Problems	23
Multivariant Problem	23
<b>Chapter 2. Geometrical Configuration of Atoms in Molecules. Elements of the Molecular Symmetry Theory</b>	<b>24</b>
Exercises	26
Problems	29
Multivariant Problem	30
<b>Chapter 3. Rotation and Rotational Spectra of Diatomic Molecules</b>	<b>30</b>
Exercises	32
Problems	33
Multivariant Problems	35
<b>Chapter 4. Rotation and Rotational Spectra of Polyatomic Molecules</b>	<b>36</b>
Exercises	38
Problems	41
Multivariant Problem	41
<b>Chapter 5. Vibration of Atoms in Molecules. Vibration and Vibration-Rotation Spectra</b>	<b>42</b>
Exercises	45
Problems	48
Multivariant Problems	51
<b>Chapter 6. First Law of Thermodynamics</b>	<b>52</b>
Exercises	56
Problems	67
Multivariant Problems	72
<b>Chapter 7. Second Law of Thermodynamics</b>	<b>75</b>
Exercises	79
Problems	97
Multivariant Problems	103

**Chapter 8. Elements of Statistical Thermodynamics 108**

- Exercises 115
- Problems 127
- Multivariant Problems 130

**Chapter 9. Gases 133**

- Exercises 138
- Problems 144
- Multivariant Problems 146

**Chapter 10. Condensed State of Matter 148**

- Exercises 153
- Problems 161
- Multivariant Problems 164

**Chapter 11. Phase Equilibrium of One-Component Systems 166**

- Exercises 168
- Problems 173
- Multivariant Problems 177

**Chapter 12. Thermodynamic Characteristics of Solutions and Processes of Their Formation 186**

- Exercises 189
- Problems 200
- Multivariant Problems 206

**Chapter 13. Dilute Solutions 210**

- Exercises 214
- Problems 219
- Multivariant Problems 224

**Chapter 14. Heterogeneous Equilibrium in Binary Systems Containing Liquid and Vapour Phases 226**

- Exercises 228
- Problems 242
- Multivariant Problems 245

**Chapter 15. Heterogeneous Equilibrium in Binary Systems Containing Liquid and Solid Phases 257**

- Exercises 258
- Problems 268
- Multivariant Problem 276

**Chapter 16. Heterogeneous Equilibrium in Ternary Systems Containing Liquid and Solid Phases 277**

- Exercises 278
- Problems 282
- Multivariant Problem 282

**Chapter 17. Chemical Equilibrium 283**

- Exercises 287
- Problems 301
- Multivariant Problems 308



<b>Chapter 18. Electrolytic Conductance. Equilibrium in Electrolyte Solutions</b>	319
Exercises	322
Problems	331
Multivariant Problems	336
<b>Chapter 19. Electromotive Force. Electrode Potentials</b>	340
Exercises	344
Problems	355
Multivariant Problems	361
<b>Chapter 20. Adsorption</b>	366
Exercises	367
Problems	370
Multivariant Problem	373
Complex Problems	375
<b>Chapter 21. Formal Kinetics</b>	376
Exercises	379
Problems	389
Multivariant Problem	395
<b>Chapter 22. Composite Reactions</b>	398
Exercises	401
Problems	405
Multivariant Problem	410
<b>Chapter 23. Temperature Dependence of the Reaction Rate</b>	411
Exercises	412
Problems	415
Multivariant Problem	418
<b>Chapter 24. Basic Theory Behind Calculation of Reaction Rate Constant</b>	421
Exercises	423
Problems	432
Multivariant Problems	437
<b>Chapter 25. Kinetics of Photochemical and Chain Reactions</b>	444
Exercises	447
Problems	452
Multivariant Problem	458
<b>Chapter 26. Diffusion. Kinetics of Heterogeneous Processes</b>	460
Exercises	463
Problems	470
Multivariant Problem	472
<b>Chapter 27. Kinetics of Reactions in Solutions. Homogeneous and Heterogeneous Catalysis</b>	474
Exercises	476
Problems	480
<b>Chapter 28. Kinetics of Electrochemical Reactions</b>	486
Exercises	487
Problems	493
Multivariant Problems	496
Complex Problems	497
Appendix	498
Answers	501

## Values of Some Physical and Chemical Constants

Avogadro constant	$N_A = 0.60229 \times 10^{24} \text{ mole}^{-1}$
Velocity of light	$c = 2.997925 \times 10^8 \text{ m/s}$
Electron mass	$m = 0.91083 \times 10^{-30} \text{ kg}$
Electron charge	$e = 0.106206 \times 10^{-18} \text{ C}$
Faraday	$F = N_A e = 96\,490 \text{ C/mole}$
Dalton	$D = 1.66033 \times 10^{-27} \text{ kg}$
Planck constant	$h = 0.66252 \times 10^{-33} \text{ J s}$
Quantum of angular momentum	$\hbar = h/2\pi = 0.105443 \times 10^{-33} \text{ J s}$
Proton mass	$m_p = 1.67239 \times 10^{-27} \text{ kg}$
Neutron mass	$m_n = 1.67470 \times 10^{-27} \text{ kg}$
Boltzmann constant	$k = 13.805 \times 10^{-24} \text{ J/deg}$
Gas constant per mole	$R = N_A k = 8.3146 \text{ J mole}^{-1} \text{ K}^{-1}$
Gas constant	$R = 0.08206 \text{ litre atm deg}^{-1} \text{ mole}^{-1}$
Standard molar volume of gas at 273 K and $1.013 \times 10^5 \text{ Pa}$	22.415 litre
Centigrade temperature	$t^\circ\text{C} = T\text{K} - 273.15$
Atmospheric pressure	$1 \text{ atm} = 101.325 \text{ kN m}^{-2}$
Electric dipole moment	$0.1602 \times 10^{-28} \text{ C m (4.8029 D)}$
Electron-volt	$1 \text{ eV} = 96.4905 \text{ kJ/mole}$

# CHAPTER 1

## Fundamentals of Quantum Chemistry. The Chemical Bonding Theory and the LCAO-MO Method

### Basic Equations and Symbols

According to the linear combination of atomic orbitals approximation (LCAO-MO method), the wave function is given by the equation

$$\psi = C_A \psi_A + C_B \psi_B \quad (1.1)$$

where  $\psi$  is the molecular wave function,  $C_A$  and  $C_B$  are coefficients, and  $\psi_A$  and  $\psi_B$  are atomic wave functions of atoms A and B. The potential energy of a system comprising atoms A and B is given by the equation

$$E_{\text{pot}} = \frac{Z_A Z_B}{r_{AB}} - \frac{Z_A e}{r_A} - \frac{Z_B e}{r_B} \quad (1.2)$$

where  $Z$  is the charge of the atomic nucleus,  $e$  is the electronic charge,  $r_{AB}$  is the internuclear distance, and  $r_A$  and  $r_B$  are the distances between the nucleus and an electron.

Schrödinger's equation is

$$\hat{H}\psi = E\psi \quad (1.3)$$

in which  $\hat{H} = -\frac{\hbar^2}{8\pi^2m} \nabla^2 + E_{\text{pot}}$  is the Hamiltonian operator,  $E_{\text{pot}}$  is the potential energy, and  $\nabla^2$  is Laplace's operator.

For the diatomic molecule A—B,

$$(H_{AA} - ES_{AA}) C_A + (H_{AB} - ES_{AB}) C_B = 0$$

$$(H_{AB} - ES_{AB}) C_A + (H_{BB} - ES_{BB}) C_B = 0$$

where  $H_{AB} = H_{BA} = \int_{-\infty}^{+\infty} \psi_A \hat{H} \psi_B dv = \int_{-\infty}^{+\infty} \psi_B \hat{H} \psi_A dv$  is an exchange integral,  $H_{AA} = H_{BB} = \int_{-\infty}^{+\infty} \psi_A \hat{H} \psi_A dv = \int_{-\infty}^{+\infty} \psi_B \hat{H} \psi_B dv$  is a coulombic integral,  $S_{AB} = S_{BA} = \int_{-\infty}^{+\infty} \psi_A \psi_B dv$  is an overlap integral, and  $v$  is the volume.