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Problems and Laboratory Experiments in Inorganic Chemistry

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ИЗДАТЕЛЬСТВО • МИР •

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ЛАБОРАТОРНЫЕ И СЕМИНАРСКИЕ ЗАНЯТИЯ ПО НЕОРГАНИЧЕСКОЙ ХИМИИ

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА»
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PREFACE

th the content of general and inorganic chemistry and the
odology of teaching have substantially changed during the past
les. Basically, an entirely new course has been worked out.
material is now discussed from the standpoint of modern con-
in quantum mechanics, thermodynamics and the structure
atter.

e course in practical general and inorganic chemistry must
the same requirements. In our opinion this can be achieved
igh exercises and laboratory experiments, which illustrate
heory and stimulate the student to independent thought and
him how to apply theory to practical needs. The student must
how to handle chemicals properly and be able to perform
atory experiments. Each experiment should be considered as
dependent piece of research (at the level of the first year student)
its own object, theoretical basis and experimental proof of
onjectured result. The experiments must lead the student from
perficial acquaintance with substances to an understanding of
properties, thorough knowledge of their structure and thermo-
mics, and further to the carrying out of an oriented experiment.
is laboratory manual will, in our opinion, serve the purpose
inging the teaching process closer to the solution of practical
lems in chemical research.

is manual is the summation of our experience in teaching
ral and inorganic chemistry at the Kazan Chemico-technological
tute. The first part of the book is devoted to general theoretical
lems in inorganic chemistry, while the second part to inorganic
istry proper. The material is presented in such a way that all
ents in a given subgroup can be characterized, while the experi-
gained in examining the properties of one element can be exten-
to the study of the other elements in the subgroup. The arrange-

ment of the material in the book facilitates the student in his independent studies.

The solution of difficult problems is given at the end of the book. Bibliographies will guide the student in his or her independent reading. The appendices will also considerably help students in their studies and in solving the problems given in this book. The data in the tables are taken from the cited literature.

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PART ONE

INTRODUCTION TO INORGANIC CHEMISTRY

I

THE STRUCTURE OF MATTER

CHAPTER 1

The Mendeleev Periodic System. The Structure of Atom

1. Formulate the main principles of quantum mechanics.

2. Calculate quantum energy of the radiation ΔE at wavelength of $\lambda = 300$ nm in joules; electron volts; joule/mole*.

3. Calculate the speed of an electron, a neutron or a particle having the mass of 1 g at which a de Broglie's wavelength is 0.1 nm.

4. Calculate the energy of the first five energy levels of an electron in the hydrogen atom and show their relative positions.

5. What is the principal quantum number of the hydrogen atom orbital if the electron energy is —3.4 eV; —13.6 eV; —0.85 eV, respectively?

6. What spectrum lines correspond to hydrogen emission as the electron passes from one energy state to another, the initial and final values of the principal quantum number being: $n = 4$ and 2; $n = 2$ and 1; $n = 3$ and 2?

To what region of the electromagnetic spectrum do these lines correspond?

7. Determine the energy of the electron transitions corresponding to the red ($\lambda = 656$ nm) and to the blue ($\lambda = 486$ nm) lines in the emission spectrum of atomic hydrogen.

Experiment 1. Observing the emission spectrum of atoms in a spectroscope. Fix a discharge tube filled with hydrogen (or helium, neon) in the vertical state in a stand and connect it to the ends of the secondary winding of the induction coil. Install a spectroscope so that its slit is at a short distance from the discharge tube and parallel to its capillary. Connect the induction coil to the D.C. source and switch on the current.

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* Data for calculations are given in the appendices.

Observe through the spectroscope a colourless flame of a gas burner. Put a piece of asbestos impregnated with a sodium chloride solution into the flame. Explain the yellow colour of the flame and the bright-yellow line in the spectrum.

Experiment 2. Observing the absorption spectrum of atoms. Using a spectroscope observe the emission of an incandescent electric lamp. Place a burner between the lamp and the slit of the spectroscope. Fix a piece of asbestos impregnated with sodium chloride solution in a stand and put it in the flame of a burner. Explain your observations.

Experiment 3. Observing the molecular spectrum. Proceed as in Experiment 1 and analyze the sulphur dioxide spectrum. Compare the spectra of the atom, molecule and solid (Experiment 2). What is the main difference between these spectra?

8. What energy changes in atom correspond to gamma-, X- and visible radiation?

9. Formulate the rules which define the number of orbitals and electrons in a given electron shell.

(a) What is the maximum capacity of electron shells K, L, M, N?

(b) What number of orbitals of a given shell is characterized by the following azimuthal quantum number: $l = 2$; $l = 1$; $l = 0$? What letters are used to designate orbitals?

(c) What number of electrons may be in the following energy states: $2s$; $4p$; $3d$; $5f$?

10. Characterize graphically the $1s$-state of the hydrogen atom electron using the following notions: (1) electron cloud; (2) boundary surface; (3) radial wave function; (4) radial probability density distribution; (5) radial probability distribution of finding an electron in an atom.

11. Characterize the $2p$-state of the hydrogen atom electron as in Problem 10.

12. Describe the form of the orbital and the electron cloud whose state is characterized by the following quantum numbers: $n = 3$, $l = 0$, $m_l = 0$; $n = 3$, $l = 1$, $m_l = 0, \pm 1$; $n = 3$, $l = 2$, $m_l = 0, \pm 1, \pm 2$. What symbols are used to designate orbitals?

13. What rules define the order of filling of the atomic shells? Give the electron configurations of unexcited atoms of Ge, Br, Mn, Ti and the ions Ba^{2+}, Fe^{3+}, Ce^{4+}.

14. Show graphically the variation of $4\pi r^2\psi^2$ with r for $3s$-, $3p$- and $3d$-states of the hydrogen atom electron. Explain the shape of the curves.

15. Plot a graph showing the variation of the orbital atomic radii with the atomic number for the elements of the 2nd and 3rd periods. Explain the shapes of the curve.

16. How does the value of the first ionization energy of atoms change with the atomic number of the element? Plot a graph showing the dependence $I_{\text{ion}} = f(Z)$ for the elements of the 2nd and 3rd periods. Explain the shape of the curve.

17. Compare the electron affinities of the nitrogen and oxygen atoms. Which of these atoms has a stronger electron affinity? Explain your answer.

18. Plot a graph of the variation of the first ionization energy of the atoms of alkali metals with the atomic number. Explain the shape of the curve.

19. Give the values of the first ionization energy of potassium, manganese and zinc atoms and their orbital atomic radii.

(a) How do the atomic radii change in the series K-Mn-Zn? Explain your answer (Fig. 1).

(b) How does the first ionization energy change in this series?

(c) Why is the first ionization energy of the rhenium atom (7.88 eV) higher than that of the manganese atom (7.44 eV)?

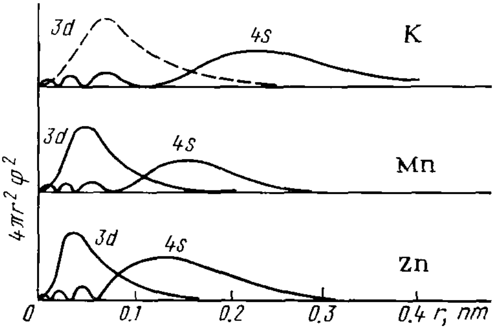

Fig. 1. Radial distribution of density of probability of finding electrons in the atoms of potassium, manganese and zinc

20. Show electron configurations of atoms of Group III elements in the ground state. What principle underlies the division of the elements of this group of the periodic system into subgroups?

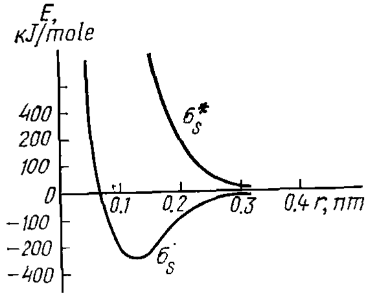

Fig. 2. Dependence of lowest energy levels of molecular hydrogen ion H_2^+ on the internuclear distance

CHAPTER 2

Chemical Bonding. The Structure of Molecule

2.1. Chemical Bonding

1. Formulate the main principles of the molecular orbital theory.

2. Figure 2 shows the lowest energy levels of the molecular hydrogen ion H_2^+ calculated with the Schrödinger equation by internuclear distance.

(a) What energy curve describes the H_2^+ ion in its ground state? How can the energy of dissociation of the molecular ion H_2^+ (to H and H^+) and the equilibrium internuclear distance be determined from the graph? What are the dissociation energy and internuclear distance of the ion H_2^+? (See Appendix 10.)

(b) Show graphically wave functions (along the axis connecting the nuclei) for the energy levels of the ion H_2^+ shown in Fig. 2.

(c) Draw the boundary surfaces and name the orbitals of the molecular ion H_2^+.

(d) Show graphically the variation of the probability of finding the electron in the bonding and antibonding orbitals of H_2^+ ion along the axis connecting the nuclei.

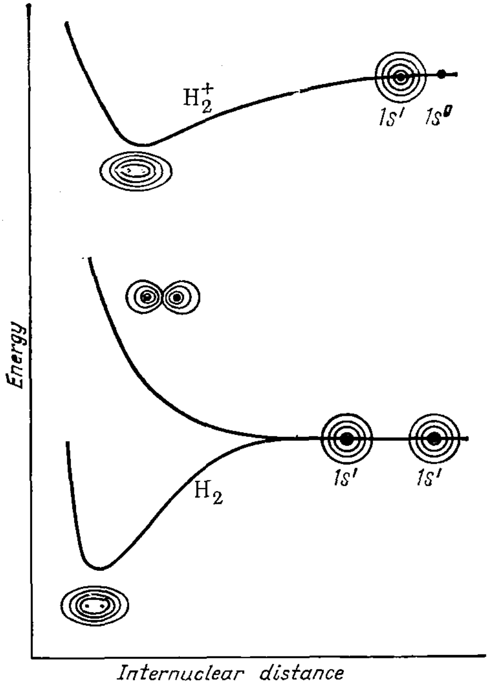

Fig. 3. Variation of potential energy of H_2 and H_2^+ with the internuclear distance

(e) Give the electron configuration of the H_2^+ ion in the ground state.

(f) Why do atoms combine into a molecule?

3. Formulate the main principles of the LCAO-MO method. How can the construction of the molecular orbitals from atomic orbitals be shown graphically for H_2^+ ion? What is the physical sense of such presentation?

4. Construct the energy diagram of the hydrogen molecule and distribute its electrons in the orbitals.

(a) Explain the difference between the ionization energies of the hydrogen molecule and the hydrogen atom in the ground state.

(b) Give the electron configurations of the ground and ionized (to H_2^+) states of the hydrogen molecule (Fig. 3).

(c) Using Fig. 3 explain the character of the variation of the energy of dissociation and the equilibrium internuclear distance with the hydrogen molecule ionization. Compare the dissociation energies and the internuclear distances of H_2 and H_2^+.

(d) Explain the difference in shape of the energy curves of H_2 and H_2^+ (Fig. 3) at the "bottom" of the energy well. In which case the bond is stronger, i.e. where higher energy is required to remove nuclei one from another to the same distance?

5. Show the overlapping in combinations of *s-s-*; *s-p-*; *p-p-*; *s-d-*; *p-d-*; *d-d-*orbitals.

(a) Indicate the cases of (1) positive, negative, zero; (2) σ-; π- and δ-overlapping (with respect to symmetry).

(b) What are the conditions for the formation of stable molecular orbitals from atomic orbitals?

6. Using the LCAO-MO method determine the number and the shape of the fluorine molecule orbitals. Draw an approximate diagram of the energy levels of the molecule and give its electron configuration.

(a) What atomic orbital combinations are suitable (from the energy standpoint) for the formation of the fluorine molecule orbitals, if the $E_{2p} \gg E_{2s}$?

(b) What combinations of atomic orbitals lead to the formation of the molecular orbitals of the σ- and π-types if the axis connecting the fluorine atoms is the z-axis?

7. Determine the number and shape of the nitrogen molecule orbitals. Show graphically the approximate diagram of the energy levels of the molecule and give its electron configuration.

(a) What effect does the energy closeness of $2s$- and $2p$-orbitals of the atoms produce on the relative position of molecular orbitals on the energy diagram of homonuclear diatomic molecules?

(b) What is the bond order in the nitrogen molecule?

8. Draw the graph of the variation of the bond order, the force constant of bond k, its length and energy with the number of valency electrons in the series B_2-C_2-N_2-O_2-F_2-Ne_2

	B_2	C_2	N_2	O_2	F_2
k, N/m . . .	350	930	2240	1140	450

(a) Explain the curves.

(b) Which of these molecules are para- and diamagnetic molecules?

9. What is the character of the variation of the dissociation energy and internuclear distance in transition: (1) from N_2 to N_2^+ and N_2^-; (2) from O_2 to O_2^+ and O_2^-? Explain your answer.

10. Give the ionization energy of N_2 and O_2 molecules and N and O atoms. In what case is the molecular ionization energy higher (lower) than the atomic ionization energy? Explain.

11. Using the LCAO-MO method determine the number and the shape of the hydrogen fluoride molecule orbitals. Draw the approximate diagram of the energy levels of the molecule and give its electron configuration. The orbital energies of hydrogen and fluorine are

	1s (H)	1s (F)	2s (F)	2p (F)
E eV . . .	-13.6	~—1000	-40	-17.4

(a) What combinations of the hydrogen and fluorine atom orbitals are most suitable for the formation of the molecular orbitals from the energy standpoint?

(b) What combinations of the hydrogen and fluorine atoms lead to the formation of the bonding, antibonding and nonbonding orbitals if the axis connecting the atoms in the HF molecule is the z-axis? Draw the diagrams of the orbital overlapping. What symbols are used to designate molecular orbitals?

(c) Why is the hydrogen fluoride molecule strongly polar? ($\mu = 0.64 \times 10^{-29}$ C·m, $\delta_F = 0.4$—).

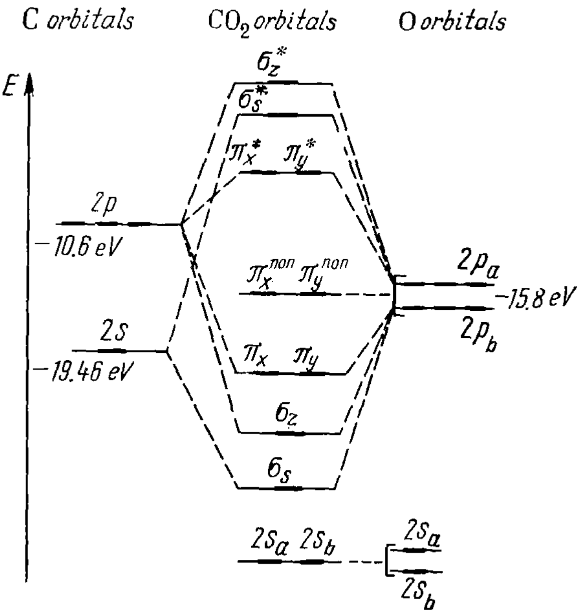

Fig. 4. Energy diagram of the orbitals of the linear molecule CO_2

12. Determine the number and the shape of the orbitals of a linear molecule of beryllium hydride, BeH_2. Draw the approximate diagram of the energy levels of the molecule and give its electron configuration.

(a) Why are the internuclear distances between Be and H in the BeH_2 molecule equal?

(b) How is the distribution of valency electrons in molecular orbitals coordinated with the positive effective charge on the beryllium atom ($\delta_{Be} = 1+$) and the negative charge on the hydrogen atom ($\delta_H = 0.5-$)?

13. Figure 4 shows an approximate diagram of the energy levels of the CO_2 linear molecule.

(a) What combinations of the central atom orbitals and group orbitals of peripheral atoms (ligands) are responsible for building molecular orbitals? Draw the overlapping diagrams.

(b) Explain the high mean energy ($E_{CO} = 803$ kJ/mole) and the force constant ($k = 1550$ N/m) of the bond CO and relatively short internuclear distance ($d_{CO} = 0.116$ nm) in the CO_2 molecule.

(c) Why is the bond in the CO_2 molecule polar while the molecule itself is nonpolar?

14. Determine the number and the shape of the molecular orbitals of a tetrahedral methane molecule. Draw an approximate diagram of the energy levels of the molecule and give its electronic configuration.

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