THE STRUCTURE
OF MATTER

M. KARAPETYANTS, S. DRAKIN

MENDELEEV'S PERIODIC

					G R O	
Periods	Series	I	II	III	IV	V
I	1	(H)				
II	2	Li 3 6.939 1 2	Be 4 9.0122 2 2	5 B 10.811 3 2	6 C 12.01115 4 2	7 N 14.0067 5 2
III	3	Na 11 22.9898 1 8 2	Mg 12 24.305 2 8 2	13 Al 26.9815 3 8 2	14 Si 28.086 4 8 2	15 P 30.9738 5 8 2
IV	4	K 19 39.102 1 8 8 2	Ca 20 40.08 2 8 8 2	Sc 21 44.956 2 9 8 2	Ti 22 47.90 2 10 8 2	V 23 50.942 1 11 8 2
IV	5	1 18 8 2 29 Cu 63.546	2 18 8 2 30 Zn 65.37	3 18 8 2 31 Ga 69.72	4 18 8 2 32 Ge 72.59	5 18 8 2 33 As 74.9216
V	6	Rb 37 85.47 1 8 18 8 2	Sr 38 87.62 2 8 18 8 2	Y 39 88.905 2 9 18 8 2	Zr 40 91.22 2 10 18 8 2	Nb 41 92.906 1 12 18 8 2
V	7	1 18 18 8 2 47 Ag 107.868	2 18 18 8 2 48 Cd 112.40	3 18 18 8 2 49 In 114.82	4 18 18 8 2 50 Sn 118.69	5 18 18 8 2 51 Sb 121.75
VI	8	Cs 55 132.905 1 8 18 18 8 2	Ba 56 137.34 2 8 18 18 8 2	La 57 138.91 2 9 18 18 8 2		
VI	8			Ce 58 140.12 2 8 20 18 8 2	Pr 59 140.907 2 8 21 18 8 2	Nd 60 144.24 2 8 22 18 8 2
VI	8			Tb 65 158.924 2 8 27 18 8 2	Dy 66 162.50 2 8 28 18 8 2	Ho 67 164.930 2 8 29 18 8 2
VI	8				Hf 72 178.49 2 10 32 18 8 2	Ta 73 180.948 2 11 32 18 8 2
VI	9	1 18 32 18 8 2 79 Au 196.967	2 18 32 18 8 2 80 Hg 200.59	3 18 32 18 8 2 81 Tl 204.37	4 18 32 18 8 2 82 Pb 207.19	5 18 32 18 8 2 83 Bi 208.980
VII	10	Fr 87 [223] 1 8 18 32 18 8 2	Ra 88 [226] 2 8 18 32 18 8 2	Ac 89 [227] 2 9 18 32 18 8 2		
VII	10			Th 90 232.038	Pa 91 [231]	U 92 238.03
VII	10			Bk 97 [247]	Cf 98 [251]	Es 99 [254]
VII	10				Ku 104 [260]	105
	11					

SYSTEM OF THE ELEMENTS

U P S

VI	VII	VIII			0
	1 **H** 1.00797				**He** 2 4.0026 2
8 **O** 15.9994	9 **F** 18.9984 (7/2)				**Ne** 10 20.179 (8/2)
16 **S** 32.064	17 **Cl** 35.453 (7/8/2)				**A** 18 39.948 (8/8/2)
Cr 24 51.996 (13/8)	**Mn** 25 54.9380 (2/13/8)	**Fe** 26 55.847 (2/14/8/2)	**Co** 27 58.9332 (2/15/8/2)	**Ni** 28 58.71 (2/16/8/2)	
34 **Se** 78.96	35 **Br** 79.904 (7/18/8/2)				**Kr** 36 83.80 (8/18/8/2)
Mo 42 95.94 (1/13/18/8/2)	**Tc** 43 [99] (2/13/18/8/2)	**Ru** 44 101.07 (1/15/18/8/2)	**Rh** 45 102.905 (1/16/18/8/2)	**Pd** 46 106.4 (0/18/18/8/2)	
52 **Te** 127.60	53 **I** 126.9044 (7/18/18/8/2)				**Xe** 54 131.30 (8/18/18/8/2)

Pm 61 [147] (2/8/23/18/8/2)	**Sm** 62 150.35 (2/8/24/18/8/2)	**Eu** 63 151.96 (2/8/25/18/8/2)	**Gd** 64 157.25 (2/9/25/18/8/2)
Er 68 167.26 (2/8/30/18/8/2)	**Tm** 69 168.934 (2/8/31/18/8/2)	**Yb** 70 173.04 (2/8/32/18/8/2)	**Lu** 71 174.97 (2/9/32/18/8/2)
W 74 183.85 (2/12/32/18/8/2)	**Re** 75 186.2 (2/13/32/18/8/2)	**Os** 76 190.2 (2/14/32/18/8/2)	**Ir** 77 192.2 (2/15/32/18/8/2)	**Pt** 78 195.09 (1/17/32/18/8/2)
84 **Po** [210]	85 **At** [210] (7/18/32/18/8/2)			**Rn** 86 [222] (8/18/32/18/8/2)

Np 93 [237]	**Pu** 94 [244]	**Am** 95 [243]	**Cm** 96 [247]
Fm 100 [257]	**Md** 101 [258]	**No** 102 [255]	**Lw** 103 [258]

М. Х. КАРАПЕТЬЯНЦ, С. И. ДРАКИН

СТРОЕНИЕ ВЕЩЕСТВА

THE STRUCTURE

OF MATTER

M. KARAPETYANTS, S. DRAKIN

TRANSLATED FROM THE RUSSIAN
by Y. NADLER and G. KITTELL

Treated in this book are present-day ideas on the structure of atoms, molecules and crystals, as well as the nature of chemical bonds. It is supposed that the reader is acquainted with chemistry within the scope of the secondary-school course and that he has some notion of differential and integral calculus.

The study of this book can precede the learning of a higher-school course in chemistry; it will be conducive in widening the student's knowledge of inorganic chemistry as well as in studying more deeply organic and analytical chemistry.

The book is designed for students in chemical engineering, polytechnical and other institutes of learning in which inorganic and organic chemistry are studied. It can be found useful for engineers, technicians and scientific workers whose industrial or research work is associated with chemical technology, metallurgy, biochemistry, or geochemistry.

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PREFACE

In our days, often called a period of scientific and technological revolution, reorientation in the various branches of science is constantly taking place. In particular, the study of the structure of matter, which lies in the borderland between physics and chemistry and was formerly a part of these sciences, is gradually being separated into an independent science with its own mathematical apparatus and methodology. This is so first of all because quantum mechanics has become the principal means of studying and solving problems in this field. On the other hand, the theory of the structure of matter is becoming essential for working in the most diverse branches of science and technology — from astrophysics to agriculture.

Because of the aforesaid it is now necessary that the chemical student in the first year of study in higher institutes of learning (colleges and universities) acquire a deeper knowledge of the structure of matter. This book was written to satisfy this requirement. It presents the modern concept of the structure of atoms, molecules and crystals, as well as the nature of chemical bonds; it describes some methods used in structure determination. The book is based on the course of lectures regularly delivered by the authors since 1964 in the Mendeleev Chemical Engineering Institute in Moscow. This course precedes that of general and inorganic chemistry. The authors believe that inorganic chemistry cannot be satisfactorily studied without the knowledge of the structure of matter and the energetics of chemical reactions, i.e., chemical thermodynamics[1].

The theory of the structure of matter is probably the most complicated branch of modern natural science; it utilizes practically all the achievements of physics and an enormous mathematical apparatus. It is obvious that in a book intended for students with only a rudimentary knowledge of mathematical analysis, many important

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[1] Information about the energetics of chemical reactions, necessary for studying inorganic chemistry, is given in the book by M. Karapetyants: Introduction to the Theory of Chemical Processes, 'Vysshaya Shkola' Publishing House, Moscow, 1970.

problems cannot be treated quantitatively. Accordingly, the purpose
of this book is to acquaint the reader with the fundamental laws
and concepts involved, discussing the quantitative aspect of the
problems only where this can be done in such a way that it can be
easily understood. When using the mathematical apparatus we tried
where possible to give a 'key' to a deeper understanding while avoid-
ing unwieldy calculations. As might well be expected, the discussion
of a number of problems had to be simplified.

Inasmuch as in colleges this book may be studied prior to the course
in chemistry, it was necessary to touch on certain things usually
discussed in such a course, such as oxidation state, acid and basic
properties of compounds, formation of complexes. The information
given is, however, very concise. It was also necessary to present cer-
tain facts in the field of physics; these are given in the appendices
at the end of the book. In the appendices are also given the deduction
of a number of relationships and other information that can be omitt-
ed in an initial discussion of the problems considered.

The authors welcome any comments and suggestions that would
improve the contents of the book.

PART I

ATOMIC STRUCTURE

CHAPTER ONE

INTRODUCTION

1.1. Atoms

According to the latest investigations matter consists of protons, neutrons and other *elementary particles* that are now considered indivisible. Thanks to the powerful accelerators now available and the intensive study of cosmic rays, about 200 elementary particles have come to be known in the last decades. Sometimes instead of 'elementary particles', they are called ·fundamental units of matter'. *Atoms* are the simplest electrically neutral systems made up of elementary particles. More complex systems, *molecules*, consist of several atoms. Chemists deal with atoms which form *substances*, i.e., with atoms of the chemical elements; they are the smallest particles. of an element which can take part in a chemical reaction. An atom of an element consists of a positively charged *nucleus* containing *protons* and *neutrons* and of *electrons*[1] moving around the nucleus. Many atoms are *stable*, i.e., they can exist indefinitely. There are also a great many *radioactive* atoms that after the elapse of some time, are converted to other atoms as a result of changes that take place in the nucleus.

The number of electrons in neutral atoms of elements is equal to the positive charge of the nucleus (expressed in units of elementary charge). The charge carried by the nucleus is equal to the sum of the charges of the electrons and is opposite in sign to that of the latter. A positive ion is formed when one or more electrons are removed from an atom, while a negative ion is formed when an electron is added to it.

The number of electrons in an atom, and consequently the positive charge of its nucleus, determines the behaviour of atoms in chemical reactions. *A chemical element is a combination of atoms with identically charged nuclei.* The charge of the nucleus determines the position of an element in the Mendeleev Periodic System: *the atomic number of an element in the periodic system is equal to the positive charges on the nucleus of an atom of the element* (expressed in units of elementary electric charge).

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[1] There exist atoms that are positron-and-electron systems (positronium), meson-and-proton systems (mesoatoms), and others. The lifetime of such atoms is less than a millionth fraction of a second.

The ancient Greek philosophers already supposed that matter consists ultimately of indivisible discrete particles, atoms. The present concept of atoms as minute particles of chemical elements capable of combining to form larger particles, molecules, of which matter consists was first stated by M. Lomonosov in 1741 in his work "Elements of Mathematical Chemistry" and subsequently in other works. Although these works were published by the St. Petersburg Academy of Sciences whose publications were available to all the large libraries of that time, they were passed unnoticed by Lomonosov's contemporaries at the time.

At the beginning of the XIX century Dalton (England) stated that matter consists of atoms and that chemical action takes place between the atoms which combine in simple proportions. Dalton advanced the concept of relative masses of atoms (atomic weights) and pointed out the necessity of precisely determining these quantities. A few years after his works were published they attracted the attention of many researchers. From this time the atom-molecule concept has been widely used in chemistry and physics.

1.2. The Avogadro Number

The number of atoms in a gram-atom of any element is called the Avogadro number; this constant is denoted as N_0. The most exact determinations show that

$$N_0 = 6.02296 \cdot 10^{23} \text{g-at}^{-1}$$

This is also the number of molecules in a gram-molecule of any substance. This quantity equal to the ratio of the mass of a gram to $1/_{12}$ of the mass of the C^{12} atom is one of the most important *universal constants* in chemistry and physics; it does not depend on the nature of the substance or its state of aggregation (physical state).

The Avogadro number can be found by different absolutely independent methods; about 60 methods are known at present. We shall consider two of them: one of the most easy-to-understand and one of the most exact ones.

1. When certain radioactive elements decay (disintegrate), α-particles (nuclei of helium atoms) are emitted. These particles are detained by any material that lies in their path and, on adding two electrons, are converted to helium atoms. The amount of helium formed is not very great but it can be determined by micromethods. In this way it was found that 1 g of radium (containing decay products) yields 159 mm^3 of helium per annum or $5.03 \cdot 10^{-9}$ cm^3 He per second.

The α-particle from which the atom is formed possesses sufficient energy to produce a visible effect. For example, when α-particles impinge on a screen coated with zinc sulphide, scintillation is observed, which can be seen through a magnifying glass; this is made use of to count the number of α-particles. There are other methods of detecting and counting α-particles. Thus, the number of α-particles emitted by a very small but definite amount of radioactive substance can be counted. Since each α-particle is converted to a helium atom,

it is possible to calculate the number of atoms of helium obtained
from 1 g of the radioactive substance and if the volume of the helium
produced is known, it is easy to find the number of atoms contained
in 22.4 litres of helium measured under normal conditions. The
helium molecule is monoatomic and therefore the number of atoms
in a gram-molecular volume (also called molar volume) is equal to
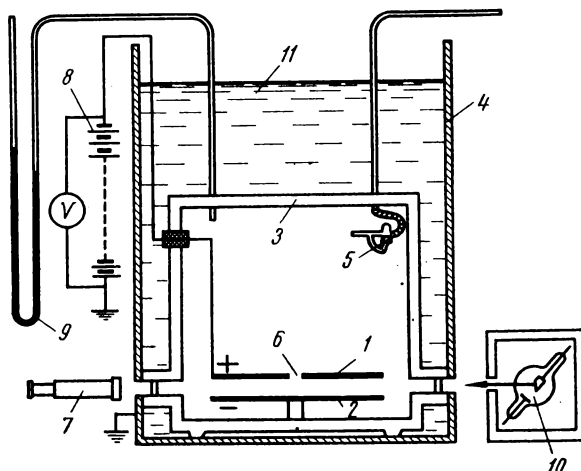
Fig. 1.1. Schematic drawing of layout used by Millikan to measure the charge
on the electron

1, 2—capacitor plates; *3*—metal chamber; *4*—thermostat; *5*—oil atomizer; *6*—aperture
in plate; *7*—eyepiece; *8*—storage batteries; *9*—pressure gauge; *10*—X-ray tube; *11*—thermostat
liquid (kerosene)

the number of molecules, i.e., to the Avogadro number. Such measu-
rements were first made by Rutherford and his co-workers in 1911.
They found that $N_0 = 6.1 \cdot 10^{23}$ which is very close to the value
established at the present time.

2. The Avogadro number can also be found with the aid of the
charge of an electron, which is a fundamental constant that is essen-
tial for the theory of the structure of matter.

The exact determination of the charge of the electron was first
effected in the years 1909-1914 by Millikan (USA).

A schematic diagram of the layout used by Millikan is shown in
Fig. 1.1. The main part of the layout was an electric capacitor
consisting of brass plates *1* and *2* contained in a metal chamber *3*
placed in a thermostat *4*. A fog composed of minute oil droplets was
created in the chamber by means of atomizer *5*. The droplets entered
the capacitor through aperture *6* in the upper plate. The motion of
the droplets between the plates could be viewed through eyepiece *7*.
Ionization was produced by exposing the air in the apparatus to

X-rays emitted from tube *10*. The free electrons (or positive ions) obtained in this way impinged on the oil droplets which received an electric charge e_d. By varying the voltage across the plates of the capacitor it was possible to attain such a voltage at which the electric field strength was balanced by the force of gravity of the charged droplet and the latter remained motionless in the field of view. Then

$$mg = e_d E \qquad (1.1)$$

where m = mass of the droplet
      g = acceleration due to gravity
      E = strength of the electric field
  For a plane capacitor

$$E = \frac{V}{d} \qquad (1.2)$$

where V = voltage applied to the plates
      d = distance between the plates
  From equations (1.1) and (1.2) it follows that

$$e_d = \frac{mgd}{V} \qquad (1.3)$$

wherefrom e_d can be found if the mass of the droplet is known (the mass of the droplet can be calculated from its velocity when falling in air in the absence of an electric field).

Millikan found that the charges on the droplets were always multiples of a certain value e, the smallest charge observed. This could be explained by the fact that a droplet can capture one, two, and so on electrons (or ions) but never a fraction of an electron because an electron is indivisible. Hence, the smallest charge of a droplet is the charge of an electron.

On taking a great number of measurements of the charge of an electron, Millikan obtained the following value:

$$e = 4.77 \cdot 10^{-10} \text{ esu}$$

This constant was subsequently determined more precisely. Its value is taken at the present time to be

$$e = 4.80286 \cdot 10^{-10} \text{ esu} = 1.60206 \cdot 10^{-19} \text{ coulomb}$$

This constant is of major importance to the chemist and physicist and can be used, in particular, to determine the Avogadro number.

Indeed, according to Faraday's law of electrolysis, it is necessary to pass a quantity of electricity equal to 1 faraday, or 96,491 coulombs, to liberate or deposit one gram-equivalent of a substance. This quantity of electricity is needed to produce from hydrochloric acid 1.008 g of hydrogen and 35.453 g of chlorine. Since in the electrolysis of HCl solution H^+ and Cl^- ions are discharged, each of which carries a charge equal to the charge of an electron, it is obvious

that the quotient obtained on dividing a faraday by the value of the charge of an electron shows how many atoms are contained in 35.453 g of chlorine or in 1.008 g of hydrogen, or in general, in a gram-atom of any element, i.e., gives the Avogadro number; hence,

$$N_0 = \frac{F}{e} \qquad (1.4)$$

where F = Faraday's constant (1 faraday). Thus,[1]

$$N_0 = \frac{96,491}{1.602 \cdot 10^{-19}} = 6.023 \cdot 10^{23}$$

The Avogadro number is enormous. If we were to gather peas in a quantity equal to the Avogadro number, and if we assumed that the volume of a pea is equal to 0.3 cm³, such a number of peas would occupy a volume equal to $0.3 \cdot 6.023 \cdot 10^{23} = 1.8 \cdot 10^{23}$ cm³ = = $1.8 \cdot 10^8$ km³. Each side of a cubic container of such a capacity would be equal to 565 km.

Two conclusions that are very important to the chemist can be drawn from the fact that the Avogadro number is so great.

1. Even very small quantities of a substance that are hardly discernible in an optical microscope contain an enormous number of atoms. That is why, macroscopically, substances seem to be continuous.

2. Any substance, even the purest one, always contains some impurities, i.e., alien atoms (atoms of different elements). At present it is impossible to obtain an appreciable amount of a pure substance that is absolutely free of impurities. Certain substances (silicon, germanium, and others) can now be obtained that contain impurities in an amount equal to 10^{-6} per cent and even from 10^{-7} to 10^{-8} per cent. But even such extra-pure substances contain milliards of alien atoms per gram.

1.3. Mass and Size of Atoms

The mass in grams and dimensions of any atom can be found from the Avogadro number. The mass of the atom m is found by dividing the gram-atomic weight[2] A by the Avogadro number:

$$m = \frac{A}{N_0}$$

[1] The descriptions of the methods for determining the Avogadro number are somewhat simplified here. Those who want to acquaint themselves with all the details of the experiments and calculations involved can do so in the following books: *R. Millikan*. Electrons (+ and —), Protons, Photons, Neutrons, and Cosmic Rays; *E. Guggenheim* and *G. Prue*. Physico-Chemical Calculations, Interscience publishers inc. New York.

[2] The terms 'atomic weight', 'molecular weight' are not absolutely correct; it would be more exact to say 'relative atomic mass', 'relative molecular mass'. However, the terms 'atomic weight', 'molecular weight' are consistently used in the chemical literature and shall be used in this book.

Hence, the mass of the hydrogen atom, for instance, is

$$m_{\mathrm{H}} = \frac{1.008}{6.023 \cdot 10^{23}} = 1.673 \cdot 10^{-24} \ \mathrm{g}$$

The mass of the uranium atom (mass number 238) is

$$m_{\mathrm{U}} = \frac{238}{6.023 \cdot 10^{23}} = 3.95 \cdot 10^{-22} \ \mathrm{g}$$

If we divide the volume of a gram-atom of an elementary substance in the solid state by the Avogadro number, we will obtain the volume v per 1 atom. The atom can be assumed to be a sphere enclosed in a cube of a volume equal to v. Since the atoms in solid bodies are very close to each other, such an assumption will not lead to considerable error. Then the diameter of the atom can be found by taking the cubic root of the volume occupied by 1 atom. Let us calculate the diameter of the copper atom.

The density of copper is equal to 8.93 g/cm³; therefore, a gram-atom of copper is equal to 63.46/8.93 = 7.10 cm³ wherefrom

$$v_{\mathrm{Cu}} = \frac{7.10}{6.023 \cdot 10^{23}} = 1.178 \cdot 10^{-23} \ \mathrm{cm^3}$$

and

$$d_{\mathrm{Cu}} \approx \sqrt[3]{v_{\mathrm{Cu}}} = \sqrt[3]{1.178 \cdot 10^{-23}} = 2.28 \cdot 10^{-8} \ \mathrm{cm}$$

Hence, the radius of the copper atom is approximately $1.14 \cdot 10^{-8}$ cm.

To find the exact dimensions of atoms it is necessary to know how they are arranged in the crystals of the solid substance; this is determined by X-ray diffraction analysis of crystal structure (see pp. 273-277). Diffraction data have shown that for most metals, including copper, the atoms are arranged the same as the most closely packed balls (see pp. 281-282); in this case the volume of the balls constitutes 74 per cent of the total volume of the space occupied by them. The exact value of the radius of the copper atom in a crystal can be found as follows.

The volume of the copper atom is $v_{\mathrm{Cu}} = 1.178 \cdot 10^{-23} \cdot 0.74 = 0.870 \cdot 10^{-23}$ cm³ and hence

$$r_{\mathrm{Cu}} = \sqrt[3]{\frac{3}{4} \frac{v_{\mathrm{Cu}}}{\pi}} = \sqrt[3]{\frac{3 \cdot 0.870 \cdot 10^{-23}}{4 \cdot 3.14}} = 1.28 \cdot 10^{-8} \ \mathrm{cm}$$

As can be seen, the exact value of the radius of the copper atom in a crystal does not differ appreciably from the approximate value determined above.

It should be noted that there is no clear demarcation between the atoms and the space surrounding them (this will be discussed at length later on). Therefore, the dimensions of atoms are given conventionally. Here, by the dimensions of the atoms are implied their radii in the crystals of the respective simple substances. The radius of

the atom is taken to be half the distance between the nuclei of neighbouring atoms.

The radii of all atoms have a value of the same order, 10^{-8} cm. In the theory of atomic structure it is convenient therefore to use a unit equal to 10^{-8} cm which is called the Ångström unit (or simply angstrom) and denoted as Å. Thus, $r_{Cu} = 1.28$ Å .

As can be seen, atoms are extremely small. Millions of copper atoms arranged in a row would form a chain that is only 0.26 mm long.

1.4. The Constituents of an Atom: Electrons and the Nucleus

As has already been stated, the atoms of chemical elements consist of a nucleus and of electrons moving around it. The properties of electrons were studied after these particles were isolated from matter
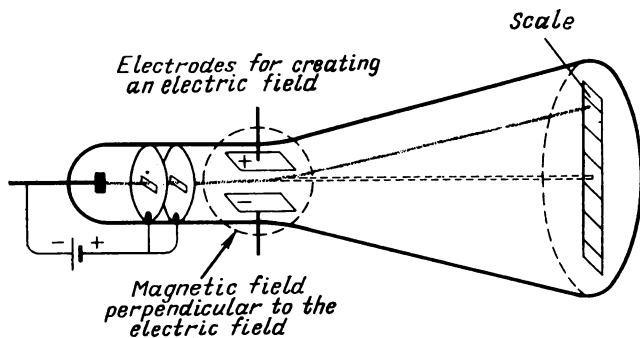
Fig. 1.2. Schematic drawing of apparatus for determining the value e/m for electrons

as cathode rays in the second half of the last century. At first the ratio of the charge of the electron to its mass, e/m_e, was measured. This ratio is determined by the deflection of a beam of electrons in electric and magnetic fields. Such measurements were first made in 1897 by J. Thomson (England). A schematic drawing of the apparatus used is shown in Fig. 1.2. Cathode ray tubes of a similar design are now being widely used (for example, in television sets). The theory on which this method is based is briefly given in Appendix I. With the aid of these experiments it was found that

$$\frac{e}{m_e} = 5.273 \cdot 10^{17} \text{ esu/g}$$

The electron charge is determined by the method described above. The mass of the electron can be calculated if e/m_e and e are known.

It proved to be

$$m_e = 0.9109 \cdot 10^{-27} \text{ g}$$

Let us compare this value with the mass of the hydrogen atom, already calculated (see p. 16):

$$\frac{m_e}{m_\text{H}} = \frac{0.9109 \cdot 10^{-27}}{1.673 \cdot 10^{-24}} = \frac{1}{1837}$$

We see that the mass of an electron is extremely small as compared to the mass of the lightest atom. Consequently, almost all the mass of the atom resides in its nucleus. The nucleus is very small; whereas the radius of an atom is of the order of 10^{-8} cm, the radius of the nucleus of the atom is within the limits of 10^{-13} to 10^{-12} cm. The nucleus and the electrons, being charged particles, create an electric field that 'fills' the space 'inside' the atom and surrounds it beyond its 'limiting boundary'. The electric field produced is material like the nucleus, electrons, and other particles are.

The presence of the nucleus in the atom was experimentally proved in 1909-1911 by Rutherford and his co-workers (England). When investigating the passage of α-particles through very thin metal films, they unexpectedly discovered that a certain part of the α-particles (approximately 1 out of 10,000) did not pass through the foil but were thrown back. This could be explained only by the collision of the α-particles with a massive positively charged particle, the nucleus of the atom.

The nucleus of the atom consists of two kinds of elementary particles, *protons* and *neutrons*; this concept of the structure of the nucleus was first stated and proved in 1932 by D. Ivanenko and E. Gapon (USSR), and Heisenberg (Germany). The proton is the nucleus of the hydrogen isotope $_1^1\text{H}$; it carries a positive charge equal in magnitude and opposite in sign to that of the electron. The neutron is an uncharged particle. The proton and neutron are approximately equal in mass, being respectively 1836.12 and 1838.65 times as massive as the electron. The charge on the nucleus is determined by the number of protons in it; the sum of the number of protons Z and the number of neutrons N gives the *mass number A*:

$$A = Z + N$$

Atoms of the same element having different nuclear masses but identical nuclear charges are called *isotopes*[1]. The isotopes of a given element differ from one another by the number of neutrons in the nuclei of their atoms.

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[1] The Greek word 'isotopes' means equally positioned (i.e., they occupy the same position in the periodic system).

CHAPTER TWO

ATOMIC SPECTRA

The study of the spectra of chemical elements constitutes the experimental basis of the theory of atomic structure. At present, the wavelengths of spectral lines can be measured with an accuracy of 0.001 per cent; in many investigations the accuracy is considerably higher. The spectral-line *intensities* can also be determined very precisely. Thus, our knowledge of the structure of atoms is based on very reliable experimental data.

2.1. Principle of Operation of Spectrographs; Kinds of Spectra

In the spectrograph the beam of light passing through a narrow slit is rendered parallel by a collimating lens and falls on a prism or diffraction grating, where it is dispersed into its constituent rays which are then focused on different parts of the photographic plate,
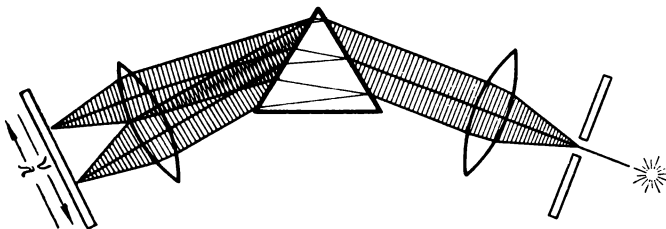
Fig. 2.1. Schematic drawing of spectrograph

according to their wavelength. Visible and ultraviolet radiation is usually investigated by means of *optical spectrographs* in which the radiation is dispersed by passing it through a glass prism (for visible light) or quartz prism (for ultraviolet radiation). A schematic drawing of the spectrograph is shown in Fig. 2.1. Light is dispersed due to the fact that the refractive index varies with the wavelength of light; for most media the index of refraction decreases with an increase in the wavelength.

The spectra obtained by dispersing the radiation emitted by bodies are called *emission spectra*. These may be *continuous*, *line*, and *band spectra*. Continuous spectra are obtained from glowing solids and liquids. The radiation of gases (which can be produced by heating them or with the aid of an electric discharge) gives a line spectrum consisting of separate lines or a band spectrum consisting of bands[1].

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[1] Many gases (H_2, Cl_2, and others) through the agency of heat or an electric discharge give continuous spectra in addition to line (or band) spectra.

The use of high-resolution spectrographs has shown that these bands consist of a great number of lines that are very close to each other. At the present time it has been established that *line spectra are obtained from the radiation emitted by atoms; while band spectra, from radiation emitted by molecules*. The atom of every element and the molecule of every substance, each has its characteristic spectrum which consists of a definite set of lines or bands that correspond to strictly definite wavelengths. In this Chapter we will consider *atomic spectra*. Examples of such spectra are shown in Fig. 2.2 in which wavelength (λ) and wave number ($\bar{v}$)[1] scales are plotted.
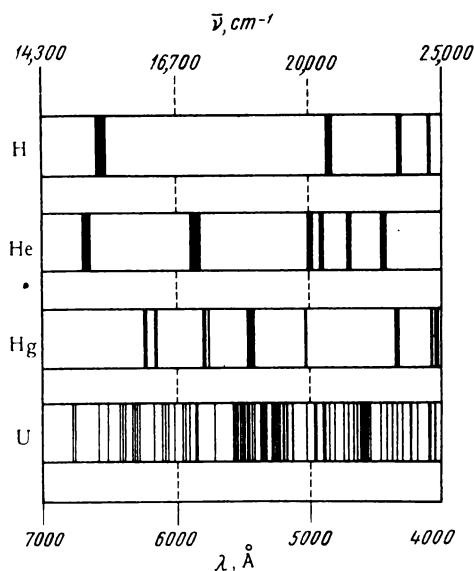
The spectra of many elements are very complex. For example, there are over five thousand lines in the spectrum of iron. Work

Fig. 2.2. Schematic representation of spectra of certain elements

The lines are of different thickness to show their relative intensity; actually the lines are of the same thickness, corresponding to the width of the spectrograph slit. Only the most intense lines are shown so as not to make the drawing too complicated

carried out with sensitive apparatus has shown that many lines in atomic spectra actually consist of several lines that are very close to each other, i.e., they are *multiplets*: double lines are called *doublets*; triple lines, *triplets* (single lines are called *singlets*). If the source of radiation is placed in a magnetic field, single lines are split and, instead of one line, a few adjacent lines will appear in the spectrum (*Zeeman effect*). A similar effect is observed when the radiation source is placed in an electric field (*Stark effect*).

2.2. The Atomic Spectrum of Hydrogen

The simplest spectrum is that of hydrogen. In the visible region there are only 4 lines (see Fig. 2.2); they are denoted as H_α, H_β, H_γ and H_δ. In the near ultraviolet region there are a number of

---

[1] The wave number $\bar{v}$ is the reciprocal of the wavelength; $\bar{v} = 1/\lambda$, i.e. the number of waves in a centimetre; it characterizes the frequency of vibrations (see Appendix II).

other lines that together with the aforementioned four lines form a series (Fig. 2.3) that is called the *Balmer series* after the Swiss scientist who in 1885 discovered that the wave numbers $\bar{\nu}$ of the lines in this series are expressed exactly by the following formula:

$$\bar{\nu} = \frac{R}{2^2} - \frac{R}{n^2}$$

where $R = 109{,}678$ cm^{-1} and $n = 3, 4, 5, \ldots$ The constant R in this formula is called the *Rydberg constant*.

Investigation of the hydrogen spectrum in the far ultraviolet and infrared regions revealed the presence of a few other series of

Fig. 2.3. Atomic spectrum of hydrogen in the visible and near ultraviolet regions (Balmer series)
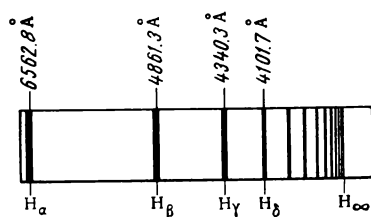
lines called by the names of the men who investigated them: the *Lyman* (ultraviolet region), *Paschen, Brackett,* and *Pfund* (infrared region) *series.* It was found that the wave numbers of the lines in these spectra are given by formulae similar to the Balmer formula, but which instead of 2^2 contained 1^2, 3^2, 4^2, and 5^2, respectively.

Therefore, the universal formula for the atomic spectrum of hydrogen is

$$\bar{\nu} = \frac{R}{n_1^2} - \frac{R}{n_2^2} \tag{2.1}$$

where n_1 and n_2 are whole numbers and $n_2 > n_1$. As seen from equation (2.1), the number of lines in the hydrogen spectrum is infinitely large (at the edges of the series which correspond to large values of n_2, the lines are very close to each other and cannot be distinguished from one other). Thus, a very simple formula describes the large number of lines observed in the spectrum of hydrogen.

2.3. The Spectra of Other Elements

Series of lines were found in the spectra of all the other elements. The spectra, however, were more complex because, unlike the hydrogen spectrum, the series are not arranged separately in different parts of the spectrum but are superimposed on one another. Nevertheless, they can be discerned by spectroscopists according to certain criteria such as the appearance of the lines (sharp or diffuse), the mode of excitation (arc or spark), multiplicity, the way they are split in magnetic and electric fields, etc.

In 1889 Rydberg (Sweden) found that the wave numbers of a particular spectral series can always be expressed as the difference between two functions of the integers n_1 and n_2:

$$\bar{\nu} = T\,(n_1) - T\,(n_2) \qquad (2.2)$$

where $n_2 > n_1$. The numerical values of these functions are called *spectral terms*.

For the hydrogen atom, the single-charged helium ion He$^+$, the double-charged Li^{2+} ion, and other particles containing only one electron the spectral term is given by the formula

$$T = \frac{RZ^2}{n^2} \qquad (2.3)$$

For the hydrogen atom, $Z = 1$; for the single-charged He$^+$ ion, $Z = 2$; for the double-charged Li^{2+} ion, $Z = 3$; etc. For the atoms of other elements, the terms can be expressed by the formula

$$T = \frac{RZ^2}{(n+\alpha)^2} \qquad (2.4)$$

where α is a fraction smaller than unity; it is a constant for the lines of a particular series[1]. The correction α for different series is denoted as s, p, d, f, i. e., the first letters in the names of the series: 'sharp', 'principal', 'diffuse', 'fundamental', respectively. As in equation (2.3), $Z = 1$ for neutral atoms; $Z = 2$ for single-charged ions, etc.

Thus, it was discovered that the vast number of spectral lines is described by relatively simple relations that *contain integer parameters*.

2.4. The Concept of Light Quantum

In 1900 Planck (Germany), in order to explain the distribution of energy in the spectra of heated bodies, developed a theory based on the assumption that energy is not emitted by atoms continuously but only in minimum indivisible quantities called *quanta*, the value of which depends on the frequency of the light emitted. According to *Planck's formula*

$$E = h\nu \qquad (2.5)$$

where E = energy of a quantum
ν = frequency of vibrations
h = *Planck's constant*

$$h = 6.62517 \cdot 10^{-27} \text{ erg-s}$$

---

[1] Equation (2.4) is most precise for the spectra of alkali metals; for the other elements there is a slight difference between the calculated and experimental values, but this discrepancy can be eliminated by introducing, in addition to α, another small correction to the integer n.

Thus, the energy of a body can change by values that are multiples of $h\nu$, just as the electric charge can change by a value that is a · a multiple of the charge of an electron.

Experimental data splendidly confirmed Planck's theory. Planck's formula expresses one of the most important laws of nature. Planck's constant, like the velocity of light and the charge of the electron, is a *fundamental constant* which cannot be expressed by any other simpler parameter.

Since every spectral line is characterized by a strictly definite wavelength, and consequently by a strictly definite frequency, this signifies that atoms can radiate only a strictly definite amount of energy which can be calculated for a given spectral line from Planck's formula. For example, for the H_α line (see Fig. 2.3)

$$\lambda = 6562.8 \text{ Å} = 0.656 \cdot 10^{-4} \text{ cm}$$

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \cdot 10^{10}}{0.656 \cdot 10^{-4}} = 4.57 \cdot 10^{14} \text{ s}^{-1}$$

where c = velocity of light; according to equation (2.5)

$$E = 6.625 \cdot 10^{-27} \cdot 4.57 \cdot 10^{14} = 3.03 \cdot 10^{-12} \text{ erg}$$

which shows that the energy of a quantum of visible light is a very small quantity.

When an atom radiates a light quantum, it passes from one energy state to another. Hence, the physical meaning of spectral terms lies in the fact that the *terms characterize the energy levels of the electrons in atoms*[1]. Thus, we come to the conclusion that the *electrons in atoms can have only strictly definite values of energy which are characterized by a series of integers*.

It follows from equations (2.2) and (2.5) that the energy of electrons in atoms is related to the values of the respective terms according to the equation

$$E = -hcT \qquad (2.6)$$

The energy is taken with a minus sign because it is assumed that when the electron is at an infinitely great distance from the atom it is in a state of zero energy; therefore, the energy of the electron in the atom is always less than zero.

It follows from equation (2.3) that equation (2.6) for the hydrogen atom will be

$$E = -\frac{hcR}{n^2} \qquad (2.7)$$

---

[1] The nucleus, being considerably heavier than the electrons, may be deemed to be at rest and therefore all the energy changes in the atom that do not affect the structure of the nucleus can be regarded as energy changes of the electrons (kinetic and potential energy).

The energy levels of the electron in the hydrogen atom is schematically represented in Fig. 2.4. The energy is expressed in electronvolts; this is a very convenient unit to use for atoms. *An electron-volt*
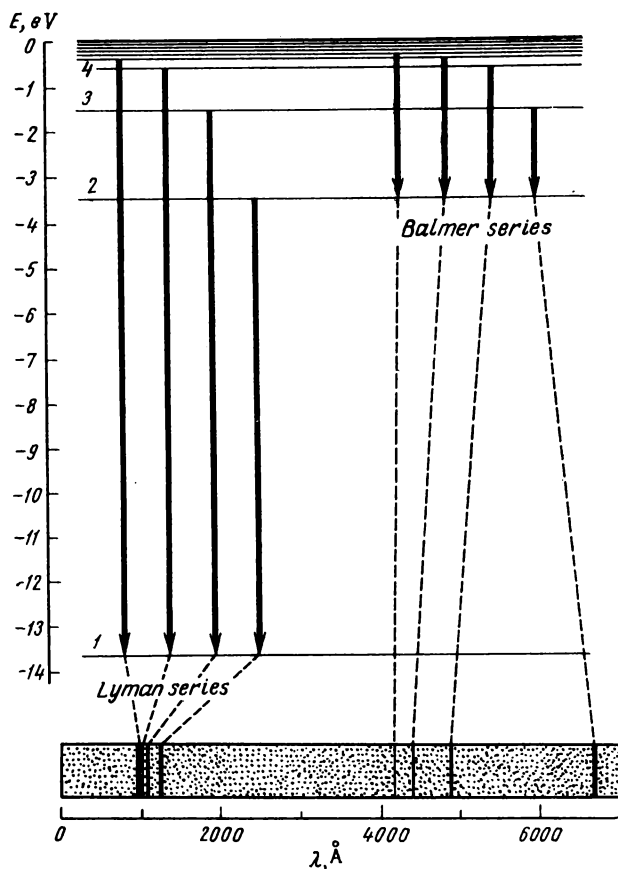
Fig. 2.4. Energy levels of the electron in the hydrogen atom

(eV) *is the energy gained by an electron which is accelerated by an electric field in the region with a potential difference of one volt:*

$$1 \text{ eV} = 1.6021 \cdot 10^{-12} \text{ erg}$$

Besides the spectral data obtained, there are many other facts that afford evidence that electrons in atoms possess strictly definite energies. This is confirmed, in particular, by the results of experiments first carried out in 1912 by Franck and Hertz to study *electron bombardment.*

In these experiments Franck and Hertz bombarded the atoms of gases (vapours of mercury, krypton, and others) with electrons and measured the loss in

energy of the electrons on colliding with the atoms of the gas. The experiments showed that if the energies of the electrons are less than a certain value, they rebound from the atoms of the gas, practically without transferring energy to them. This, for example, occurs when mercury vapours are bombarded by electrons with an energy less than 4.9 eV. When the energy of the bombarding electrons is greater than 4.9 eV, their energy is transferred to the mercury atoms. From this it can be concluded that 4.9 eV is the energy needed to transfer an electron of the mercury atom from the lowest energy level to the next energy level.

When mercury atoms are bombarded with electrons with an energy of 4.9 eV or greater, radiation of a wavelength of 2537 Å is observed, which corresponds to the energy of a quantum equal to 4.87 eV; this value practically coincides with the energy of electrons required to induce radiation (4.9 eV). This can be explained by the fact that the electrons of atoms which have been transferred to a higher energy level by electron bombardment, are transferred back to the lower energy level and emit a quantum of radiant energy.

With the aid of more powerful electron bombardment the electrons of the atoms can be transferred to the third, fourth, etc. levels; this is indicated by absorption of the energy of the bombarding electrons. When a certain amount of energy is transmitted, the electrons break away from the atoms and ionization of the gas takes place. By this method it was established that an energy of 10.4 eV is necessary for the ionization of the mercury atom.

Thus, experimental data show that a definite set of energy levels exist in the atoms of elements.

2.5. History of the Development of the Concepts of Atomic Structure

Rutherford, after establishing the presence of a nucleus in the atom in 1911, proposed the *planetary model of the atom* in which the electrons revolve around the nucleus like planets revolve around the Sun. From electrodynamics it is known however that a charge revolving around a certain centre is a source of electromagnetic waves and therefore a radiating electron would continuously lose energy and eventually fall onto the nucleus. In 1913 Bohr (Denmark) suggested that there are *stationary orbits* in atoms, in which the electron moves without radiating energy; according to Bohr, for such orbits the following equation must be satisfied:

$$m_e v r = n \frac{h}{2\pi} \tag{2.8}$$

where m_e = mass of electron
$\quad\quad v$ = velocity of electron
$\quad\quad r$ = radius of the orbit
$\quad m_e v r$ = *angular momentum* of the electron[1]
$\quad\quad n$ = 1, 2, 3, . . .
$\quad\quad h$ = Planck's constant

---

[1] The angular momentum of a particle rotating in a circle with a radius r is equal to *mvr* where *m* and *v* are the mass and velocity of the particle, respectively. In the general case, the angular momentum of a material point relative to any centre O is equal to the product of the mass and the distance r between

The value $h/2\pi$ is designated as $\hbar$ (crossed h), then

$$m_e v r = n\hbar \qquad (2.9)$$

Proceeding from this hypothesis, Bohr was able to develop his theory of the structure of the hydrogen atom. Indeed, by equating the centripetal force and attractive force of the electron to the nucleus, we can write

$$\frac{m_e v^2}{r} = \frac{e^2}{r^2} \qquad (2.10)$$

By solving the system of equations (2.9) and (2.10), we can find the velocity of the electron in a stationary orbit

$$v = \frac{e^2}{n\hbar} \qquad (2.11)$$

and the radius

$$r = \frac{n^2\hbar^2}{m_e e^2} \qquad (2.12)$$

By substituting the known values into equation (2.12), we find that

$$r = 0.529 n^2 \text{ Å} \qquad (2.13)$$

Consequently, the radius of the first Bohr orbit is 0.529 Å; the order of this value conforms with that of the known values of the sizes of atoms (see p. 17).

The energy of an electron is the sum of its kinetic and potential energies. The potential energy[1] of a system of two bodies with charges e is equal to $-e^2/r$. Hence,

$$E = \frac{m_e v^2}{2} + \left(-\frac{e^2}{r} \right) \qquad (2.14)$$

---

the particle and the centre O and the projection of its velocity on the line lying in the plane of motion perpendicular to r. The concept of angular momentum is extensively used in the theory of atomic structure. The angular momentum (also called the moment of rotation) is a vector quantity; it is directed perpendicular to the plane in which rotation occurs.

[1] The potential energy of two differently charged bodies with charges e_1 and e_2, which are at a distance r from each other, is determined by the work necessary to move these bodies from the position at which the potential energy is zero (corresponding to $r = \infty$) to the given distance r; this work, in accordance with Coulomb's law, is expressed by the integral

$$\int_{\infty}^{r} \frac{e_1 e_2}{r^2} \, dr = -\frac{e_1 e_2}{r}$$

When the charges of the bodies are of the same magnitude, as in our case, the potential energy is equal to $-e^2/r$.

Substituting the values of v and r from equations (2.11) and (2.12), respectively, we obtain

$$E = -\frac{1}{2}\frac{m_e e^4}{n^2 \hbar^2} = -\frac{\text{const}}{n^2} \tag{2.15}$$

i.e., the equation obtained resembles the one for the energy levels in the hydrogen atom [see equation (2.7)]. By equating these expressions, we can find the theoretical equation for the Rydberg constant:

$$R = \frac{2\pi^2 m_e e^4}{ch^3} \tag{2.16}$$

The value of R calculated from this equation coincides with that found experimentally.

In this way Bohr calculated theoretically the spectrum of hydrogen.

Later on (1916-1925) Sommerfeld (Germany) and other scientists developed a theory of the structure of many-electron atoms, based on the Bohr theory. It was assumed that the stationary orbits in atoms could be not only circular but also elliptical and be positioned differently in space; the size of the orbits and their position in space were determined by *quantization rules*, a generalization of equation (2.9). Many characteristics of the atomic spectra could be explained with the aid of this theory.

The Bohr—Sommerfeld theory, however, does not satisfy the present state of the art. Although it does explain many characteristics of the spectra, it has many faults because of which it must be replaced by modern concepts. The main faults of the Bohr—Sommerfeld theory are as follows.

1. It is based on quantization rules which do not stem from the laws of mechanics and electrodynamics.

2. The use of this theory in calculating a number of spectral characteristics, in particular, the intensity of spectral lines and their multiplet structure, yields results that do not agree with those obtained experimentally.

3. The Bohr—Sommerfeld theory when used for the calculation of the energy of electrons in many-electron atoms, also fails to give results that coincide with those obtained in experiments (even for the simplest case, the He atom).

4. It was found that this theory could not be used for the quantitative explanation of chemical bonding. Thus, the calculation of the bond strength (bond-breaking energy) in the simplest system, the ionized molecule H_2^+, gave a negative value, i.e., showed that such an ion cannot exist. Actually, however, it does exist and the bond strength in this case is equal to +61 kcal/mole (see p. 203).

CHAPTER THREE

THE WAVE PROPERTIES OF MATERIAL PARTICLES

The modern theory of the structure of atoms and molecules is based on laws describing the motion of electrons and other particles of very small mass, i.e., of *microobjects*. These laws were definitely formulated in 1925-1926; they differ greatly from the laws governing the motion of *macroobjects* which include all objects that are visible in an optical microscope or to the naked eye.

The basis of the modern theory lies in the concept of the dual nature of microobjects: they can be regarded as particles and as waves, i.e., *microobjects simultaneously have the properties of particles and waves.*

3.1. Dual Nature of Light

The dual wave-particle picture was first established for light. In the first half of the last century, as a result of *interference* and *diffraction* studies, it was experimentally proved that light consists of transverse electromagnetic vibrations. The occurrence of interference and diffraction under certain conditions is characteristic of any wave process (see Appendix II).

However, in the XX century a great number of phenomena became known, that showed that light consists of a stream of material particles which were named *light quanta* or *photons*.

The concept of the quantum, as has already been stated, was first introduced in 1900 by Planck. The corpuscular properties of light are most clearly manifested in two phenomena: the *photoelectric effect* and the *Compton effect*.

The photoelectric effect, which was discovered in 1887 by Hertz and developed by A. Stoletov, consists in the fact that metals (and semiconductors) emit electrons when exposed to light. The photoelectric effect cannot be explained by the wave theory of light. Calculations show that due to the extremely small size of the electron, the quantity of energy transmitted to it by the electromagnetic waves that fall on it is so small that in order that the electrons accumulate sufficient energy to leave the metal the latter would have to be exposed to sunlight for no less than several hours (and that only in the absence of transfer of the energy absorbed by the electrons to the atoms). Emission of electrons, however, is observed immediately after the metal is illuminated. Besides that, according to the wave theory, the energy E_e of the electrons emitted by the metal should be proportional to the intensity of the incident light. It was, however, established that E_e does not depend on the intensity of the light, but depends on its frequency; E_e increases with ν but an increase in the intensity of light only causes a greater number of electrons to be emitted from the metal.

In 1905 Einstein showed that the photoelectric effect could be explained very simply if light were regarded as a stream of particles, photons. The photons on colliding with the electrons transmit to them their energy equal to $h\nu$ in accordance with Planck's formula; this also explained why radiation of long wavelengths does not produce the photoelectric effect; the reason for this is that the energy of the photon in this case is not sufficient to tear the electron away from the metal.

Those electrons that escaped without giving up to the atoms of the metal any of the energy they received from the photons will

Fig. 3.1. Dependence of the voltage at which the photo-electric current is discontinued on the frequency of the incident light (for cae-sium)
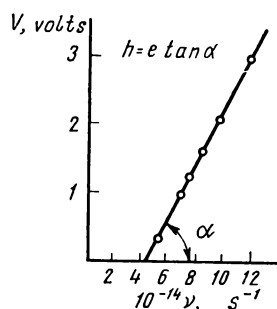
have the maximum energy. Obviously, the energy of such electrons is equal to the difference between the energy of a photon $h\nu$ and the work required to overcome the force retaining the electron in the metal, i.e., *the work function of the electron* W; hence,

$$(E_e)_{\max} = h\nu - W \tag{3.1}$$

This equation, called *Einstein's law for the photoelectric effect*, is fully consistent with experimental data. It was very thoroughly checked experimentally in 1916 by Millikan. The maximum energy of the emitted electrons was measured by applying an external electric field at which the photoelectric current is discontinued; the applied voltage does not allow the electrons to reach the electrode, and in this case

$$Ve = \frac{1}{2} m_e v^2 = (E_e)_{\max} \tag{3.2}$$

where m_e, e, and v are respectively the mass, charge and velocity of the electron; V is the potential difference of the electric field.

Planck's constant can be found on the basis of Einstein's law; for this purpose it is necessary to determine the dependence of $(E_e)_{\max}$ on the frequency of the incident light. This dependence for caesium, found experimentally, is represented in Fig. 3.1. As can be seen from equations (3.1) and (3.2), the tangent of the slope in the

V—v coordinates is equal to h/e. This method is one of the most exact ones for determining Planck's constant.

Prior to passing on to the discussion of the other phenomenon indicative of the corpuscular nature of light, the Compton effect, it is necessary to say something about the law of interdependence of mass and energy.

3.2. The Law of Interdependence of Mass and Energy

In 1903, with the aid of his *relativity theory*, Einstein proved that the mass of a body in motion exceeds its mass at rest, according to the equation

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad (3.3)$$

where m = mass of the body in motion

m_0 = mass of the body at rest

v = velocity of the body

c = velocity of light in vacuum

Hence, an increase in the velocity of the body, and consequently an increase in its energy, results in an increase in its mass.

Einstein also showed that the mass of a body is related to its energy according to the equation

$$E = mc^2 \qquad (3.4)$$

The above equation expresses the *law of interdependence of mass and energy*, i.e., it shows how mass and energy are related to each other; prior to the appearance of the relativity theory, they were deemed to be independent quantities. Equation (3.4) shows the interdependence of changes in mass Δm and energy ΔE in any process; thus, the equation can also be written as $\Delta E = \Delta mc^2$.

It cannot be concluded from equation (3.4) that mass can be converted to energy or, all the more, that matter can be converted to energy. Mass and energy are merely different properties of matter. The first is a measure of its inertness; the second, a measure of motion. Therefore, they cannot be reduced to one another, nor can they be converted to each other. The conversion of matter to motion would imply the possibility of motion without matter, which is of course absurd. Equation (3.4) only shows that one of the characteristics of material bodies, their mass, depends on their motion.

The relationship between the wavelength of light and the mass of a photon can be determined by Planck's and Einstein's formulae.

The photon has no rest mass; this is due to the fact that it moves with the velocity of light (if the mass were at rest, then in accordance with equation (3.3) the mass and energy of a photon would

be infinitely large). Therefore, all the mass of a photon is dynamic, i.e., due to motion[1], and can be calculated from the energy of a photon by means of equation (3.4).

On the other hand, according to Planck's formula

$$E = h\nu = h\frac{c}{\lambda} \tag{3.5}$$

Combining this equation with equation (3.4), we obtain

$$mc^2 = h\frac{c}{\lambda}$$

wherefrom

$$\lambda = \frac{h}{mc} \tag{3.6}$$

This equation expresses the interdependence of the *momentum*[2] of a photon mc and the wavelength of light. It can be written as

$$\lambda = \frac{h}{p} \tag{3.7}$$

where p = momentum (impulse) of a photon.

3.3. Compton Effect

In this phenomenon, when a photon collides with an electron it gives up part of its energy to it; as a result, the radiation is scattered and its wavelength is increased. This effect was discovered by Compton (USA) in 1923. He found that when various substances are exposed to X-rays, the wavelength of the scattered radiation is greater than the original wavelength. The change in the wavelength $\Delta\lambda$ does not depend on the nature of the substance or the wavelength of the original radiation; it is always a definite value that is determined by the scattering angle φ (the angle between the directions of the scattered and original radiations).

It was found that the equation for the precise expression of the Compton effect could be derived if the interaction of a photon and an electron be regarded as an elastic collision of two particles, in which the laws of conservation of energy and impulse are observed. Below we will show how the equation is derived; the derivation is somewhat simplified.

Let us suppose that a photon of energy $h\nu$ (Fig. 3.2a) collides with an electron, the energy and momentum of which are taken to be

---

[1] This conclusion may seem strange to the beginner, but it merely means that a motionless photon does not exist, i.e., that light is always in motion.

[2] The momentum (or *impulse*) of a particle is the product of its mass and velocity. The momentum, in contrast to energy, is a vector quantity; its direction coincides with the direction of the velocity.

zero. After the collision the energy of the photon becomes $h\nu'$ and the scattered photon moves at an angle φ to the original direction. The electron that has obtained from the photon a certain amount of energy, the *recoil electron*, moves in a direction that is at an angle θ to the direction of the original photon.
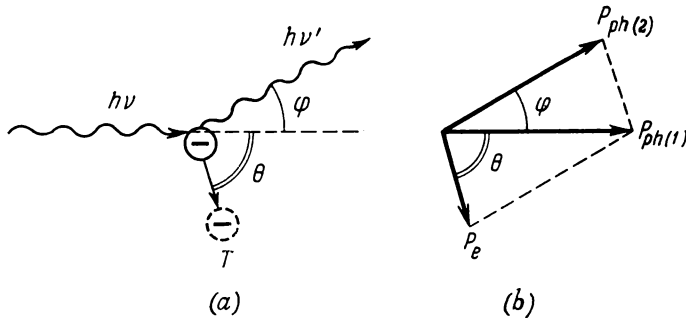

Fig. 3.2. Explanation of the Compton effect

(a) schematic representation of the motion of the photon and electron; (b) vector addition of momenta of the recoil electron and scattered photon

According to the law of conservation of energy, the kinetic energy of the recoil electron T is given by the equation

$$T = h\nu - h\nu' = -h(\nu' - \nu) = -h\Delta\nu \qquad (3.8)$$

The kinetic energy of a particle, equal to $\frac{1}{2}mv^2$, where m and v are the mass and velocity of the particle, respectively, is related to its momentum $p = mv$ according to equation

$$T = \frac{p^2}{2m} \qquad (3.9)$$

Combining equations (3.8) and (3.9) we find that the equation for the momentum of the recoil electron is

$$p_e^2 = -2m_e h\Delta\nu \qquad (3.10)$$

According to the law of conservation of momentum, the sum of the vectors of the momenta of the scattered photon and recoil electron is equal to the momentum of the original photon (Fig. 3.2b). Applying the cosine theorem we obtain

$$p_e^2 = p_{ph\,(1)}^2 + p_{ph\,(2)}^2 - 2p_{ph\,(1)}p_{ph\,(2)}\cos\varphi \qquad (3.11)$$

where $p_{ph\,(1)}$ and $p_{ph\,(2)}$ are the magnitudes of the impulses of the original and scattered photons. The difference between these magnitudes is negligible and therefore it can be taken that

$$p_{ph\,(1)}^2 \approx p_{ph\,(2)}^2$$

Then equation (3.11) can be written as

$$p_e^2 = 2p_{ph\,(1)}^2 \, (1 - \cos \varphi)$$

And since

$$1 - \cos \varphi = 2 \sin^2 \frac{\varphi}{2}$$

it can be written that

$$p_e^2 = 4p_{ph\,(1)}^2 \sin^2 \frac{\varphi}{2} \qquad (3.12)$$

The momentum of a photon, according to equation (3.7), is determined by the equation

$$p = \frac{h}{\lambda} = \frac{h\nu}{c} \qquad (3.13)$$

Substituting the expression for $p_{ph\,(1)}$ from equation (3.13) into equation (3.12) we obtain

$$p_e^2 = 4 \, \frac{h^2\nu^2}{c^2} \sin^2 \frac{\varphi}{2} \qquad (3.14)$$

Equating the right-hand sides of equations (3.10) and (3.14) we find that

$$- m_e \Delta \nu = 2 \, \frac{h\nu^2}{c^2} \sin^2 \frac{\varphi}{2} \qquad (3.15)$$

If we differentiate the ratio $\nu = c/\lambda$, we obtain

$$d\nu = - \frac{c}{\lambda^2} \, d\lambda$$

Since $\Delta \nu$ is very small as compared to ν, we can write that

$$\Delta \nu \approx - \frac{c}{\lambda^2} \, \Delta \lambda \qquad (3.16)$$

Substituting in equation (3.15) the value ν by c/λ and the value of $\Delta \nu$ from equation (3.16), we obtain the equation for the Compton effect:

$$\Delta \lambda = 2 \, \frac{h}{m_e c} \sin^2 \frac{\varphi}{2} \qquad (3.17)$$

The value $h/m_e c$ in equation (3.17) has the dimension of length and is equal to 0.0242 Å. It is often called the *Compton wavelength of the electron.*

Investigations have shown that equation (3.17) is in good agreement with experimental data.

3.4. De Broglie Waves

Whereas the photoelectric effect and the Compton effect are clearly indicative of the corpuscular (particle) nature of visible light and X-ray radiation, interference and diffraction phenomena are evidence

of their wave nature. Therefore, the conclusion can be drawn that
the motion of photons obeys special laws in which corpuscular and
wave properties are combined. The unity of such seemingly incon-
gruous characteristics is given by equation (3.6) which correlates the
mass of a photon and the wavelength of radiation.

In 1924 de Broglie (France) suggested that the dual wave-particle
nature is true not only for the photon but for any other material
particle as well. The motion of any material particle can be regarded
as a wave process for which the following relation is valid:

$$\lambda = \frac{h}{mv} \qquad (3.18)$$

similar to equation (3.6), where m and v are the mass and velocity
of the particle, respectively. These waves are called *de Broglie
waves.*

De Broglie's wave hypothesis was supported by *electron diffraction*
experiments. It was found that when a beam of electrons passed
through a diffraction grating the diffraction picture observed on the
photographic plate was the same as that obtained on passing radiat-
ion of a wavelength λ calculated from equation (3.18). Metal crystals
were used as the diffraction grating. The atoms are regularly arranged
in the crystals, thus forming a natural diffraction space lattice. In
1927 Davisson and Germer (USA) were the first to carry out such
experiments; in the same year (1927) electron diffraction was also
observed by G. Thomson (England) and P. Tartakovski (USSR).

At the present time electron diffraction is widely used in the study
of the structure of matter (see Sec. 12.1); the *electron-diffraction came-
ra* used for this purpose is now available in all physicochemical labo-
ratories. Neutron diffraction is also used in structure studies. The
diffraction of helium atoms, hydrogen molecules, and other particles
has been studied.

Thus, the dual wave-particle nature of material particles is a fact
that is well founded on experimental data.

If we were to calculate the values of λ with the aid of equation
(3.18) for various objects, we would find that for macro-objects the
values are vanishingly small. For example, for a particle of a mass
of 1 g moving with a velocity of 1 cm/s, $\lambda = 6.6 \cdot 10^{-27}$ cm. This
means that the wave properties of macro-objects are not revealed
in any way because if the wavelength is considerably less than the
size of the atom (10^{-8} cm), it is impossible to obtain a diffraction
grating or other device by which the wave nature of the particle
could be observed. It is quite another matter for micro-objects.
The motion of an electron accelerated by a potential difference of
1 V ($v = 5.94 \cdot 10^7$ cm/s) is associated with $\lambda = 1.22 \cdot 10^{-7}$ cm.

It can be proved that the velocity of propagation of de Broglie
waves w is related to the velocity of the particle v according to the

equation

$$w = \frac{c^2}{v} \qquad (3.19)$$

where c = velocity of light. Thus we see that only for photons the velocity of propagation of de Broglie waves coincides with the velocity of the particle. For all other particles, the velocity of propagation of these waves is greater than the velocity of light; therefore, de Broglie waves do not transmit energy, i.e., they cannot be regarded as real vibration. The concept of de Broglie waves is merely a convenient method for describing the motion of microparticles. As we shall see later on, this motion cannot be clearly conceived inasmuch as such concepts as trajectory and velocity are unsuitable in the microworld. We shall also see that there is a more general way of expressing the laws of motion of microparticles, which does not include the parameter λ.

3.5. Quantum Mechanics; the Schrödinger Equation

The mechanics describing the movement of microparticles was initiated by the investigations of de Broglie. In 1925-1926 Heisenberg (Germany) and Schrödinger (Austria) independently proposed two variants of the new mechanics; subsequently it was found that both variants lead to identical results. Schrödinger's method proved to be more convenient for carrying out calculations; the modern theory of the structure of atoms and molecules is based on his method. The mechanics of micro-objects is called *quantum mechanics* (or *wave mechanics*); the mechanics based on Newton's laws, applicable to the motion of ordinary bodies, is called *classical mechanics*.

In contrast to the Bohr—Sommerfeld theory, quantum mechanics is not an artificial combination of classical concepts and the quantization rules; it is a harmonious theory based on a system of concepts free of any contradictions. All the results obtained by quantum mechanics are in complete agreement with experimental data.

In quantum mechanics the laws of motion of microparticles are described by the *Schrödinger equation* which is of the same significance for it as Newton's laws are for classical mechanics. Like Newton's laws, this equation cannot be deduced from any more general assumptions. It can be obtained from the analogy between the equations of mechanics and optics.

The Schrödinger equation is a *differential equation involving partial derivatives*; in problems met with in atomic and molecular theory, the Schrödinger equation for one particle can be written as follows:

$$-\frac{h^2}{8\pi^2 m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi = E\psi \qquad (3.20)$$

3*

where h = Planck's constant
  m = mass of particle
  U = potential energy
  E = total energy
x, y, z = coordinates

The construction of the Schrödinger equation is given in Appendix III[1].

The variable ψ in this equation is known as the *wave function*. The square of this function ψ^2 has a definite physical meaning characterizing the probability of finding the particle in a given region of space; to be exact, the *value $\psi^2\, dv$ gives the probability of finding the given particle in an element of volume dv* (see footnote 2).

In accordance with the physical meaning of the wave function, *it must be finite, continuous, and single-valued and become zero where the particle cannot be found.* For example, when considering the motion of an electron in an atom, ψ should become zero at an infinitely great distance from the nucleus.

The quantum-mechanical solution of problems in atomic and molecular theory consists in finding the ψ-functions (which have the above mentioned characteristics) and the energies that satisfy the Schrödinger equation. The solution of the Schrödinger equation, in most cases, is a very complicated mathematical problem.

A special system of units is frequently used in the quantum-mechanical treatment of atoms and molecules; the use of these units makes it possible to write the equations used and obtained more simply. In this system, the unit of length is the radius of the first Bohr orbit of the electron in the hydrogen atom:

$$a_0 = \frac{\hbar^2}{me^2} = 0.529 \text{ Å}$$

and the unit of energy is the absolute value of the potential energy of the electron in this orbit:

$$E = \frac{me^4}{\hbar^2} = \frac{e^2}{a_0} = 27.2 \text{ eV}$$

The charge and mass of the electron are taken as the units of electric charge and mass. These units were proposed by the English scientist Hartree; they are called *atomic units* (or *Hartree units*): when atomic units are employed, the Schrödinger equation for one electron is

$$-\frac{1}{2}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + U\psi = E\psi$$

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[1] Equation (3.20) is applicable only in the case when the state of the system does not change with time; it is the *Schrödinger equation for stationary states.* In its general form, time is included in the equation.

[2] The wave function can be expressed by a complex quantity; in this case the probability of finding the particle in a region of space is determined by the product $\psi\psi^*$, where ψ^* is a complex conjugate quantity; the quantity $\sqrt{\psi\psi^*}$ is called the modulus of the wave function and is denoted as $|\psi|$; hence, in the general case the probability of finding the particle in an element of volume dv is given by $|\psi|^2\, dv$.

The system of concepts of quantum mechanics differs sharply from that of classical mechanics. Quantum mechanics gives the *probability of finding a particle in a region of space* and says nothing of the trajectory of the particle, its coordinates, and velocity at a given moment; such concepts mean nothing in quantum mechanics. However, the concepts of mass, energy, and angular moment of the particle retain their importance.

One of the basic assumptions of quantum mechanics is the *Heisenberg uncertainty principle* which states that it is not possible to define simultaneously the position of a particle and its momentum, $p = mv$. The more precisely the position of the particle is determined, the more uncertain is its momentum; and, on the other hand, the more exactly the momentum is known, the more indefinite is the position of the particle. The equation expressing the uncertainty principle can be written as

$$\Delta x \Delta p_x \gg \hbar \tag{3.21}$$

or

$$\Delta x \Delta v_x \gg \frac{\hbar}{m} \tag{3.22}$$

where Δx is the uncertainty of finding the position of the particle along the x-axis at a given moment; Δp_x and Δv_x are the uncertainties in the momentum and velocity values in the direction of the x-axis. Similar equations can be written for the y and z coordinates.

Many of the specific properties of microparticles can be explained by the uncertainty principle. It often affords a rapid and simple estimation of a given effect where calculation would be complicated. This can be shown by the following example. Let us consider, with the aid of the uncertainty principle, the motion of the electron in the hydrogen atom.

Let us assume that the motion of the electron occurs in a region with a radius r. Then, the uncertainty of its position can be taken to be equal to r and, according to equation (3.21), the minimum uncertainty of Δp in the value of the momentum of the electron p is equal to $\hbar/r$. It is obvious that the value of the momentum cannot be less than the uncertainty of its value; therefore, the minimum possible momentum value will be

$$p = \frac{\hbar}{r} \tag{3.23}$$

The energy of the electron is equal to the sum of its kinetic energy (which according to equation (3.9) is $p^2/2m_e$) and its potential energy (which at a distance r from the nucleus is $-e^2/r$). Hence, substituting the value of p from equation (3.23) into the expression for the kinetic energy, we find that the total energy of the electron in the hydrogen atom is

$$E = \frac{\hbar^2}{2m_e r^2} - \frac{e^2}{r} \tag{3.24}$$

This dependence of the energy of the electron on r is shown in Fig. 3.3. As can be seen, the curve has a minimum; the value of r_0 at which E has a minimum value can easily be found since at the point, corresponding to the minimum, $dE/dr = 0$. Differentiation gives
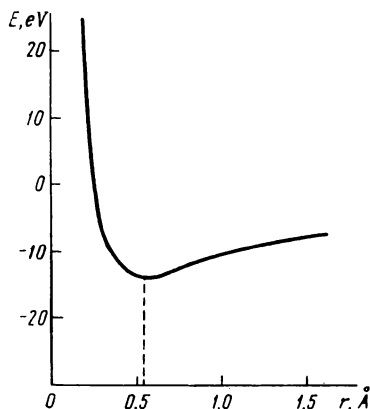
$$-\frac{\hbar^2}{m_e r_0} + e^2 = 0$$

wherefrom

$$r_0 = \frac{\hbar^2}{m_e e^2} \tag{3.25}$$

Substituting this value of r_0 into equation (3.24), we find the equation for the minimum energy of the electron in the hydrogen atom:

$$E_{\min} = -\frac{1}{2}\frac{m_e e^4}{\hbar^2} \tag{3.26}$$

The result obtained is very significant. According to the classical conception the electron would have a minimum energy when it fell onto the nucleus; however, quantum mechanics shows that the energy of the electron is minimum, not when it 'rests on the nucleus', but when

Fig. 3.3. Dependence of electron energy on the radius of the region of space in which the electron moves

it moves within a sphere with a radius r_0, its exact position within this region of space being unknown. When $r < r_0$, the energy of the electron increases.

A comparison of equations (3.25) and (2.12) shows that the value of r_0 is equal to the radius of the first Bohr orbit, and by comparing equations (3.26) and (2.15) it is seen that $E_{\min}$ found by applying the uncertainty principle coincides with the minimum energy value of the electron in the hydrogen atom according to Bohr's theory and the study of the hydrogen spectrum. This interpretation of course is approximate because the motion of an electron in an atom cannot be confined to an exactly prescribed region. It explains, however, why the electron does not fall onto the nucleus and makes it possible to correctly estimate the minimum value of the energy of an electron. This result can be obtained by solving the Schrödinger equation for the hydrogen atom, but this would involve very complicated mathematical calculations.

As we shall see further on (see p. 52) the radius of the first Bohr orbit is equal to the distance from the nucleus at which the electron of the hydrogen atom is most probably to be found (for the state of minimum energy).

Since the value of $\hbar$ in the uncertainty equation is very small, the uncertainties of the values of the coordinates and the momentum of macro-objects are negligibly small and therefore the effect due to them cannot be observed by any apparatus. When dealing with the motion of macro-objects, it is necessary to speak of precise trajectories and to apply classical mechanics.

CHAPTER FOUR

QUANTUM-MECHANICAL EXPLANATION OF ATOMIC STRUCTURE

4.1. Solution of the Schrödinger Equation for the One-Dimensional Square-Well Model

The solutions of the Schrödinger equation for problems met with in the theory of atomic and molecular structure are very complicated and cannot therefore be set forth in this book. However, to understand the nature of the results of the quantum-mechanical study of the atom discussed below, it is worth while to analyze the solution of the Schrödinger equation for at least one simple example. Let us solve it for the hypothetical *square-well* model.

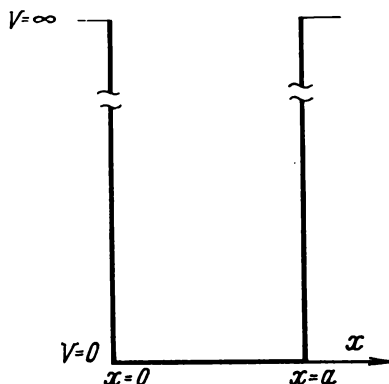First let us obtain the solution for a *one-dimensional particle-in-a-*

Fig. 4.1. One-dimensional square potential well

box problem. In this model the particle (for example, an electron) can move only in one direction, for instance, along the x-axis from $x = 0$ to $x = a$ (Fig. 4.1)[1]. Within the limits of this region the potential energy of the particle U is uniform; it is convenient to take it to be equal to zero (the potential energy can be reckoned from any

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[1] Although the model is highly simplified, it is used for the solution of actual problems. Thus, for example, the motion of π-electrons in a system of conjugated double bonds in organic compounds (see p. 194 and Appendix IX) can be regarded approximately as motion in a one-dimensional square well.

arbitrary level). Outside this region the potential V acting on the particle is infinitely high; that means that the particle cannot go beyond the region of length $0 < x < a$ (this would require an infinitely large increase in its energy).

The Schrödinger equation (3.20) for the one-dimensional square-well model is

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi \qquad (4.1)$$

To solve this equation it is necessary to find the ψ-function and the value of energy E that would satisfy the equation; the magnitude of the ψ-function should be finite, single-valued and continuous and should be equal to zero when $x = 0$ and $x = a$ (since the particle cannot be located outside this region, the probability of finding it beyond these points, determined by ψ^2, is equal to zero; in order that the function remain continuous, it must also be equal to zero at points $x = 0$ and $x = a$).

The ψ-function that satisfies the above conditions is

$$\psi = A \sin \frac{n\pi x}{a} \qquad (4.2)$$

where $n = 1, 2, 3, \ldots$ and A is a constant value.

The value of n cannot be zero because that would imply the absence of the particle in the well ($\psi^2 = 0$).

That this function satisfies the Schrödinger equation can be shown by substituting it into the left-hand and right-hand sides of equation (4.1). Then after differentiating equation (4.2) we obtain
left-hand side:

$$-\frac{h^2}{8\pi^2 m}\left(-\frac{n^2\pi^2}{a^2}\right) A \sin \frac{n\pi x}{a} = \frac{n^2 h^2}{8ma^2} A \sin \frac{n\pi x}{a}$$

right-hand side:

$$EA \sin \frac{n\pi x}{a}$$

It is evident that the two sides are equal if the energy of the particle is determined by the relation

$$E = \frac{n^2 h^2}{8ma^2} \qquad (4.3)$$

where $n = 1, 2, 3, \ldots$

Thus, we have found the ψ-function and the energy value that satisfy equation (4.1), i.e., we have solved the Schrödinger equation for the one-dimensional square-well problem. Let us analyze the solution obtained.

First of all note should be taken of the sharp difference between the result obtained and the picture observed in an analogous problem for a particle for which the laws of classical mechanics hold. Obvi-

ously, the energy of such a particle could have any value and the probability of finding it would be the same for any point on the x-axis.

On the contrary, as seen from equation (4.3), the energy of a particle for which the laws of quantum mechanics hold can have only a number of definite values characterized by the integral coefficient n. The energy levels for a particle in a one-dimensional box are shown in Fig. 4.2. Pay due attention to the fact that quantization of energy is the inevitable result of the solution of the Schrödinger equation, although the equation itself does not contain integral n-coefficients.

This solution which shows that for microparticles there are a number of permissible energy values is characteristic not only of the motion in the potential well: a similar result is obtained when considering any problem in which the microparticle is confined to a definite region of space under the action of forces (see p. 45). Thus, quantum mechanics explains
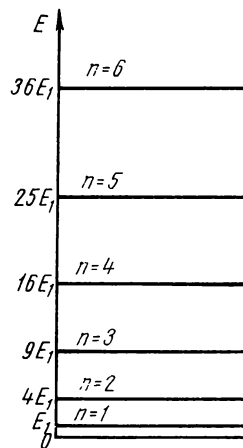
Fig. 4.2. Energy levels of a particle in a one-dimensional square potential well (E_1 is the zero-point energy corresponding to $n = 1$)

the existence of *discrete* energy levels for electrons in atoms and molecules (this is indicated by spectra) and makes it possible to theoretically calculate the magnitude of these energies.

Since in the equation for the energy of a particle in the potential well $n \neq 0$, E also cannot be equal to zero. The minimum energy (*zero-point energy*) corresponds to $n = 1$.

The fact that the particle possesses a zero-point energy is one of the specific characteristics of the microcosm. It is connected with the particle-wave nature of microparticles and stems from the uncertainty principle. We have already seen (see p. 38) that the location of an electron in a particular region of space results in the appearance in it of a certain impulse and, consequently, kinetic energy which is the greater the more the motion of the electron is restricted. The same can be said of any other microparticle. There is no state of matter in which the kinetic energy of its particles is equal to zero. Even at absolute zero, not only electrons, but even atoms as a whole, will be in constant motion, vibrating about the equilibrium position. The zero-point vibrations of atoms affect many of the properties of substances. Their actual occurrence is confirmed by studies of diffraction of X-rays by crystals. These studies show that even at temperatures close to absolute zero, there is a certain disorder in the spacial distribution of atoms due to their zero-point vibrations.

The fact that atoms and other particles have a zero-point energy, as proved by quantum mechanics, once more confirms the assertion of dialectical materialism that matter cannot exist without motion.

Figure 4.3 shows the ψ-function and ψ^2-function for a particle in a one-dimensional potential well where $n = 1$, 2, and 3. The diagram showing the dependence of ψ on x is similar to the picture of the vibration of a string fixed at two ends, where only such vibration is possible in which a whole number of half-waves go along the string.
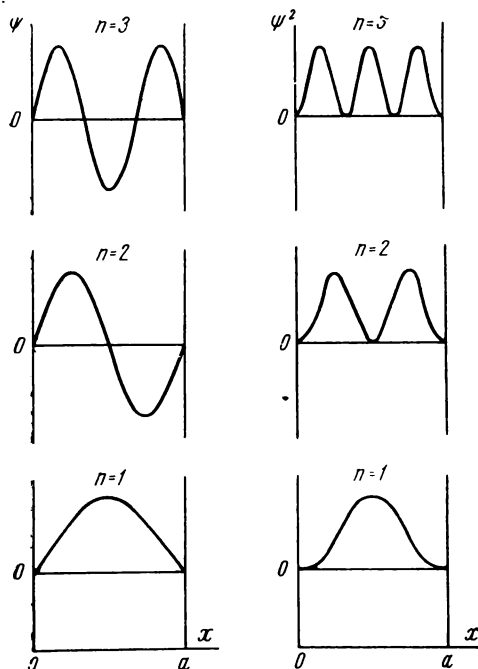
As can be seen in Fig. 4.3, the ψ^2-functions also differ considerably from the classical pattern. From Fig. 4.3 it is obvious that the probability of finding a particle at various points of the potential well is not the same. Besides that, at values of $n > 1$, the probability of finding the particle at certain points inside the well is equal to zero—which is absolutely impossible from the standpoint of classical conceptions.

However, as seen from equation (4.3), if the mass of the particle m (and,

Fig. 4.3. ψ- and ψ^2-functions of a particle in a unidimensional square potential well

consequently, the value a) and its energy E are large enough, the motion of the particle does not particularly differ from the classical one; i.e., the permissible energy levels will lie so close to each other that they cannot be distinguished experimentally, and it can be considered that the particle can have any energy value. Thus, for macro-objects, quantum mechanics leads to the same results as classical mechanics does.

As concerns the constant A, it can be of any value from the point of view of mathematical requirements. However, because of the physical meaning of the ψ^2-function, it is necessary to choose a definite value of A, namely such a value that the total probability of finding the particle in the potential well be equal to unity. This condition is expressed mathematically by the equation

$$\int_0^a \psi^2 \, dx = 1 \qquad (4.4)$$

Such a value of A must be found that satisfies equation (4.4). By substituting into equation (4.4) the expression for the ψ-function given in equation (4.2) and solving the integral we obtain

$$A = \sqrt{\frac{2}{a}}$$

This mathematical operation, called *normalization*, is performed in all cases when it is necessary to find the complete expression for the wave function, i.e., to determine the constant value that it always contains; this constant value is called the *normalization factor*. In the general form, the equation is written as follows:

$$\int \psi^2 \, dv = 1 \qquad (4.5)$$

where dv = element of volume. Integration is carried out for the entire volume from the value $-\infty$ to $+\infty$ for each of the coordinates. Equation (4.5), the same as equation (4.4), shows that the total probability of finding the particle is equal to unity, i.e., that the particle can actually be found somewhere in space.

4.2. Three-Dimensional Square-Well Model

The existence of discrete energy levels of an electron in an atom becomes clear from the above solution of the Schrödinger equation for the one-dimensional square well. To explain other characteristics of atomic structure it is advisable to consider the motion of a particle in a *three-dimensional square well.*

In this problem the particle is confined within a space inside a potential well, a cube with a side a. The
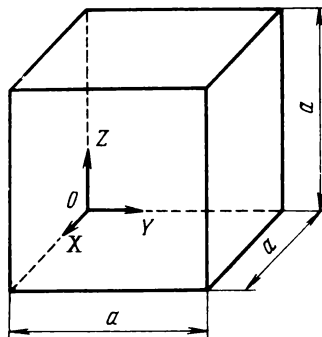

Fig. 4.4. Three-dimensional square potential well

origin of the coordinates is in one corner of the cube (Fig. 4.4). The potential energy of the particle within the square well is constant; beyond it the potential is infinitely great and therefore the particle can under no circumstances be outside the well.

As in the previous one-dimensional problem, the three-dimensional square-well model is a hypothetical one. However, there actually exists a phenomenon for which these conditions are to some extent true, namely, the motion of conduction electrons in

a piece of metal. These electrons move in all directions, but they do not go beyond the piece of metal. Therefore, the three-dimensional square-well model is used in the theory of the metallic state.

In this case it is necessary to solve the Schrödinger equation for three dimensions. When solving such problems, the following procedure is usually employed: the equation is analyzed and an attempt is made to separate it into parts each of which contains only one of the three coordinates. If this can be done, the sought function is found more simply. Let us attempt to find the ψ-function in this way.

The potential energy $U(x, y, z)$ can be regarded as the sum of three terms each of which is a function of only one coordinate:

$$U(x, y, z) = U(x) + U(y) + U(z) \qquad (4.6)$$

The total energy is separated in a similar way. The velocity of the particle v being a vector quantity can be resolved into its components along the coordinate axes, v_x, v_y, and v_z, and the kinetic energy can be expressed as the sum of the corresponding terms; accordingly, in view of this and equation (4.6) we can write

$$E = E_x + E_y + E_z \qquad (4.7)$$

Let us now assume that the sought ψ-function can be expressed as the product of three functions each of which depends only on one coordinate, i.e.,

$$\psi(x, y, z) = X(x) \, Y(y) \, Z(z) \qquad (4.8)$$

and let us see if we can solve the Schrödinger equation by means of the function thus divided. For the sake of simplicity we will denote the functions $X(x)$, $Y(y)$, and $Z(z)$ simply as X, Y and Z.

By substituting into equation (3.20) the new function given in equation (4.8) and the expressions given in equations (4.6) and (4.7) we obtain

$$-\frac{h^2}{8\pi^2 m}\left(YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2}\right) + [U(x) + U(y) + U(z)] \times$$
$$\times XYZ = (E_x + E_y + E_z)\,XYZ$$

On dividing this equation by XYZ we obtain

$$-\frac{h^2}{8\pi^2 m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right) +$$
$$+ U(x) + U(y) + U(z) = E_x + E_y + E_z$$

The resulting equation can be considered to be the sum of three identical equations of the type

$$-\frac{h^2}{8\pi^2 m}\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + U(x) = E_x$$

or

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 X}{\partial x^2} + U(x)X = E_x X \qquad (4.9)$$

We already know the solution of equation (4.9); we obtained it for the one-dimensional square-well problem (the function $U(x)$ according to the conditions of the problem can be taken to be equal to zero).

Thus, such a division makes it possible to find the ψ-function and the energy of the particle E; the wave function is expressed by equation (4.8) in which

$$\left.\begin{array}{l} X(x) = A_x \sin\dfrac{n_x \pi x}{a} \quad \text{where } n_x = 1,\ 2,\ 3,\ \ldots \\[2mm] Y(y) = A_y \sin\dfrac{n_y \pi y}{a} \quad \text{where } n_y = 1,\ 2,\ 3,\ \ldots \\[2mm] Z(z) = A_z \sin\dfrac{n_z \pi z}{a} \quad \text{where } n_z = 1,\ 2,\ 3,\ \ldots \end{array}\right\} \qquad (4.10)$$

and

$$E = E_x + E_y + E_z = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8ma^2} + \frac{n_z^2 h^2}{8ma^2} = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8ma^2} \qquad (4.11)$$

As for the one-dimensional square potential well, the values n_x, n_y and n_z can *only be whole numbers (integers)*. Thus, passing from the one-dimensional to the three-dimensional problem has resulted in the appearance of *three* integral characteristics in the expression for the wave function.

This result has a general meaning. The quantum-mechanical treatment of various cases of motion of microparticles within a confined region of space (say, in an atom, molecule, etc.)[1] shows that *the wave function of a particle always contains dimensionless parameters which can take a number of integral values.* These values are called *quantum numbers.* The number of quantum numbers contained in the solution is equal to that of the *degrees of freedom* of the particle. *The number of degrees of freedom is the number of independent components of motion of the particle.* Thus, in the one-dimensional potential square well, the particle has only one degree of freedom; in the case of translatory motion in space, it has three degrees of freedom (motion is possible in the direction of each of the three coordinates x, y and z); if, besides this, the particle can rotate round its own axis, it has a fourth degree of freedom.

Whereas in the problem of the motion of a particle in the one-dimensional potential square well different values of the quantum

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[1] The expression 'confined region of space' implies that the particle is confined to a given region by the action of some forces and the probability of finding it beyond this region is close to zero.

numbers correspond to different energies, in the three-dimensional problem there are states characterized by different quantum numbers but by one and the same energy. Thus, at $n_x = 2$, $n_y = 1$, and $n_z = 1$ the energy of the particle will be the same as when $n_x = 1$, $n_y = 2$, and $n_z = 1$. If one and the same energy corresponds to several different states (characterized by different wave functions) it is said that the given energy level is *degenerate*. Depending on the number of states, degeneration may be two-fold, three-fold, etc.

In the simplified examples considered above we have come to know some of the laws of quantum mechanics. Now we can investigate the motion of electrons in real systems, i.e., in atoms of chemical elements.

4.3. Quantum-Mechanical Explanation of Structure of Hydrogen Atom

The hydrogen atom has the simplest structure; it has only one electron moving in the field of force of the nucleus. In this case the potential-energy function U in the Schrödinger equation (see p. 26) is expressed by

$$U = - \frac{e^2}{r} \qquad (4.12)$$

This seemingly insignificant complication of the equation as compared with the square-well problem presents some mathematical complexities that cannot be dealt with in this book. We shall therefore consider only the basic peculiarities of this solution and their physical meaning.
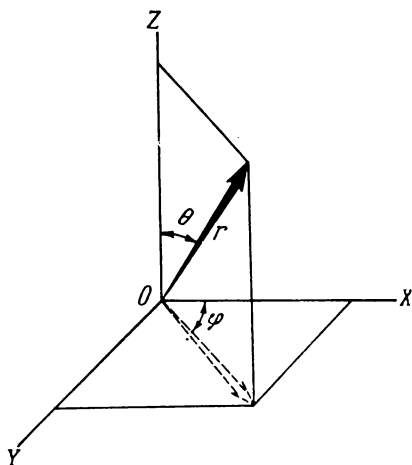
Fig. 4.5. Polar system of coordinates

It is convenient to consider the movement of the electron in such problems in polar coordinates, the centre of which coincides with the nucleus of the atom (Fig. 4.5). Whereas in the Cartesian (rectangular) coordinates the position of a particle in space is given by the coordinates x, y and z, in the polar coordinates it is defined by the radius-vector r (the distance from the centre) and the angles θ and φ. In Fig. 4.5 it can be seen that the polar coordinates are related to the rectangular coordinates as follows:

$$x = r \sin \theta \cos \varphi, \quad y = r \sin \theta \sin \varphi, \quad z = r \cos \theta \qquad (4.13)$$

As in the solution of the three-dimensional square-well problem, the ψ-function should be presented as the product of three functions, each of which contains only one variable:

$$\psi(r, \theta, \varphi) = R(r) \Theta(\theta) \Phi(\varphi)$$

The expression $R(r)$ is called the *radial component* of the wave function; the product $\Theta(\theta) \Phi(\varphi)$ is known as its *angular component*.

The presence of three degrees of freedom results in the appearance of three values which can only be integers, i.e., three quantum numbers denoted as n, l and m. These values are present in both the radial and angular components of the wave function; in its most general form the solution of the Schrödinger equation for the hydrogen atom can be expressed as follows:

$$\left. \begin{array}{l} R(r) = f_1(n, l) \\ \Theta(\theta) = f_2(l, m) \\ \Phi(\varphi) = f_3(m) \end{array} \right\} \tag{4.14}$$

The quantum numbers n, l and m can have the following values:

$$\left. \begin{array}{l} n = 1, 2, 3, 4, \ldots, \infty \\ l = 0, 1, 2, 3, \ldots, (n-1) \\ m = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l \end{array} \right\} \tag{4.15}$$

As we shall see below, the quantum numbers n, l and m characterize the motion of the electron not only in the hydrogen atom, but in any other atom as well.

As seen from equation (4.14), the quantum numbers n and l enter into the expression of the R-function; they therefore determine the *function of radial distribution of the probability of finding an electron in an atom*. These functions for the hydrogen atom are shown graphically in Fig. 4.6. Along the axis of ordinates are plotted the values $R^2(r)$ multiplied by $4\pi r^2$. These values characterize the probability of finding the electron in a thin spherical shell of radius r; this probability is proportional to $4\pi r^2 R^2(r)\, dr$ where dr is the thickness of the shell.

From Fig. 4.6 it follows that in contrast to the Bohr—Sommerfeld theory according to which the electron moves in exactly prescribed orbits, quantum mechanics shows that the electron can be found at any point in the atom although the probability of it being in different regions of space is not the same. Thus, if we could observe the electron in the atom, we would see that it is more often in certain places and less often in others. Therefore, the modern conception is that of an *electron cloud* the *density* of which at different points is determined by the probability of finding the electron there. Therefore in the scientific literature instead of the term 'orbit', the term now used is '*orbital*' meaning the *particular pattern traced out by an*
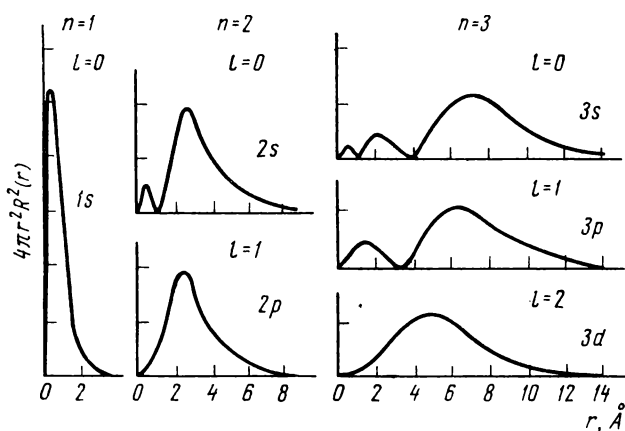
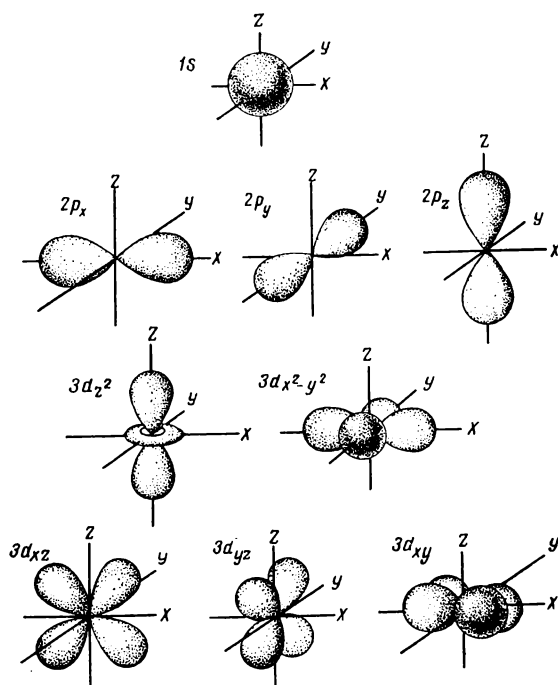Fig. 4.6. Radial distribution of the probability of finding the electron for different states of the hydrogen atom

Fig. 4.7. Shapes of electron clouds for different states of electrons in atoms

electron in an atom (*the electron distribution pattern*). Each orbital corresponds to a definite wave function ψ.

The following designations are used to represent the electron state of atoms: the quantum number n is designated by figures and l, by small letters according to the following scheme:

$$l \quad \ldots \ldots \ldots \ldots \quad 0 \ 1 \ 2 \ 3 \ 4 \ 5$$
$$\text{Designation} \quad \ldots \ldots \quad s \ p \ d \ f \ g \ h$$

The first four letters coincide with the designations of spectral series (see p. 22); the origination of these series is due to the transition of electrons, corresponding to definite values of the quantum number l. The last two letters, g and h, are the letters following f in the alphabet. Thus, $1s$ is the designation for an electron for which $n = 1$ and $l = 0$; $2p$, for an electron for which $n = 2$ and $l = 1$, etc. The number of electrons in an atom with the given values of n

Table 4.1

The Wave Functions of the Electron in the Hydrogen Atom

Designation of orbital	Radial component	Angular component
$1s$	$2e^{-r}$	$\dfrac{1}{2\sqrt{\pi}}$
$2s$	$-\dfrac{1}{2\sqrt{2}}(2-r)e^{-r/2}$	Same
$2p_x$	$\dfrac{1}{2\sqrt{6}}re^{-r/2}$	$\dfrac{\sqrt{3}}{2\sqrt{\pi}}(x/r)$
$2p_z$	Same	$\dfrac{\sqrt{3}}{2\sqrt{\pi}}(z/r)$
$2p_y$	Same	$\dfrac{\sqrt{3}}{2\sqrt{\pi}}(y/r)$
$3d_{x^2-y^2}$	$\dfrac{4}{81\sqrt{30}}r^2e^{-r/3}$	$\dfrac{\sqrt{15}}{4\sqrt{\pi}}[(x^2-y^2)/r^2]$
$3d_{xz}$	Same	$\dfrac{\sqrt{30}}{2\sqrt{2\pi}}(xz/r^2)$
$3d_{z^2}$	Same	$\dfrac{\sqrt{5}}{4\sqrt{\pi}}[(3z^2-r^2)/r^2]$
$3d_{yz}$	Same	$\dfrac{\sqrt{30}}{2\sqrt{2\pi}}(yz/r^2)$
$3d_{xy}$	Same	$\dfrac{\sqrt{15}}{4\sqrt{\pi}}(xy/r^2)$

and l is indicated by a superscript. Thus, $2s^2$ shows that in the atom there are two electrons with $n = 2$ and $l = 0$.

Table 4.1 gives the wave functions for certain electron states of the hydrogen atom. They are given in atomic units. Moreover, for the sake of abbreviation, the trigonometric functions of the angles are defined by the Cartesian coordinates x, y, and z and the distance r. The motion of the electron in ions with a single electron (He^+, Li^{2+}, etc.) is characterized by similar wave functions; to find the expressions for these ions the given wave functions must be multiplied by $Z^{3/2}$ and r must be replaced by Zr.

Figure 4.7 shows the electron clouds for different states of electrons. It presents the shape of the surfaces defining the space in which the greater part ($\sim 90\%$) of the electron cloud is enclosed. The shape of these surfaces is determined by the angular component of the wave function $\Theta(\theta)\,\Phi(\varphi)$. This pictorial representation of electron clouds will be repeatedly used in the subsequent discussion.

4.4. Quantum Numbers of Electrons in Atoms

The quantum numbers characterize the motion of electrons not only in the hydrogen atom but in any other atom as well. These characteristics are very important for understanding the properties of substances and the nature of chemical bonding. Therefore we shall discuss their significance in greater detail.

The quantum numbers n, l, and m determine the geometric pattern of the electron cloud. They are also associated with the physical characteristics of the motion of the electron.

The quantum number n is equal to the number of nodal surfaces (nodes) of the orbital. A node is the locus of points at which $\psi = 0$. Obviously, if $\psi = 0$, $\psi^2 = 0$; therefore, the density of an electron cloud in a node is equal to zero. A surface infinitely removed from the nucleus is also a nodal surface; as we already know, in this case ψ is always equal to zero.

The existence of nodal surfaces in the distribution of electron density stems from the laws of the microcosm. The motion of the microparticles is described by relations analogous to the equations of wave motion. In every wave there are points where the amplitude of vibration is equal to zero. If vibration is three-dimensional, the sum of these points form a nodal surface. Nodal surfaces (nodes) in atoms may be of two kinds: those that do not pass through the centre of the atom (the nucleus) and those that pass through it. The first are concentric spherical nodes the centres of which coincide with the nucleus; the second kind are nodal planes or cones which pass through its centre. The presence of spherical nodes is shown in the radial component of the wave function—at certain distances from the nucleus, ψ is equal to zero; this can be seen in Fig. 4.6.

The value l shows how many nodes of the wave function of the electron pass through the nucleus. As has already been pointed out, one of the nodes is always at an infinitely great distance from the nucleus. It is therefore obvious that l can vary from 0 to $n - 1$. Fig. 4.8 shows the positions of nodes that pass through the centre of the atom, for different states of the electron. It is worth comparing this Figure with Fig. 4.7.

As has been noted above, according to quantum mechanics the electron in an atom can be at any distance from the nucleus; however
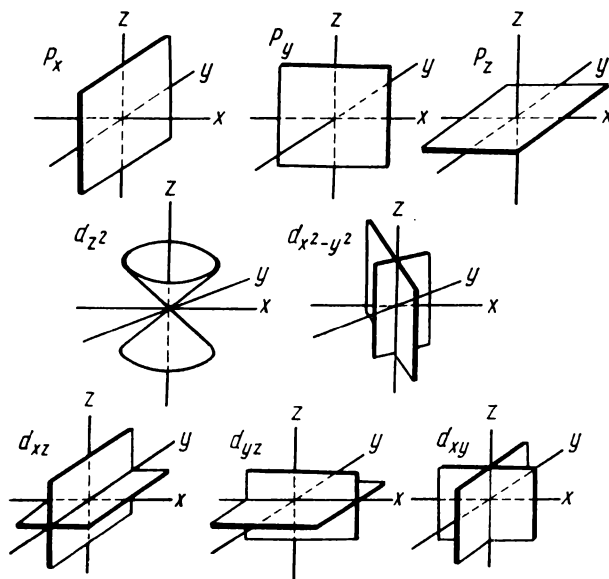
Fig. 4.8. Position of nodal planes for different states of an electron

the probability of it being in different places of the atom is not the same. Knowing the density distribution of an electron, we can calculate the *average distance* of the electron from the nucleus, r_{av}, which characterizes the size of the orbital; r_{av} can be found by integrating the function of radial distribution. The value r_{av} is determined by the values n and l. For the electron in the hydrogen atom and hydrogen-like ions, the relation between these values is expressed as follows:

$$r_{av} = \frac{a_0 n^2}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right\} \tag{4.16}$$

where Z = charge on the nucleus

a_0 = radius of the first Bohr orbit

From equation (4.16) it can be seen that r_{av} is approximately proportional to n^2. Hence, it can be stated that *n determines the size of the electron orbital.*

It should be noted that the maximum probability of finding the position of the electron in the hydrogen atom for the *1s, 2p, 3d, 4f,* etc. states coincides with the radius of the corresponding Bohr orbit (see Fig. 4.6).

The energy of the electron in the hydrogen atom depends only on the value *n*; the solution of the Schrödinger equation gives the relation

$$E = -\frac{1}{2} \frac{m_e e^4}{n^2 \hbar^2} \qquad (4.17)$$

As can be seen, it is the same expression as in the Bohr theory [see equation (2.15)], but in contrast to the latter, quantum mechanics reaches this result without having recourse to the arbitrary hypothesis that the electron can move in a definite set of orbits defined by a series of integers.

Since *n* determines the principal characteristic of the electron in the hydrogen atom, its energy, this value is called the *principal quantum number*. The quantum number *l* is called the *orbital quantum number*; the latter determines the *orbital angular momentum* of the electron *M*:

$$M = \hbar \sqrt{l(l+1)} \qquad (4.18)$$

As we already know (see p. 26), the angular momentum is a vector quantity. Its direction is determined by the quantum number *m*. In other words, *m characterizes the position of the orbital in space.* The direction of the vector can be given by its projection on one of the axes, for example, on the *z*-axis (the projection of the orbital momentum can be found only on one axis because in accordance with the uncertainty principle the other projections cannot be found; if we knew all three projections, we would know the trajectory of the electron). The projection of the orbital angular momentum is determined by the relation

$$M_z = \hbar m \qquad (4.19)$$

The quantum number *m* is called the *magnetic quantum number*[1] because the projection of the *orbital magnetic moment of the electron* depends on it (see Appendix VIII).

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[1] Since the absolute value of *m* cannot exceed *l* [see equation (4.15)], equations (4.18) and (4.19) show that the projection of the orbital angular momentum is always less than its full value. This also follows from the uncertainty principle. If the projection of the orbital momentum on the *z*-axis were equal to the full value, we would know that its projections on the *x*-axis and *y*-axis are equal to zero; hence, the value and exact direction of the vector of angular momentum of the electron would be known, but this contradicts the uncertainty principle.

The quantum numbers n, l, and m in the solution of the Schrödinger equation for the hydrogen atom do not completely describe the motion of electrons in atoms. The study of the spectra and other investigations have shown that there is an additional characteristic resulting from a fourth degree of freedom, the so-called 'spin' of the electron, or its rotation on its own axis.

The *spin*[1] or self-rotation of the electron is due to its *inherent angular momentum*. This characteristic of the electron is as fundamental as its charge and mass[2]. As shown by experimental investigations, the projection of the inherent angular momentum of the electron can have only two values, $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$; the plus and minus signs correspond to different directions of rotation of the electron. Hence, the *spin quantum number s* can have only two values, $+\frac{1}{2}$ and $-\frac{1}{2}$, i.e., these numbers differ by unity as do all quantum numbers. The spin can be allowed for in the expression for the wave function by introducing a factor (spin function).

The four quantum numbers n, l, m and s completely describe the motion of the electron in the atom. This motion can have no other characteristics independent of the quantum numbers.

Since the energy of the electron in the hydrogen atom is determined by the value n and does not depend on the other quantum numbers, it is evident that there may be several electron states with the same energy. These states are degenerate (see p. 46). Degeneration disappears when an external electric or magnetic field acts on the electron in the atom. An electron in a state with the same n but with different values of l, m, or s reacts differently with the external field; as a result the energies of these states become dissimilar. This explains the resolution of spectral lines when the source of radiation is placed in an electric or magnetic field (Stark and Zeeman effects).

It is evident that all that has been said about the hydrogen atom is completely applicable to the other one-electron systems, such as He^+, Li^{2+}. The energy of the electron in this case is equal to

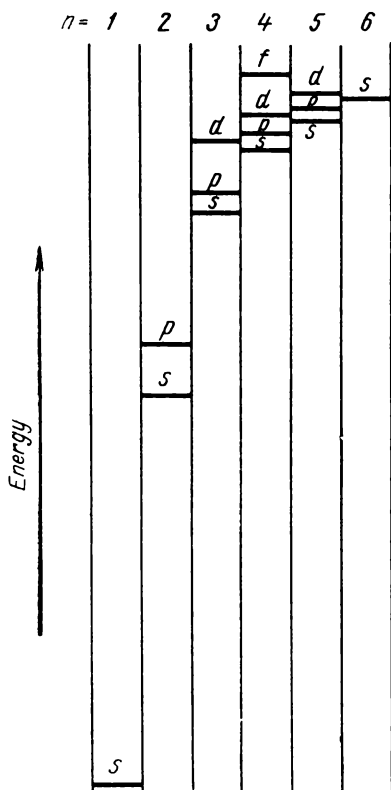$$E = -\frac{1}{2}\frac{m_e e^4 Z^2}{n^2 \hbar^2} \qquad (4.20)$$

---

[1] By spin or self-rotation is only meant that the electron possesses an inherent angular momentum. The electron cannot be considered as a rotating charged sphere; in particular, if the velocity of a point on the surface of such a sphere were to be calculated by means of electrodynamic equations, the velocity obtained would be greater than that of light. Spin, like the other characteristics of the motion of microparticles, cannot be associated with any model based on macro concepts.

[2] It should be borne in mind that there are particles that have a spin equal to a whole number (for example, zero).

4.5. Many-Electron Atoms

As in the hydrogen atom, in many-electron atoms the *state of each electron is determined by the values of the four quantum numbers n, l, m and s* that can have the same values as in the hydrogen atom.

In many-electron atoms, the electron moves not only in the field of the nucleus but also in the field of other electrons; due to this factor the energies of electrons with the same n but different l become different (the reason for this will be discussed below on p. 86). Therefore, the energy of electrons in many-electron atoms is determined by the values of the two quantum numbers n and l, increasing both with an increase in n and l. The dependence of the energy on l becomes greater as compared to its dependence on n, the greater the number of electrons in the atom. Thus, for the electron in the sodium atom that is farthest removed from the nucleus, the difference in the energies for levels with quantum numbers $n = 3$, $l = 0$ ($3s$) and $n = 3$, $l = 1$ ($3p$) is equal to 2.1 eV; this value approximates the difference between the energies of levels with $n = 3$, $l = 0$ ($3s$) and $n = 4$, $l = 0$ ($4s$) which is equal to 3.1 eV. For atoms that con-

Fig. 4.9. Sequence of energy levels in many-electron atoms (schematic representation)

tain an even greater number of electrons, the influence of l, in certain cases, can be greater than that of n; this fact determines the structure of a number of many-electron atoms.

In general, the energy levels of many-electron atoms can be described as follows. The energies of the levels ns, $(n - 1)\,d$, and $(n - 2)\,f$ do not differ considerably and are always less than that of the level np. Thus, the sequence of energy levels, in the order of increasing energy, is approximately as follows:

$$1s < 2s < 2p < 3s < 3p < 4s \approx 3d < 4p < 5s \approx$$
$$\approx 4d < 5p < 6s \approx 5d \approx 4f < 6p$$

A schematic representation of the relative placement of the energy levels in many-electron atoms is given in Fig. 4.9. In order not to make the diagram too long, the levels corresponding to $n = 1$ and $n = 2$ are positioned higher than they are actually located. The diagram is approximate (it holds for the first twenty elements) because the placement of the levels varies noticeably from atom to atom (see pp 82-83).

The state of electrons in many-electron atoms always satisfies the quantum-mechanical rule formulated by Pauli (the *Pauli exclusion principle*). This principle states that *in any atom or molecule no two electrons can have the same four quantum numbers*. The Pauli exclusion principle restricts the number of electrons in an atom that have a given value of n. Let us find the number for $n = 1$ and $n = 2$.

If $n = 1$, then l and m can only be equal to zero [see equation (4.15)]. Consequently, electrons with $n = 1$ can differ only in their spin quantum numbers. Hence, in an atom there can be only two electrons with the principal quantum number $n = 1$:

	n	l	m	s
1st electron	1	0	0	$+1/2$
2nd electron	1	0	0	$-1/2$

The same reasoning shows that in the case when $n = 2$, there can be only eight different combinations of the four quantum numbers:

n	l	m	s		n	l	m	s
2	0	0	$+1/2$		2	1	0	$+1/2$
2	0	0	$-1/2$		2	1	0	$-1/2$
2	1	-1	$+1/2$		2	1	$+1$	$+1/2$
2	1	-1	$-1/2$		2	1	$+1$	$-1/2$

In the same way it can be found that for $n = 3$ the maximum number of electrons is equal to 18; for $n = 4$ it is equal to 32, etc. In the general case the *maximum number of electrons in an atom which can have a given value of n is equal to $2n^2$*. Table 4.2 gives the quantum numbers for different electronic states.

Since the value n determines the average distance of the electron from the nucleus, we will call the system of all the electrons in an atom with the same n-value an *electron shell*. Electron shells are designated by the following capital letters:

n	1	2	3	4	5	6	7
Designation of shell	*K*	*L*	*M*	*N*	*O*	*P*	*Q*

The system of electrons with the same l-value and the same n-value we will call an *electron subshell*; subshells are distinguished as *s*-subshells, *p*-subshells, etc.

Accordingly, the number of electrons in an electron shell cannot exceed $2n^2$; thus, in the first shell there cannot be more than two

Table 4.2

Quantum Numbers for Different Electron States

n	1	2				3								
l	0	0	1			0	1			2				
m	0	0	0	± 1		0	0	± 1		0	± 1		± 2	
s	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$	$+1/2$ $-1/2$
Designation of orbitals	$1s$	$2s$	$2p_z$	$2p_x$	$2p_y$	$3s$	$3p_z$	$3p_x$	$3p_y$	$3d_{z^2}$	$3d_{xz}$	$3d_{yz}$	$3d_{x^2-y^2}$	$3d_{xy}$
Maximum number of electrons with a given value of l	2	2	6			2	6			10				
Maximum number of electrons with a given value of n	2	8				18								

electrons; in the second shell, more than eight electrons, etc. The maximum number of electrons in a subshell is equal to $2 (2l + 1)$.

Whereas there can be only two electrons (with opposite spins) in the s-subshell, the number of electrons in the p-subshell can be six. Therefore, it is necessary to ascertain how the spins of the electrons are oriented. Thus, for the nitrogen atom of the electron configuration $1s^2 2s^2 2p^3$ (2 electrons in the first shell and 5 in the second) there are two conceivable variants:
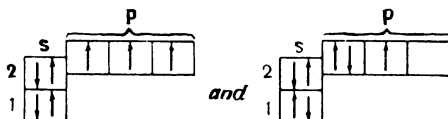
Each cell in these diagrams corresponds to a definite orbital. *On each orbital there can be two electrons with opposite spins.* In the first diagram all the p-electrons have different m-values; in the second diagram, two p-electrons have the same m-value.

Which of these variants should be preferred? This question is appropriate because for heavy atoms the number of conceivable variants is considerable, since in the d-subshell the number of orbitals is equal to five and in the f-subshell, to seven; i.e., the first subshell may have ten and the second subshell fourteen electrons.

Quantum mechanics and analysis of spectra show that filling of the orbitals (the lowest energy state of the atom) proceeds as follows. When electrons are being added to a subshell, the orbitals corresponding to different values of the magnetic quantum number are first singly occupied by electrons with parallel spin before any become doubly occupied. In other words, the *subshells are filled with electrons in such a way that the total spin is maximum*[1]. This important conclusion is known as *Hund's rule.*

In Part Two of this book it will be shown that the periodicity of the chemical and physical properties of the elements is due to the gradual filling up of the electron shells; each subsequent shell is essentially similar in construction to the preceding one.

4.6. Origination of Spectra

If the atom is not exposed to the action of any external force, its electrons are in the lowest energy state or the *ground state.* If energy is transmitted to the atom (as a result of collision with another atom, the absorption of a light quantum, impingement of electrons, etc.)

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[1] The spin due to the inherent angular momentum of the electron is a vector and is therefore designated by an arrow. The sum of the spins of two electrons with opposite spins is equal to zero.

one or several electrons in the atom may pass to a higher energy level
and become '*excited*'. As a rule the atom persists in the excited state
for a very short period of time (of the order of 10^{-5} to 10^{-8} s), after
which the electron returns to the lowest energy level and the atom
returns to the ground state. If there are intermediate levels between
the lowest energy level and the one at which the electron is located,
the return to the ground state can take place in several stages.

When an electron returns from a higher energy level to a lower
one, the atom radiates a quantum of light the frequency of which
according to Planck's equation (2.5) is determined by the relation

$$E_2 - E_1 = h\nu \qquad\qquad (4.21)$$

This frequency characterizes the respective spectral line. Thus, the
appearance of each spectral line is due to the transition of an electron
from one energy level to another (see Fig. 2.4). Therefore, the spectrum
of an element indicates the energy transitions of electrons that take
place when an excited atom returns to the ground state.

The transitions of electrons between the inner shells produce
X-rays of a wavelength much shorter than that of visible light. This
is so because the inner electrons are more strongly bound to the
nucleus; hence, their transitions are accompanied by greater energy
changes, which according to equation (4.21) results in radiation of
high frequency and, consequently, of short wavelength. X-ray spectra
consist of few lines; proceeding from one element to another their
frequencies vary continuously with an increase in the charge of the
nucleus (see p. 67).

The transitions of the outer electrons of atoms are accompanied by
smaller energy changes and produce spectra in the visible and ultra-
violet regions.

The study of spectra makes it possible to deduce the electronic
structure of atoms of elements, i.e., to find the values of the quantum
numbers and the energy of electrons in atoms (generally, by the
'electronic structure of an atom' is meant its structure in the ground
state).

The determination of electronic structure from spectral data is
often a very difficult task. For this purpose it is necessary to assign
the lines in the spectrum to definite series and to find out, with the
aid of the rules of quantum mechanics, what transition caused the
appearance of each spectral line. Because of the great number of
lines in spectra, that is not an easy task. However, as a result of the
painstaking work of a great number of investigators, the electronic
structure of most of the elements is now known. Mendeleev's Periodic
Law has played a great part in the systematization and interpretat-
ion of atomic spectra.

Figure 4.10 presents schematically the energy levels of the outer
electron of the lithium atom. The lines connecting the different

levels show the transitions of the electrons; the wavelengths of the respective spectral lines in Å are also given in the diagram. As can be seen, for the outer electron in the lithium atom, the 2s-state is the one with minimum energy. The spectrum of lithium can be plotted with the aid of this diagram. The investigator who studies spectra solves the reverse problem: his task is to construct an energy level diagram (like the one shown in Fig. 4.10) from the spectroscopic data.

The energy levels and electron density distribution in many-electron atoms, the same as in the hydrogen atom, can in principle be calculated theoretically by the methods of quantum mechanics; however, this involves complex calcula-
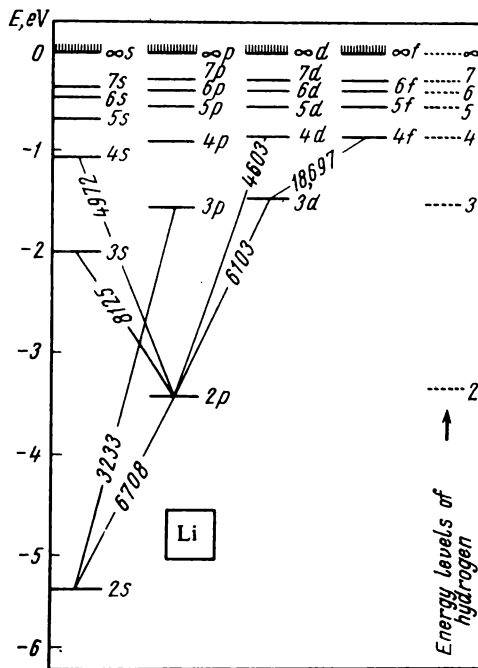
Fig. 4.10. Diagram showing the origination of the lithium atom spectrum. The energy levels of the electron in the hydrogen atom are given for comparison

tions because the Schrödinger equation must be solved for many particles. The equation in this case is

$$\sum_{k=1}^{k=N} \left[\left(\frac{\partial^2 \psi}{\partial x_k^2} + \frac{\partial^2 \psi}{\partial y_k^2} + \frac{\partial^2 \psi}{\partial z_k^2} \right) + \frac{8\pi^2 m}{h^2} \left(\frac{e^2 Z}{r_k} - U_k \right) \psi \right] + \frac{8\pi^2 m}{h^2} E\psi = 0$$

(4.22)

Here all the electrons in the atom are submitted to such mathematical treatment (r_k is the distance of the kth electron from the centre of the nucleus) and the term U_k takes into account the energy of repulsion of the given electron from the other electrons; it is equal to e^2/r_{ki} taken from $i = 1$ to $i = N$, where r_{ki} is the distance between the kth and ith electrons. Thus, even for the simplest many-electron atom, helium, the sum of the second derivatives alone contains six terms. The Schrödinger equation is not exactly soluble for such problems; however, approximate methods of solution have been

found. These methods are very complicated and the calculations involved are very laborious. At the present time, electronic computers are used for this purpose.

4.7. Energy Characteristics of Atoms:
Ionization Energy and Electron Affinity

The behaviour of atoms in chemical processes depends essentially on the strength with which the electrons are retained on their orbitals. Therefore, an important characteristic is the *ionization energy*, i.e., *the energy required to remove an electron from an atom in the ground state*. This concept also applies to molecules. The ionization energy, like the energy levels in atoms can be determined from spectral data.

The short-wavelength limit in a spectral series, indicating the transitions of electrons to the ground state, corresponds to the emission of energy when an electron outside the atom is transferred to the ground state. It is evident that the same energy is required to remove an electron from an atom. Hence, the ionization energy can be calculated by Planck's equation (2.5) from the frequency corresponding to the short-wavelength limit of the given series; the spectral term corresponding to the lowest energy level is called the *ground term*.

The ionization energy can be determined by different methods, in particular the *electron impingement* and *photoionization methods*. The ionization energy is usually expressed in electron-volts and is therefore often called the *ionization potential*, having in mind the potential difference (expressed in volts) due to which the electron acquires energy equal to the ionization energy.

The ionization energy of the hydrogen atom is easily calculated theoretically; from equation (4.17) it is apparent that it is expressed by the relation

$$I = \frac{1}{2} \frac{m_e e^4}{\hbar^2} \tag{4.23}$$

Inserting into this equation the appropriate values of m_e, e^4, $\hbar^2$, we obtain $I = 13.60$ eV.

For many-electron atoms there exist several ionization energies: I_1, I_2, . . ., corresponding to the removal of the first, second, etc. electron; in every case

$$I_1 < I_2 < I_3 < \ldots, \tag{4.24}$$

because with an increase in the number of electrons removed, the charge of the positive ion produced is increased and it attracts the electron more strongly.

Table 4.3 presents the ionization energies of certain atoms. From the Table it follows that the alkali metals have the smallest value of I_1 and that for a given element the ionization potential changes

Table 4.3

Ionization Energies of Certain Elements *

Atom	I, eV				
	1	2	3	4	5
H	13.595				
He	24.581	54.403			
Li	5.390	75.619	122.419		
Be	9.320	18.206	153.850	217.657	
B	8.296	25.149	37.920	259.298	340.127
C	11.256	24.376	47.871	64.48	392.00
N	14.53	25.593	47.426	77.450	97.863
O	13.614	35.146	54.934	77.394	113.873
F	17.418	34.98	62.646	87.23	114.214
Ne	21.559	41.07	63.5	97.16	126.4
Na	5.138	47.29	71.65	98.88	138.60
Mg	7.644	15.031	80.12	109.29	141.23
Al	5.984	18.823	28.44	119.96	153.77
Si	8.149	16.34	33.46	45.13	166.73
P	10.484	19.72	30.156	51.354	65.007
S	10.357	23.4	35.0	47.29	72.5
Cl	13.01	23.80	39.90	53.5	67.80
A	15.755	27.62	40.90	59.79	75.0
K	4.339	31.81	46	60.90	—
Ca	6.111	11.868	51.21	67	84.39

* Higher potentials, beginning with the 6th, are not included in the Table. A dash signifies that no experimental data is available.

sharply from one value of I to another. Thus, for boron the removal of the 4th and 5th electrons requires approximately a ten-fold consumption of energy as compared to the 1st, 2nd, and 3rd electrons. This affords direct evidence that the electrons are grouped in shells. In Table 4.3 sharp changes are indicated by step-shaped lines.

Figure 4.11 shows (the scale of the diagram is distorted) the energy levels and values of I_i ($i = 1, 2, 3, 4, 5$) for boron and its ions.

The increase in the binding energy between the 1s- and 2s-electrons and the nucleus with an increase in i is explained by the reduction in size of the ion with an increase in its charge.

Although in principle any degree of ionization is possible, chemists however are only interested in the first few ionization energies because, taking into account that 1 eV is equal to 23.1 kcal/gram-atom, it is obvious that the energies absorbed or emitted in chemical processes are commensurable with the first ionization potentials (see p. 135). Indeed, whereas chemical processes are accompanied by the emission or absorption of energy of the order of tens and hundreds of kcal/mole, the removal of seven electrons from the fluorine atom, for example,

$$F \longrightarrow F^{7+}$$
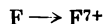
would require more than 15,000 kcal/gram-atom.
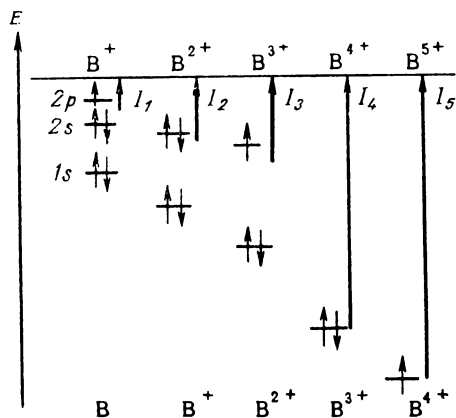
Fig. 4.11. Ionization energies and energy levels of the boron atom and ions (schematic representation)

The ionization energies are very important characteristics of atoms. This will become evident below; here the significance of these values can be illustrated by the following example. In 1962 Bartlett (Canada) synthesized the compound O_2PtF_6. By theoretical reasoning Bartlett came to the conclusion that this compound consists of the ions O_2^+ and $[PtF_6]^-$. The fact that the ionization energy of the O_2 molecule and the Xe atom are almost the same (12.2 and 12.13 eV, respectively) led him to conclude that it was possible to obtain a similar compound with xenon. Bartlett actually synthesized $XePtF_6$. In this way the synthesis of compounds of noble gases (also called rare and inert gases)[1] was initiated. This is one of the remarkable achievements of chemistry in recent years.

Electrons are retained in atoms by the field of the nucleus; this field also attracts a free electron if it happens to be near the atom. It is true that the free electron is repelled by the electrons of the atom. However, theoretical calculation and experimental data have

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[1] None of these terms is perfect. We prefer the term 'noble' because 'rare' is not absolutely appropriate (about 1 per cent of argon is contained in air) and 'inert' is contradicted by the reactability of these elements. As we know, noble metals also tend to react chemically.

shown that for many atoms the energy with which an additional electron is attracted exceeds that with which it is repelled by the electron shells; these atoms can add an electron and produce a stable negative single-charged ion. The energy required to remove the additional electron from such an ion is determined by the *electron affinity* of the atom (also defined as the energy evolved when an electron is added to an atom or ion). Like the ionization energy, electron affinity is usually expressed in electron-volts.

Quantum-mechanical calculations show that when two or more electrons are added to an atom, the repulsion energy is always greater than the attraction energy, i.e., the electron affinity in this case is always negative. Therefore, single-atom multicharged negative ions (O^{2-}, S^{2-}, N^{3-}, etc.) cannot exist in the free state. As we shall see later on (see p. 228) there are grounds for believing that neither do such ions exist in molecules and crystals. Hence, the formulae $Ca^{2+}S^{2-}$, $Cu^{2+}O^{2-}$, etc. should be considered to be only a rough approximation.

The electron affinities of all of the atoms are not as yet known. Table 4.4 gives the electron affinities of certain elements. The halogen atoms possess the maximum electron affinity. The Table shows that in passing from fluorine to iodine the electron affinity first increases but then gradually decreases. The method used for calculation of electron affinity is discussed on p. 291.

Table 4.4

The Electron Affinity of Certain Elements

Atom	E, eV	Atom	E, eV	Atom	E, eV	Atom	E, eV
H	0.747	C	1.24	Na	0.47	S	2.33
He	0.19	N	0.05	Mg	—0.32	Cl	3.81
Li	0.82	O	1.47	Al	0.52	Br	3.56
Be	—0.19	F	3.58	Si	1.46	I	3.29
B	0.33	Ne	—0.57	P	0.77		

MENDELEEV'S PERIODIC LAW
AND THE STRUCTURE OF ATOMS OF ELEMENTS

CHAPTER FIVE

INTRODUCTION

5.1. The Modern Formulation of the Periodic Law

The Periodic Law was set forth by D. Mendeleev in 1869 and was formulated by him as follows: *the properties of simple substances[1] as well as the forms and properties of compounds of elements vary periodically with the atomic weights of the elements.*

D. Mendeleev believed that the Periodic Law reflected the profound regularities in the internal structure of matter. In his book "Fundamentals of Chemistry" he wrote: "...the periodic system has not only embraced the interrelations of the elements but has perfected the knowledge of the kinds of compounds formed by the elements, shown that the physical and chemical properties of simple substances and compounds vary periodically. Such relationships make it possible to predict the properties of simple substances and compounds that have not as yet been studied experimentally and therefore pave the way to atomic and molecular mechanics".

The Periodic Law is expressed by the *periodic system of the elements.* As is known, mathematical functions can be expressed in three ways: by equations, by curves, or by tables. In the case of the Periodic Law, a table was the most appropriate way. Hundreds of periodic systems have been proposed but only those that closely resemble the table worked out by D. Mendeleev have been widely adopted.

The study of atomic structure has shown that the periodic system can be presented as a table in which the *elements are arranged in a strictly definite order in accordance with the structure of the electron shells of their atoms.* The everlasting fame of Mendeleev, rests on his setting forth a table that is simple enough yet covers all the basic details of atomic structure; therefore it has remained practically unchanged for over 100 years.

The electronic structure of an atom in the normal (ground) state is determined by the number of electrons in the atom. When the atom

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[1] A simple substance is one that consists of atoms containing nuclei of identical charge, i.e., of atoms of one and the same element. Examples of such substances are metallic sodium, diamond, graphite, argon, etc. A chemical element consists of a combination of atoms with nuclei of the same charge; these atoms can be present in simple substances or compounds.

is not excited the electrons occupy the orbitals in which their energy is minimum. The number of electrons in an atom is equal to the positive charge on the nucleus. Hence, the charge on the nucleus determines the electronic structure of atoms and, consequently, the properties of the elements. At the present time, therefore, the Periodic Law is formulated as follows: *the properties of elements and their compounds vary periodically with the nuclear charge of the atoms of the elements.*

As a rule, an increase in the nuclear charge (an increase in the number of protons in the nucleus) is also accompanied by an increase in the average mass of the isotopes that make up the element, i.e., in the atomic weight of the element. Because of this, D. Mendeleev was able to work out a periodic system by arranging all the elements in ascending order of atomic weights. Exceptions to this rule are four pairs of elements: A and K, Co and Ni, Te and I, Th and Pa; the atomic weight of the first element in each pair is a little greater than that of the second one, although the nuclear charge of the atom is smaller[1].

The Periodic Law shows that the properties of the elements vary periodically with the nuclear charge of their atoms; this is true for a great number of diverse properties of the elements. Fig. 5.1*a, b* presents curves showing the dependence of atomic volumes[2] and melting points on the atomic number of the elements; Fig. 5.1*c*, the dependence of the first ionization energies on the atomic number. These curves are periodic and have a number of maxima and minima. Similar curves show the dependence on the atomic number of other properties such as the coefficient of compressibility, the coefficient of expansion, melting and boiling points, magnetic properties, dissociation energies, ionic radii and most important of all, chemical properties (for example, the heat of formation of such compounds as oxides).

The periodicity of properties can be obscure and even remain undetected unless appropriate conditions are observed when studying the elements. Thus, many physical properties (melting point, density, hardness, etc.) depend on the structure of matter. Therefore, these properties should be compared for identical structures; for instance, atomic radii should be compared in analogous atomic surroundings.

There are only very few properties that do not vary periodically with the atomic numbers.

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[1] The first element in each of these pairs contains a relatively large amount of the heavier isotope. Thus, argon consisting of isotopes with mass numbers 36, 38, 40 contains 99% $^{40}_{18}A$; potassium consisting of isotopes with mass numbers 39, 40, 41 contains 93% $^{39}_{19}K$ (only one isotope of cobalt, $^{59}_{27}Co$, is known, but nickel is a mixture of isotopes in which $^{58}_{28}Ni$ predominates).

[2] Atomic volume is the volume occupied by a gram-atom of an element; it is equal to the quotient obtained on dividing the gram-atomic weight by the density.

VII Periods

IV V VI

m.p., °K

4000
3000
2000
1000

0   20   40   60   80   100   Z

(b)

ν, cm³/g-atom

70
60
50
40
30
20
10
0

II III IV V VI VII Periods

20   40   60   80   Z

(a)

I_r, eV

25
20
15
10
5
0

II III IV V VI VII Periods

He
Ne
A   Kr   Xe   Rn
Li Na K   Rb   Cs

20   40   60   80   Z
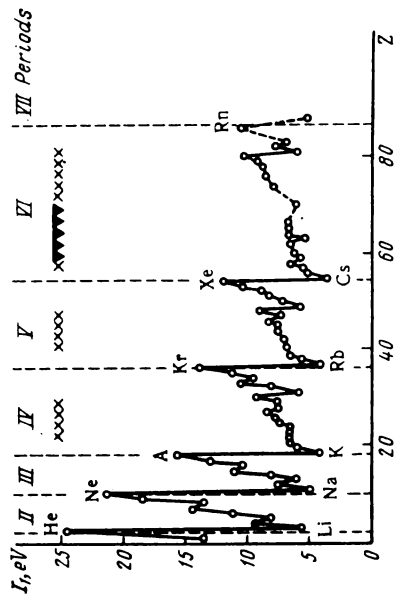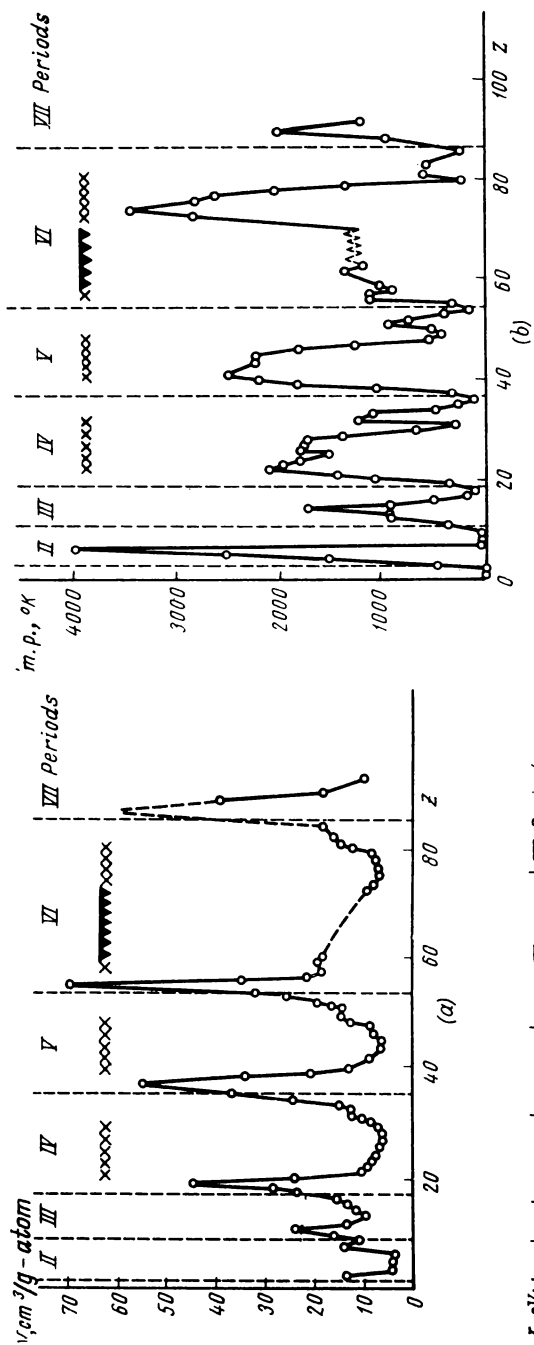
Fig. 5.1. Dependence on atomic number of
(a) atomic volume of elements; (b) melting point of elements; (c) first
ionization energy. Symbol × denotes transition elements; symbol ▼,
lanthanides and actinides

At the first glance it may appear that the specific heats of elements do not vary periodically. Indeed, the atomic heat C equal to the product of the specific heat c (cal/g·degree) and the atomic weight A, according to the rule of Dulong and Petit, is an approximately constant quantity:

$$C = cA \approx 6.3 \tag{5.1}$$

Dulong and Petit's rule was at one time of great importance for finding the correct atomic weights of elements. It shows that the
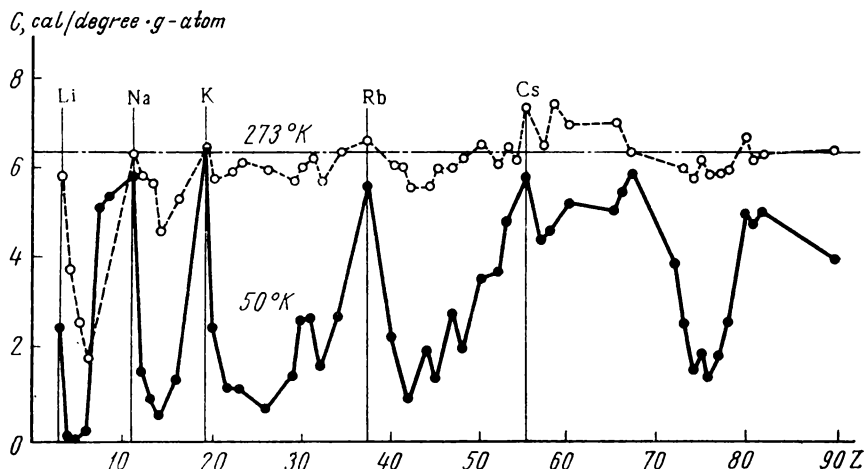
Fig. 5.2. Dependence of atomic heats of elements on their atomic number

specific heat decreases continuously with increasing atomic weight, i.e., this property does not seem to show periodicity. As can be seen in Fig. 5.2, except for the lightest elements, the points of the curve $C = f(Z)$ at $T = 273°$K fluctuate about the horizontal line corresponding to 6.3. The same Figure, however, shows that the curve at 50°K indicates that the atomic heats vary periodically with the atomic numbers. The curve for $t = 0°$C ($T = 273°$K) shows that actually periodicity occurs at this temperature also, although it is less pronounced due to the effect of the higher temperature (take note of the position of the points for the alkali metals).

The frequency of radiation (or the wave number $\overline{v}$. which is proportional to v) giving rise to X-ray spectral lines can be considered to be a nonperiodic property. This value changes continuously with an increase in the atomic number of the element according to the equation

$$\sqrt{\overline{v}} = A(Z - b) \tag{5.2}$$

5*

where $\bar{v}$ = wave number of a particular (first, second, etc.) line
  of the X-ray spectrum series
    Z = atomic number of the element
A and b = constants

Equation (5.2) is illustrated by Fig. 5.3. This regularity was esta-
blished experimentally in 1913 by Moseley, an Englishman. Mose-
ey's experimental data proved that the nuclear charge is numerically
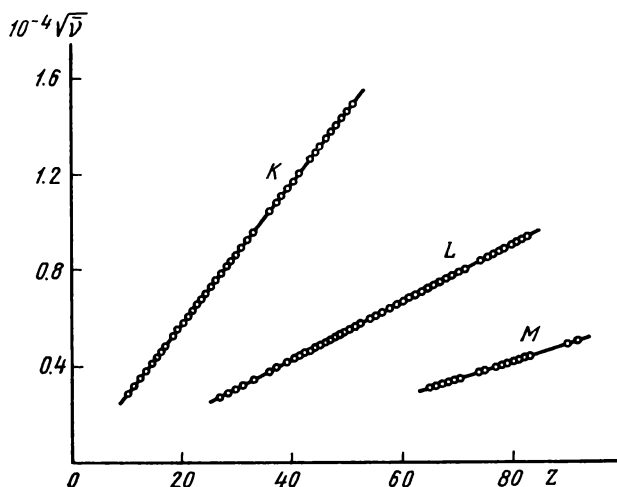
Fig. 5.3. Dependence of $\bar{v}$ for lines of the X-ray spectrum on the atomic number
of the element

equal to the atomic number of the element and gave undeniable
verification of the arrangement of the elements in the periodic
system.

Equation (5.2) can easily be obtained theoretically. As we already
know (see p. 58), the X-ray spectrum arises from transitions of
electrons between the inner shells of atoms. For atoms and ions with
one electron, the spectral term is given by equation (2.3). Somewhat
modified, this formula is applicable to an electron on one of the inner
shells of the atom. Electrons that are located at a greater distance
from the nucleus than the one under consideration affect but slightly
the energy of the latter because they are bound to the nucleus much
less strongly. Their action on the electron is so small that can
be ignored. The electrons that are located between the given
electron and the nucleus will decrease its attraction to the nucleus.
This effect can formally be considered as a decrease in the charge
acting on the electron by a certain value b known as the *screening*

constant. The expression for the spectral term will then be

$$T = R \frac{(Z-b)^2}{n^2}$$

from which we can find the wave number:

$$\bar{v} = T(n_1) - T(n_2) = (Z-b)^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

When considering the transitions of electrons between identical energy levels in different atoms, the value $R(1/n_1^2 - 1/n_2^2)$ will be a constant. If we denote this constant as A^2, we obtain the equation

$$\bar{v} = A^2 (Z - b)^2$$

which is the same as Moseley's formula [see equation (5.2)].

X-ray spectra arise as the result of the transition of electrons located near the nucleus. It may appear that Moseley's law indicates the absence of periodicity of properties of the inner electrons. Equation (5.2), however, holds true only because here under consideration is the change with increasing atomic number in the energetics of an electron having the same set of quantum numbers. In the given case the energy of the bond between the electron and the nucleus will increase continuously with an increase in the nuclear charge. If, however, we consider the high ionization energies, we see that they are periodic functions of Z since in this case the electrons in question have different sets of quantum numbers.

Hence, periodicity is characteristic of the electron shell as a whole and not only its periphery.

5.2. The Structure of the Periodic System

Mendeleev's system consists of several *periods* corresponding to the periodic variation of the properties of the elements. This is presented schematically in Fig. 5.4 in which are given the atomic numbers of the first, next to the last, and last element of each period. Three of them (I, II, III) are single-series *short periods*; the first contains only two elements, the second and third each contains eight elements. The remaining ones are *long periods*; two of them (IV and V) each contains 18 elements and one of them (VI) contains 32 elements. The seventh period is incomplete. Omitting the first period, each pair of periods, i.e., II and III, IV and V, VI and VII, are similarly constructed; this is also confirmed by Fig. 5.1.

Let us now pass from the schematic representation to the detailed structure of the periodic system (see the fly-leaf at the beginning of the book).

Each period (except the first one) begins with a typical metal (Li, Na, K, Rb, Cs, Fr, respectively) and ends at a noble gas (Ne,

A, Kr, Xe, Rn) which is preceded by a typical nonmetal (F, Cl, Br, I, At). These are the elements that are shown in Fig. 5.4 (the atomic numbers of the noble gases are enclosed in double lines). In passing from Li to F, from Na to Cl, etc. there is a gradual decline in the metallic properties and an increase in those characteristic of nonmetals.

The noble gas is the element that separates the typical nonmetal of the given period from the typical metal at the head of the next period. In the first period, besides helium, there is only one element, hydrogen; hence, it may be expected that hydrogen has some properties typical of metals and some typical of nonmetals. This will be confirmed below (see p. 103, 109).

The two-series fourth and fifth periods, in contrast to the second and third periods, contain *transition groups comprising ten elements*: after the second element of Period IV, Ca, come the 10 *transition elements* (Sc — Zn) after which come the other 6 main elements of the period (Ga — Kr). Period V is constructed similarly. Since the elements of the transition groups are all metals, the even series of Periods

Fig. 5.4. Schematic representation of Mendeleev's Periodic System of the Elements

IV and V contain only metals. In these two periods |the presence of 16 elements between the typical metal and typical nonmetal (between K and Br and between Rb and I, respectively) instead of 5 elements as in the short periods accounts for the fact that the adjacent elements in the fourth and fifth periods differ from each other much less than in the second and third periods. As we shall see below this is explained by the fact that whereas in the group Mg—S the number of outer electrons is not the same, in the groups Sc—Zn and Y—Cd it is, apart from a few exceptions, identical (two outermost s-electrons).

The two following periods are characterized by the presence of groups of ten and fourteen elements in addition to the main elements. Immediately after the second element of Period VI, Ba, there should come the ten transition elements La—Hg, but actually

after the first transition element, La, there come the 14 elements Ce—Lu. After Lu the transition group is continued and completed (Hf—Hg) and after that come the other 6 main elements of Period VI (Tl—Rn). The incomplete Period VII is constructed similarly: the transition group here contains as yet only three elements which are separated by the 14 elements Th—Lw. This group of elements also contains only metals that resemble each other even more than do the ten transition elements as is clearly shown in Fig. 5.1. Because of this, all 14 elements can be regarded as occupying a single position in the periodic system (together with La and Ac, respectively). If this is done, Periods VI and VII also become two-series periods, i.e., similar to Periods IV and V. The similarity of these elements to La and Ac, respectively, explains why they are called *lanthanides* (Ce—Lu) and *actinides* (Th—Lw). The difference in the properties of the lanthanides and actinides is attributed to some difference in the $(n-1)\,d$ and $(n-2)\,f$ energy levels.

Although, as we have seen above, in passing from an 8-element to an 18-element period and from an 18-element to a 32-element period the increasing resemblance of adjacent elements mainly concerns the middle of a given period, it is however true for the period as a whole. Thus, for example, whereas there is hardly any resemblance between C and N, the resemblance between Pb and Bi is considerable.

The arrangement of the elements in periods (horizontal rows) results in the formation of vertical rows of allied elements, i.e., of families or *groups*. Because of the presence of transition elements in Periods IV, V, VI, and VII and actinides and lanthanides in the last two periods, there are three types of *subgroups*.

The *main subgroups* are formed by the main elements of each period. They are the longest ones; they begin with the elements of the second period. The main subgroups are the Li, Be, B, C, N, O and F subgroups; to them should be added the noble gases which form the zero group (see footnote on p. 112).

The transition elements form the *supplementary subgroups*. They are shorter than the main subgroups and begin with elements in Period IV. There are ten of them corresponding to the number of transition elements in this period: the Cu, Zn, Sc, Ti, V, Cr, Mn, Fe, Co and Ni subgroups. The elements of the first seven supplementary subgroups together with the elements of the respective main subgroups make up the first seven groups. The elements constituting the main and supplementary subgroups are arranged alternately (see the fly-leaf at the beginning of the book) in order to show that they form different families of closely related elements. The elements of the last three supplementary subgroups constitute the eighth group.

Thus we see that the zero and eighth groups differ from the others: the zero group does not contain elements of supplementary sub-

groups; the eighth group does not contain elements of the main subgroups (see footnote on p. 112).

The shortest subgroups are those made up of two elements; one lanthanide and one actinide. They begin in Period VI. There are fourteen of them. They are all included in Group III. Hence, Group III is the largest of all the groups; it contains 5 elements of the main subgroup, 4 elements of the supplementary subgroup, and 28 elements of the lanthanide and actinide series. In all, it contains 37 elements.

Within each group the properties of the elements of the main and supplementary subgroups differ from one another, but the degree of difference varies from group to group. In the first group the difference in the properties of the elements is considerable; in the following groups at first it is less, then greater, and in the seventh group very great. Thus, the copper subgroup includes the low-activity metals Cu, Ag, Au, that differ sharply from the active metals of the lithium subgroup (in particular from K, Rb, Cs); the elements of Group III are relatively close to each other in their properties; while the elements of the Mn subgroup differ greatly from the halogens.

Table 5.1

Mendeleev's Periodic System of the Elements
(long-form table, first variant)

Table 5.2

Mendeleev's Periodic System of the Elements
(long-form table, second variant)

Periods	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 A
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Ku	105													
	s		d						d								p	

f

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

Nevertheless, when noting the degree of difference, it should always be remembered that all the elements of a given group have characteristics in common; this is discussed in detail in courses of inorganic chemistry (see also p. 112).

As has already been mentioned, there are many different representations of the periodic system of the chemical elements. Tables 5.1 and 5.2 present two long-form variants. These, in addition to the short-form table discussed above, are the most widespread.

In Table 5.1 the elements of the supplementary subgroups are positioned separately between the beryllium (IIA) and boron (IIIA) subgroups as 10 vertical columns and the lanthanides and actinides are placed outside the Table as two horizontal series. In Table 5.2, in contrast to the preceding one, the lanthanides and actinides are included within the Table and are arranged as fourteen vertical columns between the scandium (IIIB) and titanium (IVB) subgroups. In this book we shall use the short-form table.

5.3. Predicting the Properties of Substances with the Aid of the Periodic Law

Mendeleev's Periodic Law can be used to determine unknown properties of elements and their compounds. A great number of such properties were first determined by D. Mendeleev himself; he even calculated the properties of elements then not discovered yet. As is known, the predictions made by D. Mendeleev were fully verified. The history of natural science knows no other examples of such brilliantly confirmed prognosis. To predict the properties of elements and their compounds D. Mendeleev made use of the following procedure: he found the unknown property as the *arithmetic mean* of the properties of the elements surrounding the given element in the periodic system: to the right of, to the left of, above and below it. This procedure can be called the *Mendeleev method*.

Thus, for example, the elements next to selenium are arsenic (to the left) and bromine (to the right) which form H_3As and HBr, respectively; evidently, selenium can form H_2Se and the properties of this compound (melting and boiling points, solubility in water, density in the liquid and solid states, etc.) will be close to the arithmetic mean of the corresponding properties of H_3As and HBr. In the same way the properties of H_2Se can be determined as the average of the properties of H_2S and H_2Te, i.e., of similar compounds of sulphur and tellurium, the elements placed in the periodic system above and below selenium. Obviously the results obtained will be more accurate if the properties of H_2Se are calculated as the average of the properties of the four compounds, H_3As, HBr, H_2S, and H_2Te. At the present time this method is widely used to estimate the properties of uninvestigated substances.

There are however other methods of using the Periodic Law to determine unknown physical and chemical constants. It is worth-

while to dwell on the use of the periodic law in the *methods of comparative calculation* worked out and studied by M. Karapetyants.

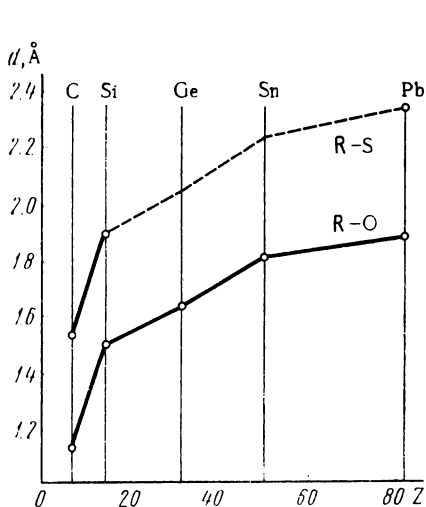Fig. 5.5. Dependence of the distances R—S and R—O on the atomic number of the element
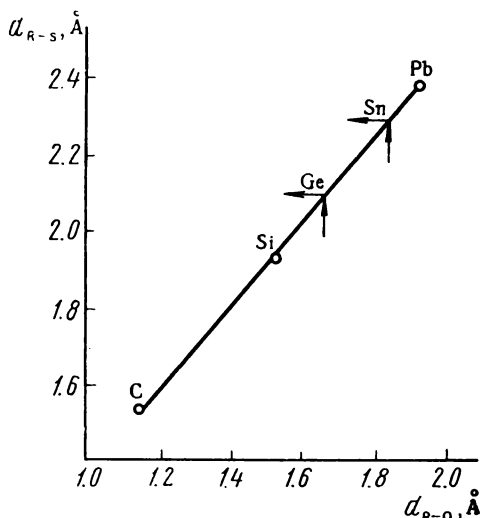

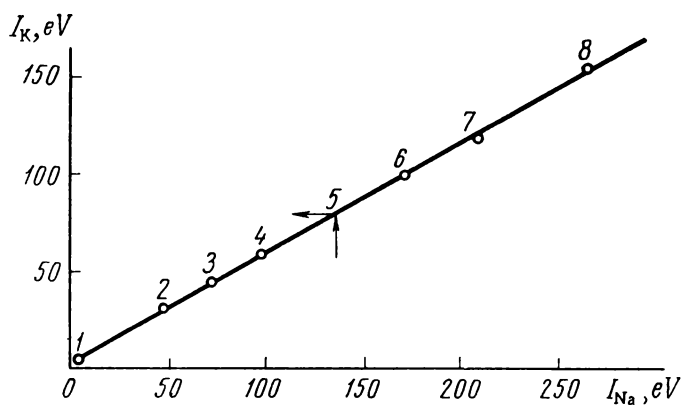**Fig.** 5.6. Comparison of interatomic distances R—O and R—S

Fig. 5.7. Comparison of ionization potentials of sodium and potassium

In these methods, the same as in Mendeleev's method, the physicochemical constants are found by comparing the known values of properties. Let us consider two examples of how the Periodic

Law is used in the method known as the *first method of comparative calculation*. There are six methods in all.

In Fig. 5.5 the distances between the atoms of sulphur and the elements of the fourth group, C, Si, Pb, combined with it in gaseous CS_2, SiS_2, and PbS_2 are plotted against the atomic numbers of the elements. As can be seen, there is no simple relationship by which the unknown distances Ge—S and Sn—S can be determined. Similarly, in the compounds CO_2, SiO_2, GeO_2, SnO_2 and PbO_2, the dependence of the distances R—O (where R—atom of the given element) on the atomic numbers of the elements is complex. However, if the idstances R—S and R—O are correlated as is shown in Fig. 5.6, the points form a straight line from which the unknown distances Ge—S and Sn—S can be found.

Figure 5.7 shows how the unknown fifth ionization potential of the potassium atom can be found by a similar method.

As can be seen, in both cases the properties of *closely related* (*allied*) *substances* are compared. The Periodic Law indicates which inorganic substances can be compared in this way (see also Figs 7.2, 8.1, 11.7, 11.8 and others).

CHAPTER SIX

THE PERIODIC SYSTEM OF THE ELEMENTS
AND THEIR ATOMIC STRUCTURE

6.1. Filling of Electron Shells and Subshells

Let us consider the connection between the electronic structure of atoms and the position of the elements in the periodic system. The electronic structure of atoms of the elements is presented in Table 6.1.

Hydrogen is the first element in the periodic table. The minimum energy of its single electron corresponds to the K-shell ($n=1$), i.e., the $1s$-state. Helium has two electrons ($1s^2$) of opposite spin.

Beginning with lithium the L-shell ($n=2$) is formed since in accordance with the Pauli exclusion principle the first shell cannot be occupied by more than two electrons of opposite spin. In neon the second shell is completely filled; the s- and p-subshells are fully occupied. The third shell is progressively occupied from sodium to argon in the same way as the second shell.

Although in the third shell there are still 10 vacancies because the $3d$-subshell remains entirely unoccupied, in potassium and calcium (the elements following argon) the fourth shell begins to be filled and only beginning with scandium the $3d$-subshell begins to be formed and is completed in copper. In the transition elements Sc—Zn, the d-subshell is not filled consecutively: in the Cr and

Table 6.1

Electronic Structure of Atoms of Elements in the Ground State

Symbols

☐ *completely filled electron shell*

* *transition elements*

▼ *lanthanides and actinides*

1	H	$1s$	
2	He	$\boxed{1s^2}$	1st period

3	Li	$\boxed{K}\,2s$	
4	Be	$\boxed{K}\,2s^2$	
5	B	$\boxed{K}$,, $2p$	
6	C	$\boxed{K}$,, $2p^2$	
7	N	$\boxed{K}$,, $2p^3$	2nd period
8	O	$\boxed{K}$,, $2p^4$	
9	F	$\boxed{K}$,, $2p^5$	
10	Ne	$\boxed{K\;2s^22p^6}$	

11	Na	$\boxed{K\quad L}\;3s$	
12	Mg	$\boxed{K\quad L}\;3s^2$	
13	Al	$\boxed{K\quad L}$,, $3p$	
14	Si	$\boxed{K\quad L}$,, $3p^2$	
15	P	$\boxed{K\quad L}$,, $3p^3$	3rd period
16	S	$\boxed{K\quad L}$,, $3p^4$	
17	Cl	$\boxed{K\quad L}$,, $3p^5$	
18	A	$\boxed{K\quad L}$, $3p^6$	

19	K	$\boxed{K\quad L}$,, ,,		$4s$	
20	Ca	$\boxed{K\quad L}$,, ,,		$4s^2$	
*21	Sc	$\boxed{K\quad L}$,, ,, $3d$	,,		
*22	Ti	$\boxed{K\quad L}$,, ,, $3d^2$			
*23	V	$\boxed{K\quad L}$,, ,, $3d^3$			4th period
*24	Cr	$\boxed{K\quad L}$,, ,, $3d^5$		$4s$	
*25	Mn	$\boxed{K\quad L}$,, ,, $3d^5$		$4s^2$	

*26	Fe	K | L		$3s^2 3p^6 3d^6$ $4s^2$	
*27	Co	K | L		,, ,, $3d^7$	
*28	Ni	K | L		,, ,, $3d^8$	
*29	Cu	K | L		$3s^2 3p^6 3d^{10}$ $4s$	
*30	Zn	K | L | M		$4s^2$	
31	Ga	K | L | M		,, $4p$	
32	Ge	K | L | M		,, $4p^2$	
33	As	K | L | M		,, $4p^3$	
34	Se	K | L | M		,, $4p^4$	
35	Br	K | L | M		,, $4p^5$	
36	Kr	K | L | M		,, $4p^6$	

4th period

37	Rb	K | L | M	,, ,,		$5s$
38	Sr	K | L | M	,, ,,		$5s^2$
*39	Y	K | L | M	,, ,, $4d$		,,
*40	Zr	K | L | M	,, ,, $4d^2$		,,
*41	Nb	K | L | M	,, ,, $4d^4$		$5s$
*42	Mo	K | L | M	,, ,, $4d^5$		$5s$
*43	Tc	K | L | M	,, ,, $4d^5$		$5s^2$
*44	Ru	K | L | M	,, ,, $4d^7$		$5s$
*45	Rh	K | L | M	,, ,, $4d^8$		$5s$
*46	Pd	K | L | M	,, ,, $4d^{10}$		
*47	Ag	K | L | M	,, ,, ,,		$5s$
*48	Cd	K | L | M	,, ,,		$5s^2$
49	In	K | L | M	,, ,, ,,	,,	$5p$
50	Sn	K | L | M	,, ,, ,,	,,	$5p^2$
51	Sb	K | L | M	,, ,,		$5p^3$
52	Te	K | L | M	,, ,, ,,	,,	$5p^4$
53	I	K | L | M	,, ,, ,,	,,	$5p^5$
54	Xe	K | L | M	,, ,, ,,	,,	$5p^6$

5th period

No.		K	L	M	N				
55	Cs	K	L	M		$4s^2 4p^6 4d^{10}$	$5s^2 5p^6$		$6s$
56	Ba	K	L	M		,, ,,			$6s^2$
*57	La	K	L	M		,,	,, ,, $5d$		
▼58	Ce	K	L	M		,, ,, $4f^2$			
▼59	Pr	K	L	M		,, ,, $4f^3$			
▼60	Nd	K	L	M		,, ,, ,, $4f^4$			
▼61	Pm	K	L	M		,, ,, ,, $4f^5$			
▼62	Sm	K	L	M		,, ,, ,, $4f^6$			
▼63	Eu	K	L	M		,, ,, ,, $4f^7$			
▼64	Gd	K	L	M		,, ,, ,, $4f^7$	,, ,, $5d$		
▼65	Tb	K	L	M		,, ,, ,, $4f^9$			
▼66	Dy	K	L	M		,, ,, ,, $4f^{10}$			
▼67	Ho	K	L	M		,, ,, ,, $4f^{11}$			
▼68	Er	K	L	M		,, ,, ,, $4f^{12}$			
▼69	Tm	K	L	M		,, ,, ,, $4f^{13}$	,, ,,		,,
▼70	Yb	K	L	M		,, ,, ,, $4f^{14}$	,, ,,		,,
▼71	Lu	K	L	M	$4s^2 4p^6 4d^{10} 4f^{14}$	,, ,, $5d$			
*72	Hf	K	L	M	N	,, ,, $5d^2$	,,		
*73	Ta	K	L	M	N	,, ,, $5d^3$	,,		
*74	W	K	L	M	N	,, ,, $5d^4$	,,		
*75	Re	K	L	M	N	,, ,, $5d^5$			
*76	Os	K	L	M	N	,, ,, $5d^6$	,,		
*77	Ir	K	L	M	N	,, ,, $5d^7$			
*78	Pt	K	L	M	N	,, ,, $5d^9$	$6s$		
*79	Au	K	L	M	N	,, ,, $5d^{10}$	$6s$		
*80	Hg	K	L	M	N	,, ,,	$6s^2$		
81	Tl	K	L	M	N	,, ,,	,, $6p$		
82	Pb	K	L	M	N	,, ,, ,,	,, $6p^2$		
83	Bi	K	L	M	N	,, ,, ,,	,, $6p^3$		
84	Po	K	L	M	N	,, ,, ,,	,, $6p^4$		
85	At	K	L	M	N	,, ,, ,,	,, $6p^5$		
86	Rn	K	L	M	N	,, ,, ,,	,, $6p^6$		

6th period

Continued

		K	L	M	N	$5s^2$	$5p^6$	$5d^{10}$	$5f$	$6s^2$	$6p^6$	$6d$	$7s$
87	Fr	K	L	M	N	$5s^2$	$5p^6$	$5d^{10}$		$6s^2$	$6p^6$		$7s$
88	Ra	K	L	M	N	..	..	..		..	..		$7s^2$
*89	Ac	K	L	M	N	..	..	..		..	..	$6d$	..
▼90	Th	K	L	M	N	..	..	..		..	..	$6d^2$	..
▼91	Pa	K	L	M	N	..	..	..	$5f^2$	..	..	$6d$	..
▼92	U	K	L	M	N	..	..	..	$5f^3$	..	..	$6d$	..
▼93	Np	K	L	M	N	..	..	..	$5f^5$	..	..		..
▼94	Pu	K	L	M	N	..	..	..	$5f^6$	..	..		..
▼95	Am	K	L	M	N	..	..	..	$5f^7$	..	..		..
▼96	Cm	K	L	M	N	..	..	..	$5f^7$	..	..	$6d$	..
▼97	Bk	K	L	M	N	..	..	..	$5f^9$	..	..		..
▼98	Cf	K	L	M	N	..	..	..	$5f^{10}$	..	..		..
▼99	Es	K	L	M	N	..	..	..	$5f^{11}$	..	..		..
▼100	Fm	K	L	M	N	..	..	..	$5f^{12}$	..	..		..
▼101	Md	K	L	M	N	..	..	..	$5f^{13}$	..	..		..
▼102	No	K	L	M	N	..	..	..	$5f^{14}$	..	..		..
▼103	Lw	K	L	M	N	..	..	..	..	..	..	$6d$	..
*104	Ku	K	L	M	N	..	..	..	..	..	..	$6d^2$	..
*105													

7th period

Cu atoms, an outer s-electron 'descends' onto the preceding d-sub-shell. The energies of the $3d$- and $4s$-states in the elements Sc—Zn are so close to one another that the addition of electrons can cause a change in the distribution of electrons on these energy levels. As a result of the 'descent' of an electron in the chromium atom, the d-subshell is half-filled (configuration d^5) and in copper is comple-tely filled (configuration d^{10}). Similar irregularities in the building up of the d- and f-subshells are also observed in the following periods (see Table 6.1).

After zinc, down to krypton, the fourth shell ($4p$-subshell) conti-nues to be filled. Thus, after the two-element period and two eight-element periods there follows a long period containing 18 elements.

The electron subshells of the following 18 elements (Rb—Xe) are filled in the same way as the electron subshells of the 18 elements of Period IV (K—Kr): after Rb ($5s$) and Sr ($5s^2$) the $4d$-subshell is filled in the transition elements from Y ($4d$) to Cd ($4d^{10}$) with several 'descents' of outer s-electrons. Then, although the $4f$-subshell

is not occupied at all, electrons are added to the p-subshell of the fifth shell.

Further building-up (*aufbau*) is accompanied by two deviations from the consecutive order of filling the subshells within one period: although after Cs (6s) and Ba (6s^2) comes La (5d), filling of the incomplete fifth shell is temporarily stopped after this element. The 4f-subshell is then formed, i.e., from Ce (4f^2) to Lu (4f^{14}) electrons fill the fourth shell that was previously left unfilled. After

Fig. 6.1. Sequence of filling of electron subshells
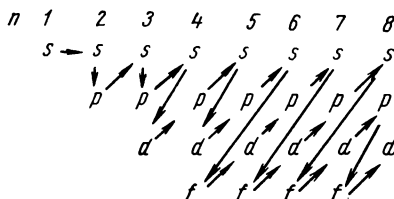
lutecium, from Hf (5d^2) to Au (5d^{10}), the 5d-subshell is filled completely, and beginning with Hg and ending with Rn filling of the sixth shell is continued. In this way, the sixth period containing 32 elements is completed.

The seventh period is formed similarly to the sixth one: after the 7s-elements (Fr, Ra) begins the Ac (6d) group of transition elements which is interrupted by the 14 actinides, from Th to Lw (5f^{14}). Only after that the group of transition elements is continued; kurchatovium Ku ($Z=104$), is already known and according to published data an element with an atomic number of 105 has been discovered. The seventh period is not complete[1].

The sequence in which the shells and subshells are filled is shown in Fig. 6.1.

Irregularities in the sequence of filling the electron shells, observed once in the fourth and fifth periods and twice in the sixth and seventh periods, are explained by the fact that it is energetically more favourable to temporarily leave a given subshell unfilled. Thus, the reason for the sequence $3p^6 \rightarrow 4s^2 \rightarrow 3d^{10}$ (instead of $3p^6 \rightarrow 3d^{10} \rightarrow 4s^2$) is that it is very difficult for a new electron to occupy the

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[1] The completion of this period is connected with the upper limit of the synthesis of transuranian elements (the heaviest naturally occurring element is uranium). The following must be kept in mind: the lifetime of the new elements should be greater than the time it takes for nuclear transitions to occur (estimated to be of the order of 10^{-20} s); with increasing atomic number, the size of the electron shells decreases, so that at $Z \approx 137$ the radius of the first shell would be so small that the electrons on it would be instantly captured by the nucleus; calculations show that the nuclei of elements with atomic numbers higher than 114-116 would undergo instantaneous *spontaneous fission*. It is true however, that lately it has been supposed that there exist ranges of stability for very heavy nuclei with a surplus of neutrons.
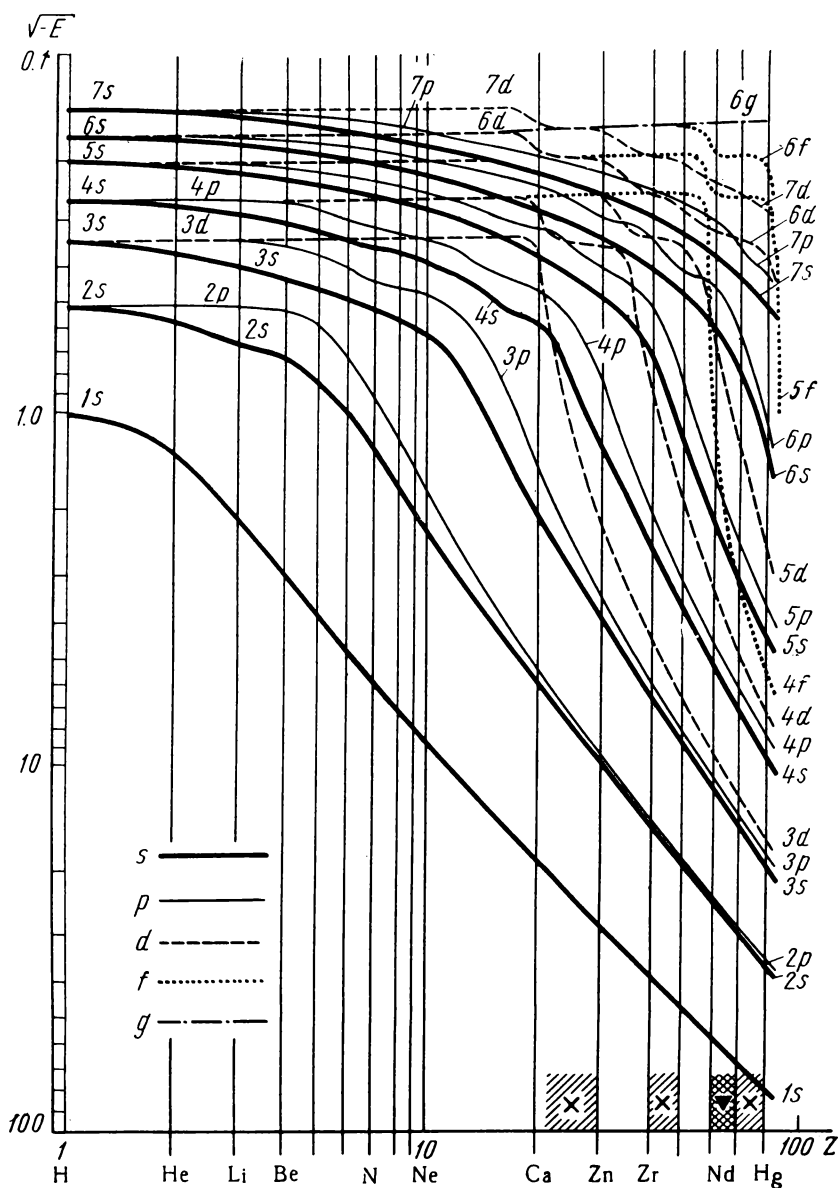
Fig. 6.2. Dependence of the energy of electrons in different shells and subshells on the atomic number of the elements. The unit of energy used here is 13.6 eV (the energy of the electron in the hydrogen atom in the ground state)

third shell due to the repulsion of the eight electrons already there. An increase in the nuclear charge, however, makes filling of the previously unfilled subshells more favourable as it compensates the repulsive forces of the electrons. With increasing nuclear charge the degree of screening (shielding) of the nucleus by electrons is also increased and that is why a large number of shells are filled irregularly; the effective nuclear charge becomes smaller and the preceding electrons are repulsed by those that follow to a greater extent. The 'descent' of electrons to lower electron subshells in Cr, Nb and other elements (see Table 6.1) is also energetically more favourable.

It should also be borne in mind that the energy of the electrons of each subshell depends not only on the number of the subshell but also on the nuclear charge; in other words, the energy of a given level varies from atom to atom. This is schematically shown in Fig. 6.2 where the atomic number is plotted (to logarithmic scale) on the axis of abscissae and the square root of the energy of the electron (with a minus sign) is plotted (also to logarithmic scale) on the axis of ordinates[1]. The curves show that there is a decrease in the energy of each level with an increase in the nuclear charge. The sharp drop in the *d*-curves is caused by the appearance of the transition elements (the diagonal shading above the axis of abscissae); and the still steeper drop in the *f*-curve, by the appearance of the lanthanides (the crosshatching above the axis of abscissae) and the actinides.

The irregularities in the sequence of filling of the electron subshells should not be regarded as a violation of the Pauli exclusion principle; this principle only gives the *maximum number of sets* of quantum numbers, but gives no indications as to the *sequence* of filling the energetic levels corresponding to these sets.

Thus, each successive element in the periodic system differs from the preceding one in that it contains one more electron. This electron may begin a new shell (Li, Na, . . .), may occupy an outer shell that already exists (Be, Mg, . . .), or may occupy a previously formed inner shell (Sc, Ti, . . .).

The filling of the electron shells and subshells of atoms of the elements in the periodic system makes evident the following general principles:

1. Each period begins with the formation of a new electron shell. A period is a consecutive series of elements the atoms of which differ in the number of electrons in the outermost shells. Each period ends in a noble gas the outer shell of which (besides helium) consists of 8 electrons and is denoted as ns^2np^6 (where $n > 1$).

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[1] The logarithmic scale is used because it makes it possible to plot a large range of values of the independent variable and function on relatively short regions of the axes.

2. The elements of the main and supplementary subgroups differ in which electron subshells are being filled. In all the elements of the main subgroups, either the outer ns-subshells (Groups I and II) or the outer np-subshells (Groups III to VII) are being filled; the former are called *s-elements*, the latter *p-elements*. In the elements of the supplementary subgroups (except for Mn, Zn, Tc, Ag, Cd and Hg) the inner $(n - 1)$ d-subshells are being filled. The elements of these supplementary subgroups form three groups of ten transition elements: 21 (Sc) — 30 (Zn); 39 (Y) — 48 (Cd); 57 (La), 72 (Hf) — 80 (Hg). A fourth group begins with 89 (Ac) in the incomplete seventh period. The transition elements are called *d-elements*.

3. In the lanthanide series, 58 (Ce) — 71 (Lu), and the actinide series, 90 (Th) — 103 (Lw), the $(n - 2)$ f-subshells, the $4f$- and $5f$-subshells respectively, are being filled. Therefore, these elements are called *f-elements*.

Because of the above-specified characteristics of electronic structure the properties of the elements in the periodic system vary in accordance with the principal regularities given below.

To clearly understand these regularities it should be borne in mind that in passing from one shell to the next one the change in the energy of the outer electrons (those determining the chemical properties of the element) decreases with an increase in n (see Fig. 6.2).

1. The elements of the first period, hydrogen and helium, in which the first electron shell of the atoms is being filled, are unique in many of their properties, i.e., they have some properties that no other element possesses (the properties of the H^+ ion, of liquefied He, etc.).

2. The elements of the second period, in which the second shell of the atoms is being filled, differ considerably from all the other elements. This is explained by the fact that the energy of the electrons in the second shell is much lower than that of the electrons in the following shells (see Fig. 6.2) and that there cannot be more than 8 electrons in the second shell.

3. The transition elements, in which the inner d-subshells are being filled, within a given period differ from each other much less than the elements of the main subgroups do, in which the outer shells are being built up.

4. The differences in the properties of the lanthanides, in which the $(n - 2)$ f-subshell (namely, the $4f$-subshell) is being filled, are insignificant[1].

The actinides are also similar to each other in many of their properties; in them the $(n - 2)$ f-subshell is also being filled. The differences in the properties of the actinides, however, are greater than

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[1] For this reason it is very difficult to separate the compounds of these elements from one another.

those of the lanthanides because the $5f$-subshell being filled is farther from the nucleus than the $4f$-subshell of the lanthanides, i.e., the former is 'more outer' than the latter. Because of this, the difference between the energies of the electrons in the $5f$- and $6d$-subshells in the atoms of the actinides becomes small (see Fig. 6.2); it is much less than the difference between the energies of the electrons in the $4f$- and $5d$-subshells of the lanthanides. Hence, the addition of electrons to the $5f$-subshell in the actinides causes approximately the same change in the properties as does the addition of d-electrons in the transition elements.

6.2. Variation of Ionization Energies

The ionization energy is a very important characteristic of atoms. As we shall see below, the nature and stability of chemical bonds depend on it as do the reducing properties of atoms, because an atom gives up an electron the more readily the smaller the ionization potential.

The dependence of the first ionization energies on the atomic number is shown in Fig. 5.1 c. It has already been noted that the ionization potential varies periodically. It is now necessary to examine this dependence more closely.

The ionization energy is equal in magnitude but opposite in sign to the energy of the most weakly bound electron when the atom (or ion) is in the ground state. Therefore, in order to find out how the ionization energy varies, it is necessary to consider the factors that determine the energy of electrons in atoms in greater detail.

If the electron under consideration were the only one in the atom, the energy of the electron, in accordance with (4.20), would depend only on the nuclear charge Z and principal quantum number n. The greater the value of Z and the smaller the value of n, the lower the energy level in a one-electron system and the stronger is the bond between the electron and the nucleus. The presence of other electrons in the atom (in addition to the one in question) greatly affects this simple relationship. The effect of the other electrons can be ascertained with the aid of two correlated conceptions; the concepts of *screening (shielding) of the nuclear charge* and *penetration of electrons to the nucleus.*

The screening effect, already referred to on p. 68, consists in a reduction of the effective positive charge of the nucleus that acts on the given electron due to the presence of other electrons between the electron under consideration and the nucleus. This effect can be taken into account by introducing the screening constant. The concept of screening affords a formal means of allowing for the mutual repulsion of electrons. It is evident that screening increases with an increase in the number of electron shells surrounding the nucleus.

The penetration effect arises from the fact that according to quantum mechanics an electron can occupy any point in the atom. Hence, some of the time even the outermost electrons are in the near-nuclear region where the screening effect is negligible; it can be said that the outer electron penetrates through the inner electron shells to the nucleus. It is obvious that the penetration effect strengthens the bond between the electron and the nucleus. At the same value of n, the smaller the value of l the greater the part of the electron cloud concentrated in the vicinity of the nucleus; hence, s-electrons penetrate to a greater degree, p-electrons to a lesser degree, and d-electrons to a still smaller degree. This explains the already familiar sequence of energy levels of s-, p-, d- and f-electrons; at equal values of n and Z, the s-state has the lowest energy, the p-state has a higher energy, etc.

In addition to the above factors, the repulsion of the electrons in one and the same shell also affects the strength with which the electrons are bound in an atom; this effect is also sometimes called a screening effect. The repulsion is stronger when two electrons of opposite spin occupy the same orbital.

The information given above can be used to explain how the ionization energies vary in the periodic system. Let us consider the first ionization energies.

The first ionization energies of atoms of the alkali metals (I_1, eV) are: 5.39 (Li), 5.14 (Na), 4.34 (K), 4.18 (Rb), 3.89 (Cs). They are the lowest ionization energies. This is explained by the strong screening effect on the nuclear charge of the electron shells of the atoms of the noble gas, that precede the outer electron. The decrease in the ionization energy from lithium to caesium is due to the increase in the distance of the electron from the nucleus as the size of the atom grows.

Let us now see how the ionization energy varies in the second period. The elements of this period have the following values of I_1, eV: 5.39 (Li), 9.32 (Be), 8.30 (B), 11.26 (C), 14.53 (N), 13.61 (O), 17.42 (F), 21.56 (Ne). As can be seen, in passing from Li to Ne the ionization energy increases. This is explained by the increase in the nuclear charge, the number of electron shells remaining the same. The values given above show, however, that I_1 does not increase uniformly; there is even a slight decrease in I_1 in the elements following beryllium and nitrogen, i.e., in boron and oxygen, respectively. This occurs in conformance with the electronic structure of the atoms. Beryllium has the configuration $1s^2 2s^2$; i.e., the outer s-subshell is filled and therefore in boron which follows it an electron occupies the p-subshell and because the p-electron is less strongly bound to the nucleus than the s-electron is, the first ionization energy of boron is less than that of berrylium. The structure of the outer electron shell of the nitrogen atom in accordance with Hund's

rule is expressed schematically as follows:
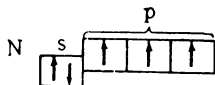
from which it can be seen that there is one electron in each *p*-orbital. In the element that follows nitrogen, i.e., in oxygen, a second electron is added to a *p*-orbital which is already occupied by one electron
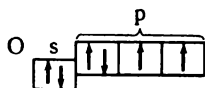
The two electrons on one and the same orbital strongly repulse each other, and therefore it is easier to tear away an electron from an oxygen atom than from a nitrogen atom.

The same sequence is observed in all the periods: the alkali metal that begins the period has the lowest ionization energy and the noble gas that ends it has the highest ionization energy. In passing from one transition element to another the ionization energies vary relatively slightly; they are greater than for the metals of the main subgroups because the outer *s*-electrons penetrate under the 'screen' of the other electrons.

Thus we see that the variation of the ionization energies is readily explained on the basis of the electronic structure of the atoms of the elements.

6.3. Secondary Periodicity

It would be wrong to suppose that the properties of elements (and their compounds) within the subgroups always vary monotonically with the atomic number. Let us plot, for example, the sum of the first four ionization potentials of the Group IV elements as ordinates and their atomic number as abscissae. In the resulting graph (Fig. 6.3) it can be seen that the points for the C, Si, Ti, Zr and Hf atoms can be connected by a continuous curve. For the group C, Si, Ge, Sn, Pb, however, the slope of the curve is not monotonic (hence, for instance, the sum of the potentials for Sn cannot be found as half the sum of the values for Ge and Pb). The same result is obtained on plotting a curve showing the dependence on the atomic number of the amount of energy evolved when oxides of the RO_2 type are formed by the Group IV elements. Here also the properties do not vary monotonically. This has come to be known as *secondary periodicity*. It was discovered by Y. Biron, a Russian, in 1915 and has since been established for many properties. Secondary periodicity was explained by S. Shchukarev in 1940. It is

associated with the filling of the respective d- and f-subshells, leading to the strengthening of the bond between the outer s- and p-electrons and the nucleus. This affects the s-electrons most strongly, the p-electrons to a smaller extent, and the d-electrons even less. Secondary periodicity is therefore most noticeable in the properties of compounds of the elements of the main subgroups in which their valency is equal or close to the group number.

Let us examine another example. In the fourth period in passing from K to Cu and from Ca to Zn there is an increase in the first
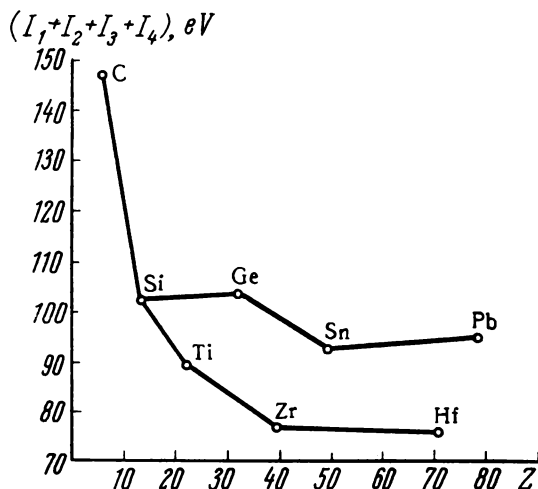

Fig. 6.3. Dependence of the sum of the first four ionization potentials of the Group IV elements on their atomic number

ionization energy by 3.4 and 3.3 eV, respectively. This is due to the penetration of the $4s$- and $4s^2$-electrons under the screen of the $3d$-electrons that progressively fill the third shell and to the resulting increase in the effective charge on the nucleus, attracting the outer electrons. A similar picture is observed in the fifth period. In the sixth period, in passing from Cs to Au and from Ba to Hg there is a much greater increase in I_1 (by 5.33 and 5.22 eV, respectively) which is explained by the penetration of the $6s$- and $6s^2$-electrons under the double screen of the $5d$- and $4f$-electrons; additional f-strengthening occurs. That is why the elements that come after the lanthanides have particularly high ionization energies. The strengthening of the bond of the s-electrons resulting from their penetration under the d- and f-orbitals gives rise to the considerable differences in the properties of the elements of the two subgroups in the first and second groups (see p. 72).

Of course the prediction of the properties of uninvestigated elements and their compounds by Mendeleev's method, based on vertical and horizontal interpolation, reduces possible error due to secondary periodicity.

CHAPTER SEVEN

ELEMENTARY PRINCIPLES OF FORMS AND PROPERTIES OF CHEMICAL COMPOUNDS

Now that we know the modern theory of the electronic structure of atoms of elements, we can pass over to the discussion of its influence on the form and properties of compounds of the elements. Prior to doing so, however, it is necessary to acquaint ourselves with certain basic concepts current in this field.

7.1. Oxidation State

One of the basic concepts in inorganic chemistry is the concept of *oxidation state*[1]. *By the oxidation state or oxidation number is meant the charge of the atom of an element in a compound found on assuming that the substance is made up of ions.*

We shall denote the oxidation number by a superscript, as Arabic numerals with a + or − sign in front of the numeral (for example, Cl^{+7})[2]. When there are grounds for believing that there are actually ions in a compound or solution, in denoting their charge the + or −sign is usually placed after the numeral (the charges 1 + and 1 − are denoted simply as + or −), for example, Ba^{2+}, Na^+, etc.

The following rules are helpful in determining the oxidation state:

1. The oxidation number of the atoms of simple substances is equal to zero.

2. In neutral molecules the algebraic sum of the oxidation numbers is equal to zero; for ions the sum is equal to the charge of the ion.

3. The oxidation number of the alkali metals is always equal to + 1.

4. Hydrogen in all its compounds, except the metal hydrides (NaH, CaH_2, etc.), has an oxidation number equal to + 1; in the metal hydrides the oxidation number of hydrogen is equal to − 1.

5. The oxidation number of oxygen is equal to − 2. Exceptions are peroxides, i.e., compounds that contain the −O—O— group in which the oxidation number of oxygen is −1, and certain other substances (superoxides, ozonides, oxygen fluorides).

[1] Synonyms for 'oxidation state' are 'oxidation number', 'electrochemical valency'.

[2] The oxidation state is also denoted in the literature by Roman numerals placed in parentheses after the symbol of the element, for example, $Mo(VI)$.

The oxidation numbers of elements in various compounds is readily found with the aid of the above rules. Thus, for example, in the compounds $Na_2^{+1}SO_3^{-2}$ and $Na_2^{+1}SO_4^{-2}$ the oxidation numbers of sulphur are equal to $+4$ and $+6$, respectively; manganese in $KMnO_4$ exhibits the oxidation state of $+7$, etc. There are cases when the oxidation number is a fraction; thus, in H_2O the oxidation number of oxygen is equal to -2, in H_2O_2 to -1, but in KO_2 and KO_3 it is equal to $-1/2$ and $-1/3$, respectively.

It should be pointed out here that the concept of oxidation state is a formal one and it usually fails to give an idea of the actual charge of the given atom in a compound. In many cases the oxidation number is not equal to the valency of the given element. For example, in methane (CH_4), methyl alcohol (CH_3OH), formaldehyde (CH_2O), formic acid ($HCOOH$), and carbon dioxide (CO_2), the valency of carbon is equal to four but the oxidation numbers of carbon are equal to -4, -2, 0, $+2$, and $+4$, respectively.

The concept of oxidation state is however very useful for classifying substances and for writing chemical equations. Thus, for instance, on determining the oxidation number of phosphorus in the compounds $HP^{+5}O_3$, $H_3P^{+5}O_4$ and $H_4P_2^{+5}O_7$, we see that all these compounds are closely related and should differ considerably in their properties from the compound $H_3P^{+3}O_3$ in which the oxidation state of phosphorus is different.

The concept of oxidation state is particularly widely used when studying *oxidation-reduction reactions*, i.e., chemical reactions in which the oxidation numbers of the elements change. Such reactions are discussed at length in the course of inorganic chemistry. Here we shall only note that in the process of oxidation there is an increase in the oxidation number, whereas in the process of reduction a decrease in the oxidation number occurs. Hence, substances in which there is an increase in the oxidation number of the element are called *reducing agents*, while substances in which a decrease in the oxidation number of the element takes place are called *oxidizing agents*. Atoms in the higher oxidation states exhibit only oxidizing properties; in the lower oxidation states, only reducing properties. In the intermediate oxidation states, the atom can be both an oxidizing and a reducing agent.

An example of an oxidation-reduction reaction is

$$2KMn^{+7}O_4 + S^0 = 2Mn^{+4}O_2 + K_2S^{+6}O_4$$
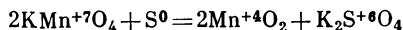
The oxidizing agent in this reaction is $KMnO_4$; the reducing agent, sulphur. As a result of the reaction, manganese is reduced; its oxidation number decreases from $+7$ to $+4$. Sulphur is oxidized; its oxidation number increases from 0 to $+6$.

The ability of a substance to react as an oxidizing or reducing agent can be characterized quantitatively by the change in the

thermodynamic potential ΔG (Gibbs' function or free energy), which takes place during a given oxidation-reduction reaction; the values of ΔG have been determined for a great number of processes. Nevertheless, oxidizing and reducing agents are characterized as 'strong', 'moderate', or 'weak', without indicating the exact value of ΔG. In this book we shall use the above terms.

7.2. Atomic and Ionic Radii

The concept of atomic and ionic radii is often used in chemistry and allied fields. These values are conventional; they are calculated from the interatomic distances which depend not only on the nature of the atoms but also on the type of chemical bond between them and on the state of aggregation of the substance.

Atoms and ions cannot be considered to be incompressible spheres resting motionless in contact with one another. We know (see pp 41,168) that the nuclei of atoms in molecules and crystals are always vibrating, even at absolute zero. In many cases the electron density practically falls to zero at distances less than the atomic and ionic radii; on the other hand, the distance at which an atom or ion acts on other particles can be much greater than its conventional radius. Finally, the sizes of atoms and ions depend on their interaction with neighbouring particles.

When considering simple substances and also organic compounds, use is usually made of the concept of *atomic radii*, r_{at}; when studying inorganic compounds, of *ionic radii*, r_{ion}.

Atomic radii are subdivided into atomic radii of metals, covalent radii of nonmetal elements, and atomic radii of the noble gases.

The structures of most of the metals are now well known. The atomic radius is found by dividing the distance between the centres of any two adjacent atoms in half[1]. The magnitudes of the atomic radii of metals are given in Table 7.1. In a given period the atomic radii of the metals decrease because, the number of electron shells being the same, the nuclear charge increases and consequently the electrons are attracted more strongly to the nucleus; thus, $(r_{at})_{Na} =$ $=1.89$ Å; $(r_{at})_{Mg} = 1.60$ Å; $(r_{at})_{Al} = 1.43$ Å. The r_{at} in the groups of ten transition elements decreases relatively slowly, especially in the two series of three elements in Group VIII; thus, whereas $(r_{at})_{Sc} =1.64$ Å and $(r_{at})_{Ti} =1.46$ Å, r_{at} for Fe, Co, Ni are equal to 1.26 Å, 1.25 Å and 1.24 Å, respectively. In the lanthanide and actinide series, r_{at} decreases even more slowly; thus, from Ce (1.83 Å) to Lu (1.74 Å) r_{at} decreases only by 0.09 Å.

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[1] The methods of determining the interatomic distances in crystals are described on pp 273-277.

Table 7.1
Atomic Radii of Metals *

Metal	r_{at}, Å	Metal	r_{at}, Å	Metal	r_{at}, Å	Metal	r_{at}, Å
Li	1.55	Cu	1.28	Cs	2.68	Pr	1.82
Be	1.13	Zn	1.39	Ba	2.21	Eu	2.02
Na	1.89	Rb	2.48	La	1.87	Gd	1.79
Mg	1.60	Sr	2.15	Hf	1.59	Tb	1.77
Al	1.43	Y	1.81	Ta	1.46	Dy	1.77
K	2.36	Zr	1.60	W	1.40	Ho	1.76
Ca	1.97	Nb	1.45	Re	1.37	Er	1.75
Sc	1.64	Mo	1.39	Os	1.35	Tm	1.74
Ti	1.46	Tc	1.36	Ir	1.35	Yb	1.93
V	1.34	Ru	1.34	Pt	1.38	Lu	1.74
Cr	1.27	Rh	1.34	Au	1.44	Th	1.80
Mn	1.30	Pd	1.37	Hg	1.60	Pa	1.62
Fe	1.26	Ag	1.44	Tl	1.71	U	1.53
Co	1.25	Cd	1.56	Pb	1.75	Np	1.50
Ni	1.24	In	1.66	Ce	1.83		

* The table is taken from data of G. Boky. Proceedings of the Academy of Sciences of the USSR, 69, 459, 1953.

In the main subgroups the atomic radii increase from top to bottom with an increase in the number of electron shells.

In the supplementary subgroups there is also an increase in r_{at} in passing from the first element to the second one, but there is even a slight decrease in passing from the second to the third element. Thus, in the titanium subgroup, r_{at} is respectively equal to 1.46 Å, 1.60 Å, 1.59 Å. This is explained by the lanthanide contraction (see p. 97).

Table 7.2 gives the covalent radii of nonmetals. They are also found by dividing in half the interatomic distances in the molecules or crystals of the corresponding elementary substances. As in the case of the atoms of metals, in the groups of the periodic system, the atoms of nonmetals with higher atomic numbers have larger radii. This is due to the increase in the number of electron shells. In the periods, the dependence of the atomic radii of nonmetals on the atomic number is more complicated. Thus, in the second period r_{at} first decreases, then increases once more; this is explained by the change in the strength of the chemical bond (see p. 210).

The atomic radii of the noble gases He, Ne, A, Kr and Xe are equal to 1.22, 1.60, 1.91, 2.01 and 2.20 Å, respectively. The above

Table 7.2

Covalent Radii of Nonmetals

Element	H	B	C	N	O	F	Si	P
r, Å	0.37	0.80	0.77	0.55	0.60	0.71	1.18	0.95

Element	S	Cl	Ge	As	Se	Br	Te	I
r, Å	1.02	0.99	1.15	1.25	1.16	1.14	1.35	1.33

values were obtained from the interatomic distances in the crystals of the given substances at low temperatures. Here is also observed an increase in r_{at} with an increase in the atomic number. The atomic radii of the noble gases are considerably greater than the radii of atoms of the nonmetals in the respective periods (see Table 7.2). This is so because in the crystals of the noble gases the interaction between atoms is very weak (see p. 265), whereas in the molecules of the nonmetals the covalent bond is strong.

Of special importance to the inorganic chemist are the ionic radii: we shall therefore discuss them in detail. If a crystal consists of ions (for example, Na^+Cl^-, $Ca^{2+}F_2^-$), the internuclear distance can be regarded as the sum of the ionic radii r_{ion}. But in order to find the value of one of the radii it is necessary to know the value of the other radius in addition to their sum. On the basis of experimental and theoretical investigation it has been assumed that the ionic radii of O^{2-} and F^- are equal to 1.32 Å and 1.33 Å, respectively. With the aid of these values the radii of other ions are found from the interionic distances in crystals. Their values are presented in Table 7.3; Fig. 7.1 shows the relative sizes of individual ions.

A comparison of r_{at} and r_{ion} shows that the cation radius r_{cat} is smaller than r_{at}; thus, $r_{Mn} = 1.30$ Å, whereas $r_{Mn^{2+}} = 0.80$ Å. The value of r_{ion} differs from that of r_{at} the more, the greater the charge on the ion; thus, $r_{Mn^{2+}} = 0.80$ Å, while $r_{Mn^{4+}} = 0.60$ Å; $r_{Cr^{3+}} = 0.63$ Å, while $r_{Cr^{6+}} = 0.52$ Å. This is explained by the fact that the conversion of atoms to cations results in contraction of the electron shells, the more so the greater the number of electrons missing.

An examination of Table 7.3 and Fig. 7.1 shows that the values of the radii of elemental ions vary in accordance with the following four rules.

1. For ions with the same charge and of similar electronic structure the radius is the larger the greater the number of electron shells in the ion.

2. The radii of ions that contain the same number of electrons (*isoelectronic ions*) decrease with an increase in the charge on them. Thus, in the group S^{2-}, Cl^-, K^+, Ca^{2+} the radii are equal to 1.74, 1.81, 1.33, 0.99 Å, respectively. This decrease is greater for positive
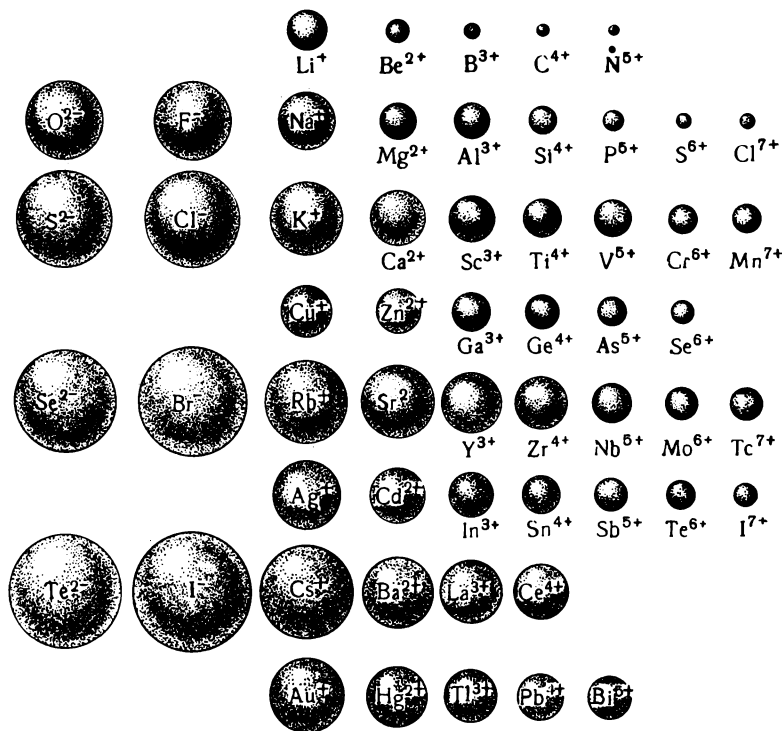

Fig. 7.1. Relative sizes of ions

ions. This is so mainly for two reasons: in the first place, with an increase in the charge on the ion the electrons are more strongly attracted to the centre of the ion; in the second place, ions with a greater charge react more strongly with ions of the opposite sign which results in a decrease in the interionic distances, and consequently, in the ionic radii. In the case of negative ions, on the contrary, as the charge increases the electrons are more strongly repulsed from the centre of the ion; the effect of the second factor, however, remains the same and as a rule it exceeds the repulsion of the electrons from the centre of the ion.

Table 7.3

Ionic Radii *

Ion	r, Å	Ion	r, Å	Ion	r, Å	Ion	r, Å
Li^+	0.68	Mn^{7+}	0.46	Cd^{2+}	0.97	Lu^{3+}	0.85
Be^{2+}	0.35	Fe^{2+}	0.74	In^{3+}	0.81	Hf^{4+}	0.78
B^{3+}	0.23	Fe^{3+}	0.64	Sn^{2+}	0.93	Ta^{5+}	0.68
C^{4+}	0.16	Co^{2+}	0.72	Sn^{4+}	0.71	W^{6+}	0.62
N^{3+}	0.16	Co^{3+}	0.63	Sb^{3+}	0.76	Re^{7+}	0.56
N^{5+}	0.13	Ni^{2+}	0.69	Sb^{5+}	0.62	Os^{6+}	0.69
O^{2-}	1.32	Cu^+	0.96	Te^{2-}	2.11	Ir^{4+}	0.66
F^-	1.33	Cu^{2+}	0.72	Te^{4+}	0.70	Pt^{2+}	0.80
Na^+	0.97	Zn^{2+}	0.83	Te^{6+}	0.56	Pt^{4+}	0.65
Mg^{2+}	0.66	Ga^{3+}	0.62	I^-	2.20	Au^{3+}	0.85
Al^{3+}	0.51	Ge^{2+}	0.73	I^{5+}	0.62	Hg^{2+}	1.10
Si^{4+}	0.42	As^{3+}	0.58	I^{7+}	0.50	Tl^+	1.47
P^{3+}	0.44	As^{5+}	0.46	Cs^+	1.67	Tl^{3+}	0.95
P^{5+}	0.35	Se^{2-}	1.91	Ba^{2+}	1.34	Pb^{2+}	1.20
S^{2-}	1.74	Se^{4+}	0.50	La^{3+}	1.14	Pb^{4+}	0.84
S^{4+}	0.37	Se^{6+}	0.42	Ce^{3+}	1.07	Bi^{3+}	0.96
S^{6+}	0.30	Br^-	1.96	Ce^{4+}	0.94	Bi^{5+}	0.74
Cl^-	1.81	Br^{5+}	0.47	Pr^{3+}	1.06	Po^{6+}	0.67
Cl^{5+}	0.34	Rb^+	1.47	Nd^{3+}	1.04	At^{7+}	0.62
Cl^{7+}	0.27	Sr^{2+}	1.12	Pm^{3+}	1.06	Fr^+	1.80
K^+	1.33	Y^{3+}	1.06	Sm^{3+}	1.00	Ra^{2+}	1.43
Ca^{2+}	0.99	Zr^{4+}	0.87	Eu^{3+}	0.97	Ac^{3+}	1.18
Sc^{3+}	0.81	Nb^{5+}	0.69	Gd^{3+}	0.97	Th^{4+}	1.02
Ti^{4+}	0.68	Mo^{6+}	0.62	Tb^{3+}	0.93	Pa^{4+}	0.65
V^{5+}	0.59	Tc^{7+}	0.56	Dy^{3+}	0.92	U^{6+}	0.80
Cr^{3+}	0.63	Ru^{4+}	0.67	Ho^{3+}	0.91	Np^{4+}	0.95
Cr^{6+}	0.52	Rh^{3+}	0.68	Er^{3+}	0.89	Pu^{4+}	0.93
Mn^{2+}	0.80	Pd^{2+}	0.80	Tm^{3+}	0.87	Am^{3+}	1.07
Mn^{4+}	0.60	Ag^+	1.26				

* The cation radii are taken from data of Arens (1952); the anion radii, from data of Goldschmidt (1926) (Landolt-Börnstein, Zahlenwerte und Funktionen, Berlin, 1955, Band I, Teil 4, Seite 523-525). The ionic radii given here correspond to the coordination number 6.

3. Ions of the noble-gas type, i.e., with outer subshells of the noble gases (*s*- and *p*-subshells) have larger radii than ions with *d*-electrons in the outer shell. For example, the radii of the K^+ and Rb^+ ions are equal to 1.33 Å and 1.47 Å, whereas the radius of the
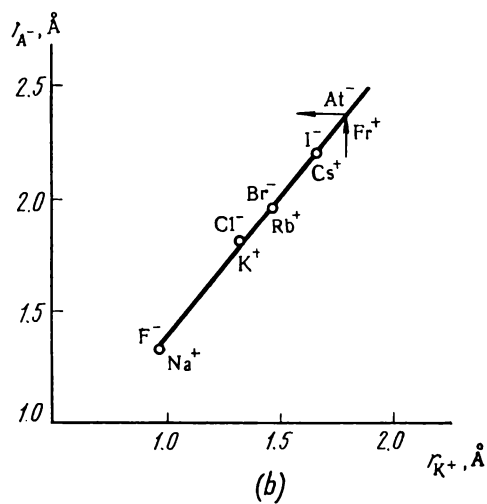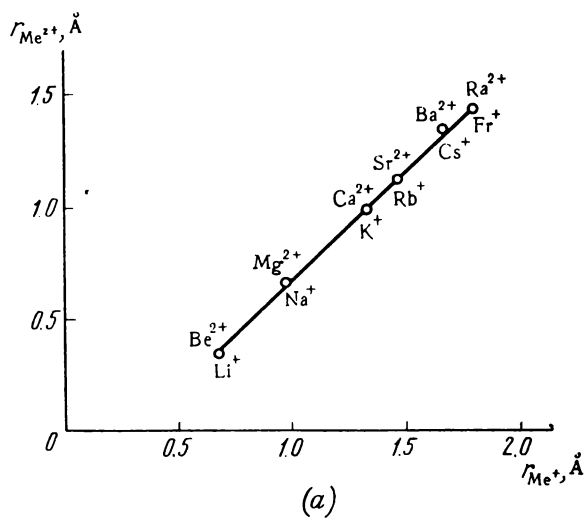
Fig. 7.2. Comparison of radii
(a) of ions of the metals of the main subgroups of Groups I and II; (b) of isoelectronic ions of the alkali metals and the halogens

Cu^+ ion is equal to 0.96 Å. The reason for this is that within each period the nuclear charge increases in passing from the s- and p-elements to the d-element; thus, $Z_K = 19$, but $Z_{Cu} = 29$. In each period, the radii of ions of d-elements with the same charge also decrease with an increase in Z; thus, $r_{Mn^{2+}} = 0.80$ Å, while $r_{Ni^{2+}} = 0.69$ Å. The decrease in the ionic radii is called *d-contraction*; it is particularly noticeable in the Group VIII elements.

4. With increasing atomic number of the elements, there is a similar decrease in the radii of ions formed by the lanthanides (the radius of the Ce^{3+} ion is equal to 1.07 Å, whereas that of Lu^{3+} is 0.85 Å). This is known as *lanthanide contraction*. In the lanthanide ions the number of electron shells is the same. An increase in the nuclear charge increases the attraction of the electrons to the nucleus, and, as a result, the radius of the ions decreases.

Figure 7.1 also shows that the *ionic radii vary periodically*. Consequently we would obtain a curve for r_{ion} similar to the one in Fig. 5.1 *a*. The variation of r_{ion} can be expressed quantitatively by the method of comparative calculation. This is shown for two cases in Fig. 7.2. In Fig. 7.2*a* are correlated the values of the ionic radii of the metals of the main subgroups of Groups I and II of the periodic system of the elements; in Fig. 7.2*b*, the values of r_{ion} of isoelectronic ions of the alkali metals and the halogens. The value of r_{At^-} can be found from the curve in Fig. 7.2*b*.

As has already been stated above, the concept of ionic radii in many cases is conventional; the value of a given r_{ion} in different compounds is only approximately constant. Moreover, the term ionic charge actually applies only to single-charged and double-charged ions since ions with a greater charge practically do not exist in crystals. In compounds containing elements in oxidation states higher than $+2$, the bond is generally not ionic and therefore the concept of ionic radius in these cases is also formal, like the concept of oxidation state. Nevertheless, the change in ionic radii characterizes the change in interatomic distances and this makes it possible to understand many properties of substances containing elements in given oxidation states.

The variation of ionic radii of elements in accordance with their position in the periodic system is also very important for understanding certain properties of compounds discussed below. Besides, it should be taken into consideration that multicharged ions actually do exist in solutions.

7.3. Coordination Number

Each atom or ion in a crystalline substance is always surrounded by other atoms, ions, or molecules. In the polyatomic ions of acids containing oxygen, such as the anions $(SO_4)^{2-}$, $(PO_4)^{3-}$, $(ClO_4)^-$,

the nonmetal atom is surrounded by oxygen atoms. Investigations have shown that the number of atoms or ions surrounding the central atom or ion is not arbitrary; it is, as a rule, a definite number which depends both on the nature of the central atom (ion) under consideration and on the surrounding atoms (ions). *The number of particles (ions, atoms, or molecules) that directly surround a given atom (ion) is called the coordination number.* Thus, in the ions $(SO_4)^{2-}$, $(PO_4)^{3-}$, $(ClO_4)^-$, the coordination number of the sulphur, phosphorus, and chlorine atoms is equal to four; in the ions $(SO_3)^{2-}$, $(CO_3)^{2-}$, $(NO_3)^-$, the coordination number of sulphur, carbon and nitrogen is equal to three.

For most of the metals, the coordination number is twelve, which corresponds to close packing (see p. 281). *The radii of atoms and ions depend on the coordination number.* Thus, when the coordination number n is reduced from 12 to 8, 6 and 4, the r_{at} corresponding to $n = 12$ should be multiplied by coefficients equal to 0.97, 0.96 and 0.88, respectively. For ions, in passing from the coordination number 6 to 12, 8 and 4, the r_{ion} should be multiplied by 1.12, 1.03 and 0.94, respectively.

The coordination numbers 3, 4 and 6 are most frequently met with in compounds. For example, in the crystals of sodium chloride, in which the Na^+ and Cl^- ions are arranged alternately, the coordination number for both ions is identical and is equal to six (see p. 283). For ions that have a similar electronic structure, the coordination number generally increases with increasing ionic size; this can be illustrated by the anions of oxygen-containing acids of elements of the main subgroup of Group IV. As the size of R^{+4} increases in the ions $(C^{+4}O_3)^{2-}$, $(Si^{+4}O_4)^{4-}$ and $[Sn^{+4}(OH)_6]^{2-}$, the coordination numbers of R^{+4} increase accordingly and are equal to 3, 4 and 6.

7.4. Compounds Containing R—H and R—O— Bonds

Later on we shall see how the properties of substances depend on the oxidation state, ionic (atomic) radii and on the coordination number. But let us first investigate some important classes of chemical compounds.

Among the compounds that play a very important role are substances in which atoms of elements are bound to hydrogen or oxygen. The importance of these substances is due to the great quantity of oxygen and hydrogen present on our planet and, consequently, to the very frequent occurrence of their compounds. Therefore, we shall confine ourselves to discussing these compounds of the elements of the periodic system, all the more so that the principles characteristic of these two types of compounds are largely applicable to other classes of compounds.

We shall, moreover, confine ourselves to discussing only those of

the afore-mentioned substances which can exist in the presence of water.

Examples of compounds containing the R—H bond are CH_4, SiH_4, PH_3, H_2O, HCl. These compounds formed by the union of hydrogen with other elements are called hydrides. The R—O— bond is present in NaOH, KOH, $Ca(OH)_2$, TlOH and other bases (hydroxides), and also in oxygen-containing acids (H_3BO_3, H_3PO_4, HNO_3, etc.) and their salts.

In the laboratory as well as in the industry, chemists often have to deal with hydrides, hydroxides, and oxy-acids. The *acid and basic properties* of substances are of great importance in laboratory research and industrial processes.

7.5. Acids, Bases, and Amphoteric Compounds[1]

An acid is a substance containing hydrogen, which dissociates in aqueous solution with the formation of hydrogen ions, H^+. *A base is a substance containing the hydroxyl group* OH, *which dissociates in water to form hydroxyl ions,* OH^-. Some substances containing H^+ and OH^- ions do not dissociate as readily as others. The facility with which substances dissociate into ions is characterized by the *degree of dissociation* in solutions. *The degree of dissociation* α *is the ratio of the number of dissociated molecules to the total number of molecules in solution.* It is expressed by a fraction (0.1, 0.2, etc.) or in per cent (10%, 20%, etc.) and depends on the concentration of the dissolved substance and the temperature. The degree of dissociation also depends on the nature of the solvent. Here we shall consider only the degree of dissociation of acids and bases in aqueous solutions and discuss the effect of only one variable, the nature of the dissolved substance.
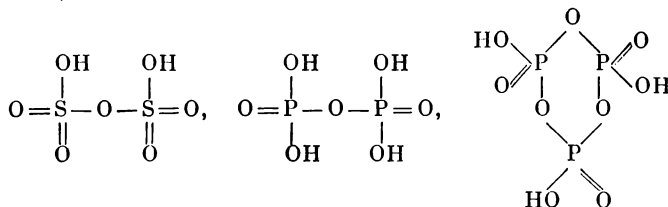
Depending on the degree of dissociation, an acid may be *strong*, *weak*, or *moderate*. The same terms apply to bases. An acid is conventionally considered to be strong if $\alpha > 30\%$ in a 0.1 N solution; weak, if $\alpha < 3\%$ in a solution of the same concentration; moderate, if in a 0.1 N solution $30\% > \alpha > 3\%$. The same pertains to bases also.

Some substances can dissociate both as acids and bases; such substances are called *amphoteric*. Some of them are: $Al(OH)_3$, $Zn(OH)_2$, $Cr(OH)_3$. Both the acid and basic properties are usually feebly marked. They react as weak bases with strong acids and as weak acids with strong bases.

There are many acids in which the atoms of an element alternate with atoms of oxygen. Acids containing the —R—O—R— chain

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[1] The definitions of acids and bases given here are somewhat simplified and incomplete. More general and exact definitions are set forth in courses of inorganic chemistry.

are called *isopolyacids*; for example, $H_2S_2O_7$ (pyrosulphuric or disulphuric acid), $H_4P_2O_7$ (pyrophosphoric acid), $(HPO_3)_3$ (trimetaphosphoric acid). These acids have the following structure:

$$O=\overset{\overset{\textstyle OH}{|}}{\underset{\underset{\textstyle O}{||}}{S}}-O-\overset{\overset{\textstyle OH}{|}}{\underset{\underset{\textstyle O}{||}}{S}}=O,\qquad O=\overset{\overset{\textstyle OH}{|}}{\underset{\underset{\textstyle OH}{|}}{P}}-O-\overset{\overset{\textstyle OH}{|}}{\underset{\underset{\textstyle OH}{|}}{P}}=O,$$

Acids containing the $-R_1-O-R_2-$ chain, i.e., derivatives of oxy-acids in which the O^{2-} ions are completely or partially replaced by acid radicals of other acids are called *heteropolyacids*. An example of such a compound is phosphotungstinic acid containing the $-P-O-W-$ chain. A great many silicon, phosphorus and boron isopolycompounds are known. The very large variety of silicates is due to the formation of compounds of the above type. Almost all the silicates, both naturally occurring and synthetic, contain the $-Si-O-Si-$ chain.

7.6. Dependence of the Strength of Acids and Bases on the Charge and Radius of the Ion of the Element Forming Them

Prior to discussing the compounds of elements and their properties, it is necessary to determine the factors on which the character of
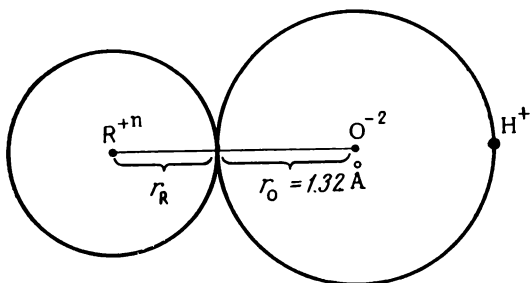
Fig. 7.3. Kossel diagram

dissociation of substance depends; to find out, for example, why $Ca(OH)_2$ is a base whereas $B(OH)_3$, which has a similar formula, is an acid.

For this purpose it is worthwhile to examine a simplified diagram which, nevertheless, gives a clear idea of the essence of the problem. This diagram was proposed by Kossel, a German.

The Kossel diagram (Fig. 7.3) presents the atomic group $R-O-H$. The R^{+n} and O^{-2} ions are shown as spheres with radii corresponding

to the radii of the ions; their interaction is determined by Coulomb's law. The radius of the hydrogen ion (proton) is very small in comparison with the radius of the R^{+n} and oxygen ions. It is assumed, therefore, that the distance between the hydrogen ion and the centre of the oxygen ion is equal to the radius of the oxygen ion.

The character of dissociation of compounds containing the R—O—H group depends on the relative strength of the R—O and O—H bonds. The strength of a chemical bond is determined by the energy required to break the given bond (see p. 133). It is necessary to distinguish bond breaking that yields neutral atoms (or groups of atoms) from bond breaking that results in the formation of ions. In the present case we are considering the dissociation of substances into ions. If the R—O bond is the stronger one, the O—H bond is broken on dissociation, i.e., the hydrogen ion is formed and the compound behaves like an acid. Conversely, if the O—H bond is the stronger one, it is the R—O bond that is broken on dissociation and the OH^- ion is formed, i.e., the substance behaves like a base. If the R—O and O—H bonds are approximately equal in strength, the compound is amphoteric.

According to the Kossel diagram the R—O bond becomes stronger with increasing charge and decreasing radius of the ion of the element R[1]. On the other hand, an increase in the charge and decrease in the radius of the ion of an element weakens the O—H bond because the proton is more strongly repulsed by the ion of the element. Hence, *the higher the oxidation state of an element and the smaller the ionic radius of the element, the more pronounced are the acid properties of the compound.* Consequently, strong oxy-acids are formed by elements in the top right-hand corner of the periodic system. On the contrary, the lower the oxidation state and the greater the ionic radius, the more pronounced are the basic properties of the substance. Consequently, strong bases are formed by the elements positioned in the bottom left-hand corner of the periodic system.

In compounds containing the R—H bond, by similar reasoning we can conclude the following. If this bond, as a first rough approximation, is considered to be ionic, it will be the stronger the higher the absolute value of the oxidation number of the element and the smaller the radius of its ion. Hence, a decrease in the oxidation

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[1] When discussing the dissociation of substances it is necessary to take into consideration not only the interaction of the ions with each other, but also their reaction with water molecules, i.e., their hydration (see p. 297). To a first approximation this effect can be allowed for by introducing the dielectric constant into the formula for Coulomb's law (see p. 301). As a result of hydration, the interaction of ions in aqueous solution is approximately 80 times weaker than in vacuum. The relationships indicated by the Kossel diagram hold true if the peculiarities of the reactions of the RO^- and H^+ and R^+ and OH^- ions, respectively, with water molecules are ignored.

number of an element (absolute value) and an increase in the radius of its ion lead to an increase in the acid properties of hydrogen compounds.

It should be stressed once more that the Kossel diagram is a very rough simplification. The O—H bond is not ionic and the distance between the centres of the oxygen and hydrogen atoms is never equal to 1.32 Å because the hydrogen ion penetrates into the electron shells of oxygen (see p. 228). Moreover, in the upper oxidation states, the bond between the element R and oxygen is likewise not ionic, and the oxidation number, as stated above, does not correspond to the charge of the ion of the element. Nevertheless, in most cases, the Kossel diagram enables qualitatively correct conclusions to be drawn on comparing like compounds, say, the hydroxides of the elements of one and the same group in the periodic system. This rough diagram can be used with such unexpected results because even in the case of bonds that differ greatly from ionic ones, the strength of the bonds increases with decreasing interatomic distances (and, consequently, with decreasing 'ionic radii' calculated from them) and with increasing oxidation numbers. The oxidation number usually indicates approximately the number of electrons of the given atom that take part in the formation of a chemical bond. Therefore the use of the Kossel diagram is very convenient for a first general orientation in the diversified data of inorganic chemistry.

CHAPTER EIGHT

ELECTRONIC STRUCTURE AND PROPERTIES OF ELEMENTS AND THEIR COMPOUNDS

Let us examine the acid-basic and oxidizing-reducing properties of the elements and their compounds in the various groups of the Mendeleev Periodic System, confining ourselves to the most characteristic oxidation states.

8.1. First Group

The first group consists of the lithium subgroup (Li, Na, K, Rb, Cs and Fr) and the copper subgroup (Cu, Ag, Au).

Lithium, sodium, potassium, rubidium, caesium and francium exhibit the oxidation state of $+1$ in their compounds. The atoms of these elements readily give up the single electron in their outer shell and are therefore strong reducing agents, the strength of which increases in passing from lithium to francium. Francium is the strongest reducing agent of all the elements because its atoms are larger than those of the other elements of the subgroup. The alkali metals dissolve in water to form R^{1+}—O—H compounds which are

strong bases that are readily soluble, i.e., alkalies. The reasons for this are the small charge and large radii of the ions.

Hydrogen is often included in the first main subgroup because, like the alkali metals, it is an s-element; however, notwithstanding the characteristics that they have in common (similar spectra, formation of the univalent positive ion R^+, reducing properties, mutual replacement of metals and hydrogen), there are essential differences between metals and hydrogen: the proton is incomparably smaller than the cations of the alkali metals and it always penetrates deeply into the electron shells of the atom with which it is united; the ionization energy of hydrogen is almost three times greater than the approximately equal first ionization energies of the alkali metals; the behaviour of hydrogen is similar to that of metals only in aqueous solutions; it acts as a reducing agent only at high temperatures. On the other hand, hydrogen in many of its properties resembles the halogens (see p. 109). That is why it is more appropriate to include hydrogen in the fluorine subgroup.

The Cu, Ag and Au atoms also have one electron in the outermost shell. The single-charged ions of these elements, however, are smaller than the ions of the alkali metals. Hence, the R—O bond is stronger than in compounds of the elements of the main subgroup. Indeed, their hydroxides are weaker bases than the hydroxides of the alkali metals. A second difference is that the shell next to the outermost one is an 18-electron shell $(s^2 p^6 d^{10})$, i.e., it contains d-electrons that are less strongly bound to the nucleus than are the s- and p-electrons of the same $(n - 1)$ electron shell of the alkali metals. Therefore, the elements of the supplementary subgroup can have an oxidation number greater than $+1$. As a matter of fact in aqueous solutions these elements exhibit the following oxidation states: Cu^{+1}, Cu^{+2}, Ag^{+1}, Au^{+3}. The compound $Cu(OH)_2$ is a weak base and exhibits slight amphoteric properties; $Au(OH)_3$ is an amphoteric compound in which the acid properties predominate because of the strengthening of the R—O bond caused by the increase in the charge and the corresponding decrease in the size of the R^{+3} ion.

8.2. Second Group

The oxidation state characteristic of all the elements of this group is $+2$. The elements of the main subgroup (Be, Mg, Ca, Sr, Ba and Ra) have two s-electrons in their outermost shell. The reducing properties of the elements of this subgroup are weaker than those of the alkali metals (the atoms of which are larger in size), although due to the increase in their atomic radii Ca, Sr, Ba, and Ra are strong reducing agents. The Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Ra^{2+} ions, like the ions of the lithium subgroup, have the configuration of noble gases, but they differ from R^+ ions in their charge and radii.

Because of their greater charge and smaller radii, their hydroxides are weaker than those of the alkali metals. The increasing of ionic radii in the Be^{2+}—Ra^{2+} subgroup explains why $Be(OH)_2$ is an amphoteric compound, $Mg(OH)_2$ is a weak base, $Ca(OH)_2$ is a strong base and $Ba(OH)_2$ is a very strong base that readily dissolves in water; it is an alkali and hence it is called caustic baryta.

The elements of the supplementary subgroup are weaker reducing agents than those of the main subgroup because their atoms have relatively small radii. The radii of Zn^{2+}, Cd^{2+} and Hg^{2+} ions are also smaller than those of the neighbouring elements of the main subgroup due to the effect of the 18-electron subshells. Hence, the hydroxides of these metals are weak bases. The compound $Zn(OH)_2$, like $Be(OH)_2$, is amphoteric; $Cd(OH)_2$ is only slightly amphoteric; HgO is not amphoteric at all[1]. Since the elements of the zinc subgroup are the last d-elements (they conclude the group of the transition elements), they exhibit some similarity to the elements following them, i.e., to Ga, In, Tl.

8.3. Third Group

The elements of the boron subgroup (with the exception of thallium) exhibit the characteristic oxidation number of $+3$ and form $R(OH)_3$ compounds. Just as the elements of Group II are less alkaline than those of Group I, so is there a further weakening of basic properties in passing from Group II to Group III: $Li(OH)$ is a base; $Be(OH)_2$ is an amphoteric compound; $B(OH)_3$ is an acid. Thus, in the third group for the first time we meet an element that forms an acid (in this respect boron differs from all the other elements in Group III) and with isopolyacids which are also characteristic of boron. The basic properties become more pronounced as the ionic radii of the elements increase from $Al(OH)_3$ to $Tl(OH)_3$: the degree of dissociation of $Ga(OH)_3$ into OH^- and H^+ ions is practically equal; the basic properties of $In(OH)_3$ predominate; $Tl(OH)_3$ is only slightly amphoteric. It can be noticed that the basic properties increase very slowly in these compounds. The reason for this is that whereas the atoms of the elements of the third main subgroup have structural identity (their outer electron shell has the configuration s^2p), the B^{3+} and Al^{3+} ions differ greatly from the Ga^{3+}, In^{3+} and Tl^{3+} ions. The former have the outer shells of noble gases; the latter have 18-electron shells containing 10 d-electrons. Consequently, the ionic radii after aluminium increase to a lesser extent and because of this the basic properties of the compounds increase slowly. Here, as in the preceding group, a diagonal similarity is observed: the amphoteric hydroxides of Al and Be closely resemble each other in their properties.

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[1] $Hg(OH)_2$ is unstable and decomposes into HgO and H_2O.

We have already stated that thallium is an exception among the elements of the boron subgroup. Its characteristic oxidation number is $+1$ and TlOH is a strong base. This is explained by the greater stability of compounds of Tl in which the atom retains the electrons on the s-orbital. Therefore, it is the p-electron that first of all determines the valency of Tl (and also of the following elements of Period VI as we shall see below). This is not characteristic of In, and even less so of Ga. Hence, Ga^+ is a very strong reducing agent, while Tl^{3+} is a strong oxidizing agent. The fact that TlOH is a strong base is explained by the considerable size of the Tl^+ ion and its small charge.

The elements of the supplementary subgroup (Sc, Y, La and Ac) also exhibit the characteristic oxidation number of $+3$ and form $R(OH)_3$ compounds. The electronic structure of the Sc, Y, La and Ac atoms is not similar to that of B and Al; these atoms have 2 s-electrons in their outermost shell. The B^{3+}, Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+} and Ac^{3+} ions, however, all have the same electronic structure, that of atoms of the noble gases. Therefore in passing from B to Ac, the properties of their compounds vary more continuously than in passing from B to Tl; in particular, in the group $B(OH)_3$—$Al(OH)_3$—$Sc(OH)_3$—$Y(OH)_3$—$La(OH)_3$—$Ac(OH)_3$, the basic properties grow more rapidly: whereas $Sc(OH)_3$ is a weak base with hardly any signs of amphoteric properties, $La(OH)_3$ is already a strong base. Because of the large radii of the La^{3+} and Ac^{3+} ions, the R—O bond is weak, which makes their hydroxides approximately as strong as the hydroxides in the main subgroup of the second group.

The elements of the lanthanide series closely resemble one another in their properties. For the most part, they exhibit the characteristic oxidation number of $+3$. Their hydroxides, $R(OH)_3$, as a rule, are not amphoteric; in passing from Ce to Lu the basic properties decline, which is associated with a decrease in the ionic radii (lanthanide contraction). Since $r_{Ce4+} < r_{Ce3+}$, the basic properties of $Ce(OH)_4$ should be weaker than those of $Ce(OH)_3$. As a matter of fact $Ce(OH)_4$ is a base that is slightly amphoteric.

The actinides exhibit various oxidation states from $+2$ to $+7$. As the atomic number increases, the oxidation state of $+3$ becomes the predominant one. We shall discuss the oxidation states of only the three most important elements: Th, U and Pu. For Th the characteristic oxidation number is $+4$. The compound $Th(OH)_4$ is a nonamphoteric base; this is explained by the large radius of the Th^{4+} ion. The oxidation state most characteristic of U is $+6$. It forms the compound $UO_2(OH)_2$, uranyl hydroxide. This is an amphoteric compound; it can react both with acids and alkalis. Uranyl hydroxide contains the $(UO_2)^{2+}$ ion which is also contained in many other uranyl compounds where the oxidation number of uranium is $+6$, for instance, uranyl chloride, UO_2Cl_2, uranyl nitrate,

$UO_2(NO_3)_2$. The formation of similar groups is characteristic of many elements in the upper oxidation states. For example, the formula of sulphuric acid can be written as $SO_2(OH)_2$; the compounds SO_2F_2, SO_2Cl_2, and others are analogues of the uranyl salts. The formation of compounds containing $(RO_2)^{2+}$ is less characteristic of sulphur than of uranium because the radius of S^{+6} ($r_{S+6} = 0.30$ Å) is much smaller than that of U^{+6} ($r_{U+6} = 0.80$ Å); hence, S^{+6} usually retains four oxygen ions rather than two oxygen ions; the $(SO_4)^{2-}$ ion is more stable than the $(UO_4)^{2-}$ ion. Uranyl hydroxide reacts with alkalis to form uranates, M_2^+ $(UO_4)^{2-}$, and diuranates, M_2^+ $(U_2O_7)^{2-}$; it reacts with acids to form uranyl salts. The characteristic oxidation state exhibited by Pu is $+4$. The compound $Pu(OH)_4$ is a weaker base than $Th(OH)_4$ due to actinide contraction.

8.4. Fourth Group

Whereas the elements of the boron subgroup mainly exhibit the oxidation number of $+3$ and only in rare instances $+1$ (because of which the oxidation-reduction processes in the transition from one state to another were not typical), the elements of the carbon subgroup (C, Si, Ge, Sn, Pb), in accordance with the structure of the outer electron shell, exhibit two oxidation states $+2$ and $+4$. In the first state the element has reducing properties; in the second state, oxidizing properties. In passing from C to Pb, the oxidation state of $+2$ becomes more characteristic, and, as a result, substances containing R^{+2} are more stable. For C and Si the oxidation state of $+2$ is exhibited only in very few compounds (for example, CO and SiO). The characteristic oxidation state of these elements is $+4$. $Ge(OH)_2$, $Sn(OH)_2$ and $Pb(OH)_2$ are amphoteric compounds in which the basic properties increase from Ge to Pb; acidic ionization predominates for $Ge(OH)_2$, basic ionization, for $Pb(OH)_2$. Compounds containing the Ge^{2+} ion are strong reducing agents; those containing Pb^{+4} are strong oxidizing agents.

Since $r_{R+4} < r_{R+2}$, the R^{+4}—O bond is stronger than the R^{+2}—O bond. That is why compounds containing the R^{+4}—O—H group exhibit acid properties. Carbon in the oxidation state of $+4$ forms carbonic acid, H_2CO_3; this is a very weak acid. The acids H_4SiO_4, $H_2[Ge(OH)_6]$, $H_2[Sn(OH)_6]$ and $H_2[Pb(OH)_6]$ are even weaker ones. With increasing size of R^{+4}, the coordination number in this group of compounds increases from 3 (for C^{+4}) to 6 (for Pb^{+4}).

All these substances are unstable; they decompose with the formation of water. Their salts, however, are quite stable. The acid properties disappear very slowly for the same reason that the basic

properties increase very slowly in the third group: the Ge^{4+}, Sn^{4+} and Pb^{4+} ions have 18-electron shells and consequently their ionic radii increase slowly. Here there is also observed diagonal similarity. Thus, Si^{+4} resembles B^{+3}. Silicon and boron resemble each other, in particular, in that they both form a large number of iso-polycompounds.

Boron forms a number of hydrides, which is not characteristic of the other elements in the third group; but hydrides are formed by all the elements in the fourth group. Their stability, however, sharply decreases in the carbon subgroup. Thus, carbon forms a great number of hydrides, silicon forms a much smaller number of such compounds; germanium, only a few; tin, only two; lead, only one, PbH_4, which is, moreover, very unstable. Because of the high oxidation number of these elements, none of the hydrides are acids.

The elements of the supplementary subgroup (Ti, Zr and Hf) also exhibit the characteristic oxidation state of $+4$. The compounds corresponding to the formula $R(OH)_4$ are amphoteric; their acid properties diminish from Ti to Hf.

8.5. Fifth Group

The elements of the main subgroup (N, P, As, Sb and Bi) with outermost electron shell of the configuration s^2p^3 exhibit three oxidation states: $+5$, $+3$ and -3.

The oxidation state of $+5$ becomes more stable in passing from nitrogen to phosphorus, after which it becomes less stable. From the formulae HNO_3, H_3PO_4 (also $H_4P_2O_7$, $(HPO_3)_3$, and a great number of other isopolycompounds), H_3AsO_4 and $H[Sb(OH)_6]$ it can be seen that the coordination number increases from 3 to 6 in passing from nitric acid to antimonic acid. HNO_3 is a strong oxidizing agent.

In passing from nitrogen to bismuth, the oxidation state of $+3$ becomes more and more stable and the basic character of the compounds increases: HNO_2 and H_3PO_3 are acids; H_3AsO_3 is an amphoteric compound in which the acid properties predominate; $Sb(OH)_3$ is an amphoteric compound in which the basic properties predominate; $Bi(OH)_3$ is a nonamphoteric hydroxide. These compounds can exhibit both oxidizing and reducing properties.

The hydrides of these elements have the formula $R^{-3}H_3$; they are not acids. These compounds are reducing agents; the reducing properties increase in the main subgroup from N to Bi.

V, Nb and Ta, constituting the supplementary subgroup, exhibit the characteristic oxidation number of $+5$. They form weak acids having the formula HRO_3; the strength of the acids declines from V to Ta.

8.6. Sixth Group

In the main subgroup the elements S, Se, Te and Po exhibit the characteristic oxidation states of $+6$, $+4$, and -2, respectively in conformance with the electronic configuration of their outermost shell. Oxygen exhibits the oxidation state of -2 (exceptions are discussed on p. 89).

Compounds containing R^{+6} have the following formulae: H_2SO_4, H_2SeO_4 and H_6TeO_6. Thus, in passing from selenium to tellurium, the coordination number increases from 4 to 6 due to the increase in the ionic radii from S^{+6} to Se^{+6} to Te^{+6}. H_2SO_4 and H_2SeO_4 are strong acids of almost equal strength; H_6TeO_6 is a weak acid. The oxidizing activity increases in passing from H_2SO_4 to H_2SeO_4 and decreases in passing on to H_6TeO_6. Thus, we see that the group of acids H_2SO_4—H_2SeO_4—H_6TeO_6 presents a typical example of secondary periodicity. That is why H_2SeO_4 does not have properties that are the average of the properties of H_2SO_4 and H_6TeO_6.

Compounds containing R^{+4} have the formula H_2RO_3 and are acids of moderate strength. In the group of acids H_2SO_3—H_2SeO_3—H_2TeO_3 there is a decline in the acid properties and tellurous acid shows amphoteric properties. Whereas H_2SO_3 is a rather strong reducing agent, H_2TeO_3 exhibits oxidizing properties.

The hydrides $R^{-2}H_2$ can dissociate with the formation of the hydrogen ion; there is an increase in the acid properties as we pass from H_2S to H_2Te, corresponding to an increase in the ionic radii. The compounds H_2S, H_2Se, and H_2Te are strong reducing agents; their reducing power increases from H_2S to H_2Te.

The elements of the supplementary subgroup (Cr, Mo, W) form compounds corresponding to oxidation states from $+2$ to $+6$; the most characteristic oxidation state is $+6$, and for chromium $+3$ as well. Simple compounds have the formula H_2RO_4. They are all acids. The strength of the acids declines from H_2CrO_4 to H_2MoO_4 to H_2WO_4. Besides, for the oxidation state of $+6$ there are known a great number of isopolycompounds (for example, $H_2Cr_2O_7$). The acids H_2CrO_4, $H_2Cr_2O_7$ and their salts are strong oxidizing agents. In this subgroup, compounds containing R^{+6} are progressively weaker oxidizing agents. The ionic radius of Cr^{3+} (0.63 Å) is close to that of Al^{3+} (0.51 Å). That explains why $Cr(OH)_3$, like $Al(OH)_3$, is an amphoteric compound.

8.7. Seventh Group

The main subgroup of this group contains the halogens, i.e., the elements F, Cl, Br, I, At. Free halogens are oxidizing agents. The first element of the halogen subgroup, fluorine, is the strongest of all known oxidizing agents. It differs considerably from the other

elements of the subgroup and exists solely[1] in the oxidation state of —1. The aqueous solution of HF is a moderate acid.

The oxidation state of —1 is also characteristic of chlorine, bromine, and iodine; these elements, however, can exhibit other oxidation states as well. In aqueous solution HR compounds are acids; the strength of the acids increases from HCl to HI with increasing ionic radius, r_{R-}. The HR acids react as reducing agents, the reducing power increasing from HCl to HBr to HI.

Besides the oxidation state of —1, chlorine, bromine, and iodine form compounds in which they exhibit positive oxidation states. The most important of these compounds are the following:

+1	+5	+7
HClO	$HClO_3$	$HClO_4$
HBrO	$HBrO_3$	
HIO	HIO_3	H_5IO_6

The stability of the acids increases with an increase in the oxidation number and in passing from Cl to I. The strength of the acids declines from top to bottom; it increases from left to right. This increase is especially noticeable for the acids formed by chlorine. Indeed, whereas HIO is amphoteric, $HClO_4$ is the strongest of all the known acids.

As has been stated above, hydrogen can also be classed together with the halogens since it can form H^- ions which like the halogen ions (F^-, Cl^-, Br^-, I^-, At^-) are isostructural with the atoms of the noble gases (He, Ne, A, Kr, Xe, Rn, respectively). There are other resemblances between hydrogen and the halogens: the gaseous state of hydrogen, the fact that its molecule contains two atoms, the ease with which hydrogen is replaced by halogens in organic compounds, the closeness of the energies of decomposition of H_2 and Hal_2 molecules, the comparability of the ionization potentials of hydrogen and the first ionization potentials of the halogens, etc. Of course it should be kept in mind that hydrogen differs from the halogens (because the latter being *p*-elements, form compounds in which the oxidation number is higher than unity). However, the properties of hydrogen bear a greater resemblance to those of the halogens than to the properties of metals (see p. 103). There is another argument in favour of this statement: namely, the results of comparative calculation. This is illustrated, for example, in Fig. 8.1 which correlates the melting point (m.p.) and melting heats (ΔH_m) in the halogen group; the point for hydrogen lies on one straight line with the points for the halogens. Consequently it is more proper to consider hydrogen to be a partial analogue of fluorine and to place it above F in the table of elements, placing it above Li only in parentheses.

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[1] This is true for the compound formed with oxygen; therefore, $O^{+2}F_2^-$ is not fluorine oxide—it is oxygen fluoride.

The elements of the supplementary subgroup (Mn, Tc, Re), with the electron configuration $(n-1)\, s^2p^6d^5ns^2$, exhibit many oxidation states, from $+2$ to $+7$. The oxidation numbers characteristic of manganese are $+2$, $+4$, $+6$ and $+7$. The compounds corresponding to these oxidation numbers are $Mn^{+2}(OH)_2$, $Mn^{+4}(OH)_4$, $H_2Mn^{+6}O_4$ and $HMn^{+7}O_4$. In accordance with the Kossel diagram, the acidity of the compounds increases with increasing oxidation number: $Mn(OH)_2$ is a base; $Mn(OH)_4$ is a very weak base which is slightly
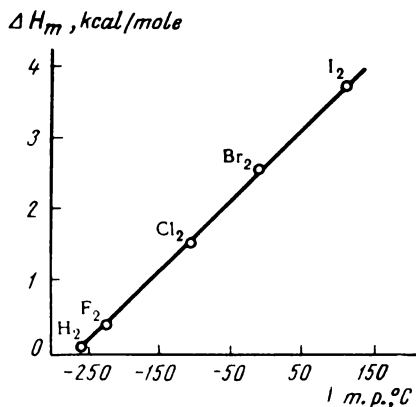
Fig. 8.1. Comparison of the melting points and melting heats of the halogens and hydrogen

amphoteric (this compound readily decomposes to form MnO_2 and H_2O); H_2MnO_4 and $HMnO_4$ are acids. $HMnO_4$ readily decomposes into Mn_2O_7 and H_2O; H_2MnO_4 is also an unstable compound, but many salts of these acids are stable. In the group $Mn^{+2}-Mn^{+4}-Mn^{+6}-Mn^{+7}$, the oxidizing properties grow and the reducing properties decline; $Mn^{+2}(OH)_2$ is readily oxidized, i.e., it is a reducing agent; the salts of $HMnO_4$ are very strong oxidizing agents. The most characteristic oxidation number of Tc and Re is $+7$. The corresponding compounds have the formula HRO_4. The strength of the acids and their oxidizing power decline in the groups $H_2MnO_4-H_2TcO_4-H_2ReO_4$ and $HMnO_4-HTcO_4-HReO_4$.

8.8. Eighth Group

This group has no main subgroup. It can be subdivided into two parts: elements of the *iron family* (Fe, Co, Ni) and the *family of the platinum metals* (Ru, Rh, Pd, Os, Ir, Pt). The oxidation state for these elements varies from $+2$ to $+8$.

The oxidation numbers characteristic of Fe, Co and Ni are $+2$ and $+3$; in passing from Fe to Ni, compounds in which the oxidation

number is $+3$ become progressively less stable. In passing from Fe to Ni, there is a gradual decline in the basic properties of the hydroxides corresponding to the small decrease in the ionic radii. Compounds with the formula $R(OH)_2$ are nonamphoteric bases; those with the formula $R(OH)_3$ are very weak bases with extremely feeble amphoteric properties. Compounds containing Fe^{2+} are moderate reducing agents. The reducing power decreases from Fe^{+2} to Co^{+2} to Ni^{+2}. The oxidizing power gradually increases from Fe^{+3} to Co^{+3} to Ni^{+3}.

Iron is also known to exist in the oxidation state of $+6$; the compound H_2FeO_4 corresponds to this state. Although H_2FeO_4 is an unstable acid, many of its salts have been obtained. In the group Fe^{+2}—Fe^{+3}—Fe^{+6} there occurs an increase in the oxidizing power, especially in passing from the oxidation state of $+3$ to the oxidation state of $+6$.

The platinum metals exist in a large number of oxidation states. The oxidation states of $+2$ and $+4$ are characteristic of platinum. The hydroxide $Pt(OH)_2$ is nonamphoteric due to the large radius of the Pt^{2+} ion. The compound $Pt(OH)_4$ is amphoteric; it reacts with both acids and alkalis. Only Ru and Os are known to exist in the highest oxidation state of $+8$ which they exhibit in the compounds RuO_4 and OsO_4. There are no acids or bases in this oxidation state because the compounds RuO_4 and OsO_4 are *coordinately oxygen-saturated* (consider the group of compounds H_2WO_4—H_1ReO_4—H_0OsO_4).

Not only do the properties of the elements vary progressively within each of the two families, they also vary in the three subgroups, i.e., in the three vertical groups. Thus, in the group Fe^{+6}—Ru^{+6}—Os^{+6} there is a sharp decline in oxidizing properties: K_2FeO_4 is a very strong oxidizing agent ($Fe^{+6} \rightarrow Fe^{+3}$); K_2RuO_4 is readily reduced to RuO_2; K_2OsO_4 is relatively easily oxidized to OsO_4. Whereas FeO_4 does not exist at all and RuO_4 is easily decomposed on heating (producing an explosion), OsO_4 boils without decomposing.

8.9. Zero Group

The zero group contains only a main subgroup consisting of the noble gases He, Ne, A, Kr, Xe and Rn. Up to 1962 it was believed that the atoms of the noble gases could not form stable molecules with the atoms of other elements, i.e., they exhibited a zero oxidation state. This opinion has now been disproved (see p. 62); at the present time there are already known tens of compounds of xenon and several compounds of krypton and radon (compounds of the other noble gases have not been obtained). The stability of compounds of the noble gases increases with increasing atomic numbers. The xenon compounds have been studied better than those of the other

noble gases. It has been found that xenon exhibits the oxidation states of $+2$, $+4$, $+6$ and $+8$ as, for example, in the compounds XeF_2, $XeOF_2$, XeO_3 and $Na_4XeO_6 \cdot 8H_2O$, respectively. These compounds are relatively stable and can exist at room temperature[1].

8.10. Some Conclusions

Generalizing the data on the acid and basic properties and the oxidizing and reducing properties of compounds containing $R-O-H$ and $R-H$ bonds, we can draw the following conclusions. If we examine any given oxidation state, we see that in each subgroup, in passing from top to bottom, the basic properties of the elements are progressively more pronounced and their acid properties decline. On the contrary, with increasing oxidation numbers of a given element, there is a gradual decrease in the basic properties and an increase in the acid properties.

As the number of the group grows there is a greater tendency to exhibit various oxidation states, including negative ones, the latter becoming more characteristic of the elements in the main subgroups with an increase in electron affinity. The greater variation of oxidation states is manifested in the greater probability of the occurrence of a larger number of different oxidation-reduction reactions.

We have already noted (see p. 72) that in passing from Group I to Group VII, the difference in the properties of the elements of the main and supplementary subgroups first diminishes, then increases, and finally becomes considerable. But this difference is great for the lower oxidation state and smaller for the upper states. Thus, chlorine ($1s^2\,2s^2\,2p^6\,3s^2\,3p^5$) and manganese ($1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$) have nothing in common and the properties of compounds of Cl^+ ($1s^2\,2s^2\,2p^6\,3s^2\,3p^4$) and those of Mn^{+2} ($1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5$) are not similar, but compounds containing Cl^{+7} ($1s^2\,2s^2\,2p^6$) and Mn^{+7} ($1s^2\,2s^2\,2p^6\,3s^2\,3p^6$) should have similar properties; this we know to be a fact.

Thus, although the Kossel diagram is a rough approximation, and the more so the higher the oxidation state of the elements, it has been, however, of great value not only in systematizing the voluminous data on the properties of the most important compounds but also in predicting their behaviour. That is why the material set forth above may be regarded as inorganic chemistry in miniature, its outline so to say.

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[1] Since compounds of the noble gases have been obtained, recently the zero group has often been called Group VIIIA in order to emphasize the fact that the heavier elements in this group form compounds in which the oxidation state is the highest, i.e., $+8$.

CHAPTER NINE

SIGNIFICANCE OF THE PERIODIC LAW

Friedrich Engels called the discovery of the Periodic Law by D. Mendeleev a scientific feat. Now when the Periodic Law is accepted by us since our school days as one of the fundamental laws of nature, it is difficult to overestimate and adequately appreciate the genius of Mendeleev's generalization.

At the time the Periodic Law was formulated only 63 elements were known and their atomic weights and valencies in many cases had been determined incorrectly. Nevertheless, on the basis of the Periodic Law, D. Mendeleev revised the valencies and corrected the values for the atomic weights of many elements; he placed a number of elements in the periodic table regardless of the conceptions of their relationships generally accepted at that time, not being tempted to correct certain seeming (as we now know) deviations. Moreover, he predicted the discovery of many new elements and even indicated the properties of the main compounds of some of them.

It is indisputable that the aim of true science is to know in order to predict. The significance of the Periodic Law, however, is not confined to the possibility it affords of estimating the values of the great number of physical and chemical properties of the elements and their compounds, so necessary for theoretical and practical purposes.

If the Periodic Law had not been discovered, it would have been impossible to determine the atomic structure of elements. Just like in the ancient Greek myth Thesius found his way out of the Minotaur's labyrinth by means of Ariadne's thread, so with the aid of the Periodic Law it became possible to understand the structure of atoms, i.e., to solve a problem more intricate than the legendary labyrinth.

It should be noted that although information about atomic structure is of major importance for science, it does not substitute the Periodic Law. The Periodic Law has made possible the prediction and calculation of such properties of elements and their compounds, which as yet cannot be calculated theoretically on the basis of data on the electronic structure of atoms and molecules. Obviously, with the advancement of science, there will be greater possibilities for theoretical calculation but it is also evident that it will lead to the study of a still greater number of substances and properties; therefore, apparently there will always be some difference between what can be calculated by means of the theory of atomic and molecular structure and what can be found with the aid of the Periodic Law. According to the principles of dialectical materialism, chemistry cannot be reduced to physics. All the laws of physics are also observ-

ed in chemistry; the latter, however, is governed by certain laws of its own, the most important of which is the Periodic Law.

Though the Periodic Law and Periodic System of the Elements were set forth and established when the atom was considered to be indivisible, they constitute a fundamental generalization. Many and varied are the complex regularities of nature that are expressed in this simple law. Subsequent scientific progress, as the discovery of new elements; the determination of their properties and the properties of compounds formed by them; the discovery of radioactivity, isotopes, the complex structure of atoms, artificial radioactivity and many other advances in science have only corroborated the Periodic Law, disclosed new aspects of the law, broadened and deepened its content.

The Periodic Law is the quintessence of the science of chemistry, the basis for correlating and comprehending the enormous number of facts that constitute the inexhaustible source of new discoveries and generalizations. Niels Bohr wrote that the Periodic System is "the guiding star for investigators in the fields of chemistry, physics, mineralogy, technology". It has greatly influenced the development of geology, geochemistry, nuclear physics, astrophysics, cosmogony. The Periodic Law is one of the general laws of nature by which science is constantly being enriched. In this lies its great service to science.

The philosophical significance of the Periodic Law cannot be overestimated. It vividly shows the interrelationship and interdependence of chemical phenomena. All the elements are connected like the links of a chain. Each element can be studied only in connection with others and the entire Periodic System, only in the light of the properties of each element.

It is hard to name another law which would illustrate more distinctly how quantitative changes (increase of Z) result in qualitative changes, *viz.*, the appearance of new properties of elements and their compounds.

When studying the Periodic System of the Elements, we are convinced over and over again that it contains vivid examples confirming the law of unity and conflict of opposites, constituting the gist of dialectics: the periods combine elements with opposite properties; and the same elements, depending on the conditions, can react in different ways. For example, sulphur can act as an oxidizing agent and as a reducing agent; arsenic in some of its properties resembles metals, whereas in others, nonmetals, etc.

Numerous examples can be cited that confirm the third law of dialectics, the law of negation of negation. We shall mention only one of them—the transition from one period to another as the result of the formation of a new electron shell, i.e., a repetition of the course of development of passed stages on a new and higher basis.

THE STRUCTURE OF MOLECULES AND THE CHEMICAL BOND

CHAPTER TEN

INTRODUCTION

10.1. Molecules, Ions and Free Radicals

The atoms of elements can form three types of particles involved in chemical processes—*molecules, ions* and *free radicals*.

The molecule is defined as the smallest neutral particle of a given substance possessing its chemical properties and capable of independent existence. Molecules may be *monoatomic,* diatomic, triatomic and so on, that is, *polyatomic.* In ordinary conditions the noble gases consist of monoatomic molecules; on the other hand, the molecules of high-molecular compounds contain thousands of atoms.

The ion is a charged particle comprising an atom or group of chemically bound atoms with an excess of electrons (anions) or an insufficiency of electrons (cations). The positive ions in a substance always exist together with negative ions, and since the electrostatic forces acting between ions are great it is impossible to bring about a significant excess of ions of the same sign in a substance.

The free radical is a particle possessing unsaturated valences (the term is defined on p. 203, on the basis of electronic conceptions). CH_3 and NH_2 are examples of such particles. Under ordinary conditions free radicals cannot, as a rule, exist for any considerable length of time, but they play a very important part in chemical processes, many reactions being impossible without their participation. At very high temperatures, e.g., in the solar atmosphere, the only diatomic particles that can exist are free radicals (CN, OH, CH and some others). Many free radicals are present in a flame.

Free radicals of more complex structure are known which are relatively *stable* under ordinary conditions. One such radical is triphenylmethyl and it was the discovery of the latter that marked the beginning of the study of free radicals.

In 1900 Gomberg of USA tried to prepare hexaphenylethane

$$C_6H_5-\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{C}}\text{————}\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{C}}-C_6H_5$$
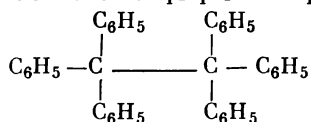
by reacting triphenylchloromethane, $(C_6H_5)_3CCl$, with zinc, copper or finely dispersed silver. Through the union of the metal with the chlorine in the tri-

8*

phenylchloromethane molecule one valence should be freed and the radicals $(C_6H_5)_3C$ — formed should unite to give hexaphenylethane (Wurtz — Fittig synthesis).

However, the properties of the substance Gomberg obtained were not like those of hydrocarbons. It formed colourless crystals which yielded bright yellow solutions when dissolved in organic solvents, and these solutions readily reacted with iodine, atmospheric oxygen and other substances. Gomberg accordingly concluded that in solution hexaphenylethane dissociated, thus forming the free radical triphenylmethyl

$$(C_6H_5)_3C - C(C_6H_5)_3 \rightleftarrows 2(C_6H_5)_3C -$$
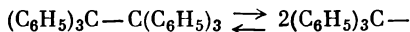
Later investigations showed that this reaction actually takes place, though not to such a degree as Gomberg supposed; the dissociation of hexaphenylethane into triphenylmethyl becomes considerable only at temperatures of 50-100°C.

The relative stability of triphenylmethyl is due, among other things, to *spatial restriction*; the large size of the phenyl groups C_6H_5 hinders union of the radicals to form hexaphenylethane. Other causes will be discussed below (see p. 193). Other stable free radicals similar to triphenylmethyl are also known.

10.2. Development of Conceptions of the Chemical Bond and Valence

The first attempt to elaborate a theory of the chemical bond dates back to the beginning of the nineteenth century when Bergman (Sweden) and Berthollet (France) advanced the idea that the tendency of particles to unite with other particles[1] was due to the force of gravity acting between them. But it was found that chemical affinity is not proportional to the mass of the atoms combined in a molecule—the mercury atom is two hundred times heavier than the hydrogen atom but water is incomparably more stable than mercuric oxide. (Give other examples, comparing the stability of compounds of a given element with that of compounds of other elements in the same subgroup of the periodic system.) Furthermore, the force of gravity acts at any distance, but chemical forces are effective for only 0.5-3 Å. The former is small and diminishes in inverse proportion to the square of the distance; the latter are colossal—roughly 10^{33} times greater than the force of gravity—and in many cases diminish with distance to a degree considerably greater than two. The force of gravity is never saturated—matter forms enormous accumulations of atoms, such as planets, for example. The hydrogen atom, on the other hand, after combining with another hydrogen atom cannot combine with a third—*chemical forces are characterized by saturability*. Moreover, unlike gravitation, chemical forces are usually associated with a definite direction in space (see p. 122).

---

[1] This tendency is usually called *chemical affinity*, a term that goes back to the alchemic period of chemistry.

Whereas the force of gravitation, according to Newton's law, acts on all bodies, the *effect of chemical forces is specific*—a chlorine atom is coupled to a sodium atom by a strong bond and to a chlorine atom by a weaker bond; it is not coupled to a helium atom by any bond. If one takes into consideration the effect of external conditions on the strength of the chemical bond, temperature, for instance, it becomes clear why the Bergman—Berthollet *gravitational theory* was untenable.

It gave way to the *electrochemical theory* formulated by the Swedish chemist, Berzelius (1810). According to this theory the atom of every element has two poles, positive and negative, the former being predominant in some elements, and the latter predominant in others. From the standpoint of the Berzelius theory, the union of electropositive magnesium with electronegative oxygen was explained by the attraction of the predominant poles, since these are of opposite signs. If there is partial compensation of the charges, the reaction product does not lose them completely. This explained the formation of more complex molecules, such as magnesium carbonate through the combining of 'positive' MgO with 'negative' CO_2. The Berzelius theory was a development of Davy's idea (1806) that the chemical bond springs from the mutual attraction of bodies bearing charges of unlike signs. On the face of it, the electrochemical theory seems plausible and would seem to be confirmed by the process of electrolysis—electrolysis would seem to restore the polarity lost by the atoms through the formation of compounds. But Hegel, criticising the Berzelius theory, wrote that such an approach took no notice of changes in specific gravity, cohesion, shape, colour and so on, which take place during a chemical process, nor of acid, corrosive, alkaline and other properties, everything disappearing in the abstraction of electricity. "Let people stop upbraiding philosophy "for abstraction from the particular and for empty abstract conceptions", if physicists chose to forget about all the enumerated properties of corporeity for the sake of positive and negative electricity." Actually the electrochemical theory soon disappeared from scientific use since it was refuted by the existence of stable molecules consisting of atoms of like polarity, e.g. H_2 and Cl_2, and by the carrying out of processes by Dumas (1834) in which elements of unlike polarity, according to the Berzelius theory, replaced one another in compounds.

In the forties of last century, the French chemists, Dumas and Gerhardt, advanced the *theory of types*. According to this theory the chemical properties of substances were associated with the analogy in the composition of their molecules, and were practically independent of the nature of the atoms. This was an attempt to elaborate a theory of chemistry based entirely on facts relating to the composition of substances. Organic compounds were considered to be deri-

vatives of a few inorganic substances. Thus, ethyl alcohol, C_2H_5OH, and diethyl ether, $C_2H_5—O—C_2H_5$, were thought to be of the H_2O type, and were regarded as substitution products of water in which one or both hydrogen atoms were replaced by the C_2H_5 group. In the same way, CH_3NH_2 and $(CH_3)_2NH$ were thought to be of the NH_3 type and so on. Thus a systematization of informa-tion was achieved, but on a strictly formal basis. Things went so far that in order to make the numerous newly discovered compounds fit into the procrustean bed of types, different formulae had to be ascribed to the same substance, depending on the reactions into which it entered. In his manual of organic chemistry, Gerhardt wrote that by confining a substance, so to say, to a single formula, one often concea-led chemical relationships which another formula would have made understandable. Attempts to elucidate the structure of molecules were rejected on the grounds that this was beyond human comprehension— the mind could not fathom the infinitesimal. It was held that studying the matter in chemical processes only made it possible to establish its past and future, and not its present; the nitration of C_6H_6 was the past of nitrobenzene, while reduction of the latter to $C_6H_5NH_2$ was its future.

Soon the results of an investigation were published which led to the idea of definite structure of molecules. In 1852 the English chemist Frankland on the basis of a study of the formation of certain metallo-organic compounds—CH_3Na, $(CH_3)_2Hg$, $(CH_3)_3Al$, $(CH_3)_4Sn$, etc.—introduced the conception of atomicity (*valence*) which expres-ses numerically the capacity of an atom of a given element to combi-ne with a definite number of atoms of a different element. If the valence of hydrogen is taken as unity, it can be considered that the valence of another element is the number of atoms of hyd-rogen (or some other monovalent element) with which it will com-bine.

The magnitude of valence depends on the state of the given ele-ment, the nature of the element with which it reacts and the condi-tions of the reaction. All elements can be divided into two catego-ries—those with a constant valence, such as sodium, and those with a variable valence, such as phosphorus or sulphur.

10.3. A. Butlerov's Theory of Chemical Structure

In 1861 A. Butlerov propounded a theory which can be formulated essentially as follows:

    (a) the atoms in a molecule are combined in a definite order;

    (b) atoms combine in accordance with their valence;

    (c) the properties of a substance depend not only on the nature of the atoms and their number, but also on their arrangement, i.e., on the chemical structure of the molecules.

This theory explained the multiformity of organic substances, and dealt a decisive blow to the agnostic theory of types. Butlerov showed that the internal structure of molecules is cognoscible and can be intentionally reproduced. On the basis of Butlerov's theory the structure of molecules can be established by the study of chemical transformations—his theory indicated *chemical methods of investigating the structure of a substance*. Thus, the empirical formula of ethyl alcohol is C_2H_6O. Taking into account the valence of the elements contained, only two structural formulae are possible

$$
\begin{array}{cc}
\begin{matrix} H & H \\ | & | \\ H-C-C-O-H \\ | & | \\ H & H \end{matrix}
& \text{and} &
\begin{matrix} H & H \\ | & | \\ H-C-O-C-H \\ | & | \\ H & H \end{matrix}
\end{array}
$$
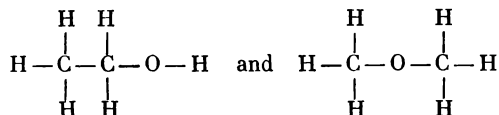
A study of the chemical reactions of ethyl alcohol shows that its molecule has the first of the above structures—when alcohol is reacted with metallic sodium only one hydrogen atom is replaced

$$2C_2H_6O + 2Na = 2C_2H_5NaO + H_2$$
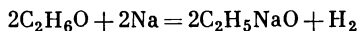
This is in accordance with the first formula in which one atom of hydrogen is different from all the others—it is joined to oxygen, not carbon. During the century which has passed since the formulation of the theory of chemical structure, chemists have worked persistently along this line, thus establishing the structural formulae of thousands of organic and elemento-organic compounds. Proving some of these formulae required tremendous effort. For instance, a large number of investigators in different countries had worked on the chemistry of quinine for over 60 years before the structure of the quinine molecule was finally elucidated.

Later study of molecular structure, employing physical methods developed in the 20th century, some of which will be considered below, confirmed the arrangement of atoms in molecules found by means of the Butlerov theory. Thus the Butlerov theory laid the foundation of present-day principles of molecular structure.

The theory of chemical structure introduced the extremely fruitful conception of the *mutual influence of the atoms* in molecules. It was found that in a molecule it is not only the directly bound atoms that act on one another—there is a mutual influence of all the atoms. It goes without saying that the effect of the mutual influence of atoms in the molecule which are not directly bound with one another, the so-called *induction effect*, is relatively small. Nevertheless, in some cases it is significant. Thus, if all the hydrogen atoms in one

$$
\begin{matrix}
& CH_3 & \\
& | & \\
H_3C-C-O-H \\
& | & \\
& CH_3 &
\end{matrix}
$$
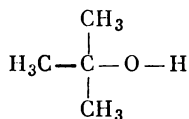
of the methyl groups of tertiary butyl alcohol are replaced by fluo-
rine, the alcohol acquires acidic properties. This is explained by the
fact that fluorine, which possesses great electron affinity, strongly
attracts electrons, and its introduction into a molecule causes
a displacement of electrons along the chain of atoms

$$
\begin{array}{c}
F \\
\quad\backslash \\
F\!\leftarrow\!\!-\!\!-\!C\!\leftarrow\!\!-\!\!-\!\!-\!C\!\leftarrow\!\!-\!\!-O\!\leftarrow\!\!-\!\!-\!\!-H \\
\quad/ \\
F
\end{array}
\qquad
\begin{array}{c}
CH_3 \\
| \\
\\
| \\
CH_3
\end{array}
$$
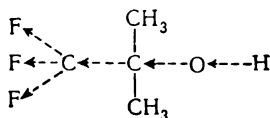
This displacement is dampened as the distance from the atom causing
the induction effect increases.

Lastly, the Butlerov theory explained *isomerism*, a phenomenon
discovered by Liebig and Wöhler in 1823, which in turn played an
important part in the formation of the theory of chemical structure.
Isomerism is the existence of several compounds of the same compo-
sition but differing in properties because of differences in the struc-
ture of their molecules. The idea of the existence of such substances
goes back to the investigations of M. Lomonosov. In his work "On
Metallic Glance" (1745) he wrote that one of the possible causes
of changes in the properties of a substance could be the shifting of
the arrangement of its parts.

There are two types of isomerism—*structural* and *spatial* or *stereo-
isomerism.*

10.4. Structural Isomerism

Structural isomerism is caused by a difference in the sequence
of the bonds between the atoms in a molecule. There are several
kinds of structural isomerism.

If molecules differ in the arrangement of the carbon atoms forming
their framework, this is termed *skeletal isomerism.* Here is an example

$$CH_3-CH_2-CH_2-CH_2-CH_3 \quad \text{and} \quad CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$$

Normal pentane   2-Methylbutane
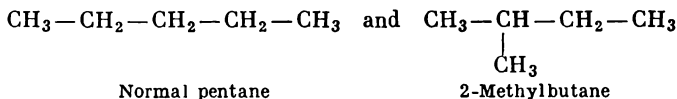
The number of isomers quickly mounts as the number of carbon
atoms in the molecule increases. For C_6H_{14} there are six isomers,
but for $C_{20}H_{42}$ there are 366,319! And compounds of the formula
$C_{100}H_{202}$ are known. Isomerism involving changes in the carbon
skeleton can be demonstrated with other examples. Here is one

$$
\begin{array}{c}
CH_2-CH_2 \\
/ \qquad\qquad \backslash \\
H_2C \qquad\qquad\qquad CH_2 \\
\backslash \qquad\qquad / \\
H_2C-CH_2
\end{array}
\quad \text{and} \quad
H_3C-HC
\begin{array}{c}
CH_2-CH_2 \\
/ \qquad\qquad | \\
\\
\backslash \qquad\qquad | \\
CH_2-CH_2
\end{array}
$$

Cyclohexane   Methylcyclopentane
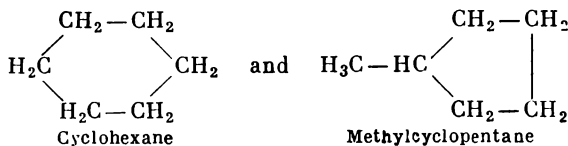
Molecules having the same carbon skeleton but differing in the position of *functional groups*[1] are termed *position isomers*

$$CH_3-CH_2-CH_2OH \quad \text{and} \quad CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Normal propyl alcohol   Isopropyl alcohol

Orthodichloro-   Metadichloro-
benzene   benzene
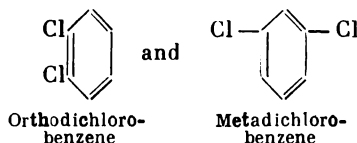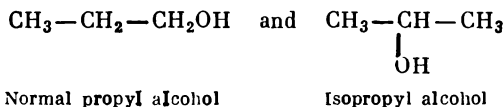
It should be noted that on the basis of his theory Butlerov foretold the existence of tertiary butyl alcohol and was the first to synthesize this isomer of normal butyl alcohol; reduction gave isobutane, the only possible isomer of butane.

A third form of structural isomerism is *metamerism*, in which molecules having the same empirical formula differ in the composition or structure of radicals attached to a non-carbon atom. Thus

$$CH_3-O-CH_2-CH_2-CH_3 \quad \text{and} \quad CH_3-CH_2-O-CH_2-CH_3$$

Methylpropyl ether   Diethyl ether
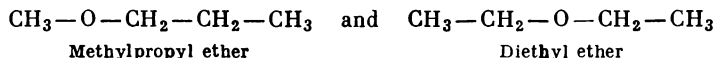
have the same empirical formula but the radicals attached to the oxygen atom differ.

There are also structural isomers which differ from one another in the character of functional groups

$$CH_3COOH \quad \text{and} \quad CH_2(OH)-C\overset{\displaystyle O}{\underset{\displaystyle H}{\Big\backslash}}$$

Acetic acid   Glycolic aldehyde
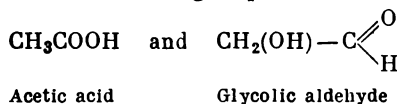
A special kind of structural isomerism is *dynamic isomerism* or *tautomerism*, in which the two isomeric forms are easily transformed from one to the other and are in a state of equilibrium. This phenomenon logically follows from Butlerov's conception of the dynamic interrelationships of the atoms in a molecule, and was first foretold and explained by him (1862). The keto-enol equilibrium is an example of tautomerism

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH_2$$

Keto form   Enol form

---
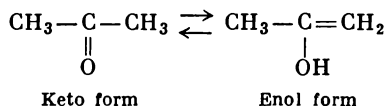
[1] Functional groups are groups of atoms, such as —OH, —NO$_2$, —NH$_2$, —COOH and —SO$_3$H, which to a considerable degree determine the chemical properties of a compound, and consequently, the class of compounds to which it belongs.

It should not be thought that structural isomerism is limited to organic compounds. It is also encountered among inorganic compounds, as illustrated by the following examples

$$HO-N=N-OH \quad and \quad O_2N-NH_2$$

Hyponitrous acid   Nitramide

$$F-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cl}}=O \quad and \quad F-O-Cl\overset{\diagup O}{\diagdown O}$$

Perchloryl fluoride   Chloryl oxyfluoride
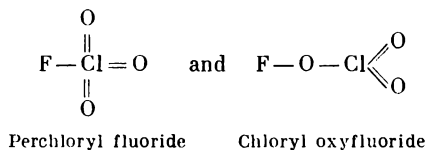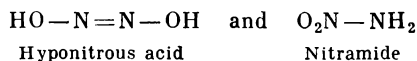
Developments in atomic physics during the last several decades have led to the discovery of a new type of isomerism, which may be termed isotope isomerism. This can be illustrated by the molecules $\overline{C}H_3COOH$ and $CH_3\overline{C}OOH$ which are tagged with radioactive carbon—the former in the methyl group, and the latter in the carboxyl group.

It was only Butlerov's work that made it possible to explain all forms of structural isomerism with a single theory. Before that, isolated instances of isomerism "wandered homelessly", as Liebig. put it, through the realm of science.

Isomerism is a manifestation of one of the forms of transition of quantity to quality—when the number of atoms in a molecule reaches a certain value, a variation in their arrangement becomes possible.

10.5. Spatial Isomerism

Butlerov's theory was significantly extended in 1874 when the Dutch chemist van't Hoff and the French chemist Le Bel working independently of one another, suggested that the four valences of carbon are directed towards the vertices of a regular *tetrahedron*, at the centre of which the carbon atom is situated (Fig. 10.1)[1]. In this case the angles between all the bonds are equal to 109.5°. This means that if the centre of the carbon atom in a molecule is connected by straight lines to the centres of the other atoms surrounding it, these lines representing the bonds will be directed towards the vertices of a tetrahedron with the carbon atom at the centre. This was the origin of the conception of the spatial structure of the molecule which developed into the branch of chemistry known as *stereochemistry*.

On the basis of van't Hoff and Le Bel's suggestion it was concluded that a particular class of isomerism—*optical isomerism* should exist.

---

[1] A regular tetrahedron is a three-faced pyramid whose faces are regular triangles.

Let us consider a carbon atom joined to four unlike atoms or groups which can be designated by the latters A, B, D and E (Fig. 10.2). Such an atom is said to be *asymmetric*. As can be seen in Fig. 10.2 two structures are possible in this case, as in *a* and *b*, which are mirror images of one another. Since all the distances between the atoms are equal to both structures, as are the angles between the bonds, the chemical properties of the two isomers, according to the Butlerov theory, should be identical.

The existence of certain compounds in several forms which could not be distinguished by their chemical properties was known long

Fig. 10.1. Spatial arrangement of valences of the carbon atom
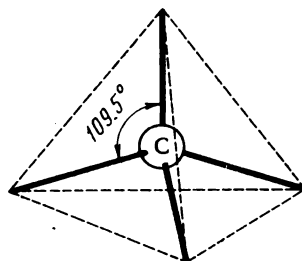
before the appearance of the works of van't Hoff and Le Bel This phenomenon was discovered in 1848 by Pasteur (France). When studying tartaric acid

$$COOH - CH(OH) - CH(OH) - COOH$$
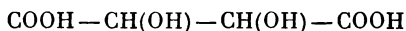
he found that this compound existed in two forms which had identical chemical properties but differed in the asymmetry of their crystals—the crystals of one form were as if the mirror images of the crystals of the other form (Fig. 10.3). Such crystals are said to be *enantiomorphous* and the compounds forming them are termed *optical antipodes*.

Van't Hoff and Le Bel explained the existence of optical antipodes as being due to the presence of asymmetric carbon atoms in their molecules; consequently there could be isomers of the structure shown in Fig. 10.2. Thus, in the tartaric acid molecule
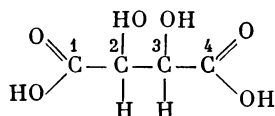
carbon atom 2 is asymmetric. It is bound to H and three different radicals, —OH, —COOH and —CH(OH)—COOH. For that reason there should be two optical isomers[1].

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[1] Carbon atom 3 is also asymmetric but since the atoms and radicals bound to atoms 2 and 3 are identical, the isomers resulting from the asymmetry of atom 3 are the same as the isomers resulting from the asymmetry of atom 2.
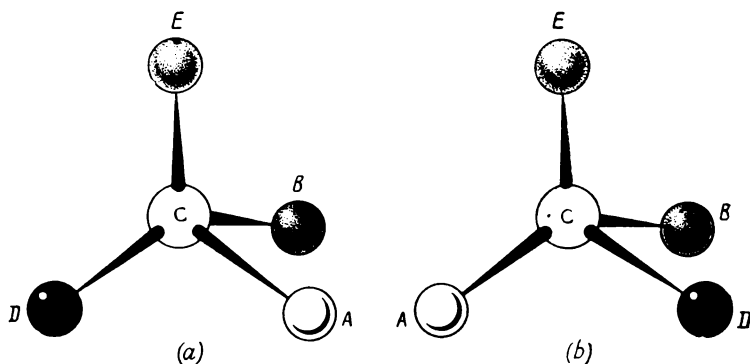
Fig. 10.2. Structure of mirror isomers
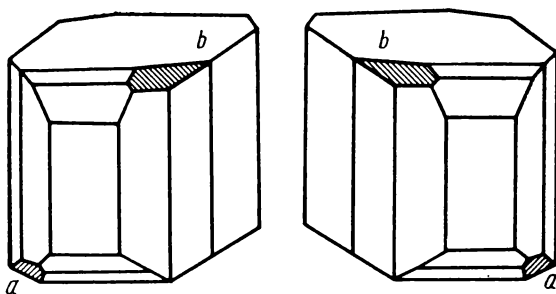
Fig. 10.3. Crystals of mirror isomers of sodium ammonium tartrate
To show the asymmetry of the crystals two faces, denoted *a* and *b,* are hatched

It should be noted that there would be no optical isomerism if all four valence lines of the carbon atom were in the same plane. In that case the distances between the atoms in the structures

$$
\begin{array}{ccc}
A \quad B & & A \quad B \\
\diagdown \diagup & & \diagdown \diagup \\
C & \text{and} & C \\
\diagup \diagdown & & \diagup \diagdown \\
D \quad E & & E \quad D
\end{array}
$$
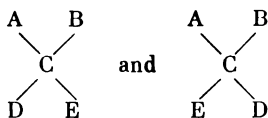
(for example, between atoms D and A) would be different and the isomers would have different chemical properties; there would be a different type of isomerism which will be discussed below.

Optical isomerism is characteristic of all compounds containing asymmetric carbon atoms. Here are some examples of such compounds,

the asymmetric atoms being indicated with asterisks

$$C_2H_5 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}} - OH \qquad\qquad CH_3 - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}} - COOH$$

Isobutyl alcohol   Lactic acid

$$\underset{O}{\overset{H}{\diagdown}}C - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}} - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}} - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}} - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}} - CH_2OH$$
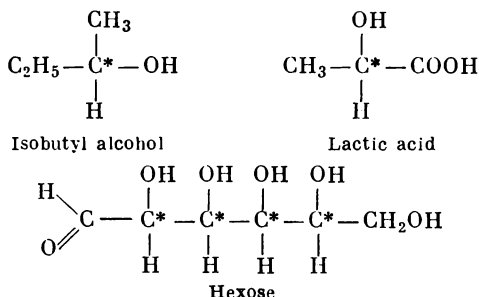
Hexose

The presence of each additional asymmetric carbon atom in a molecule doubles the number of possible isomers, i.e., if there are n asymmetric atoms the number of isomers is 2^n. Consequently for
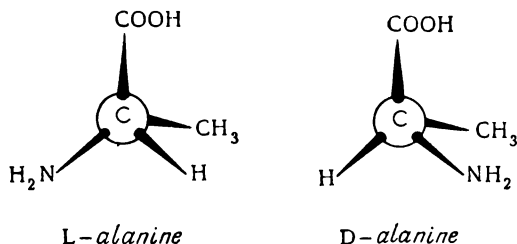
L-*alanine*   D-*alanine*

Fig. 10.4. Optical isomers of alanine

hexose, the last compound shown above, 16 isomers are possible, and all have been found. Four occur in nature, and the others have been prepared.

As stated above the chemical properties of optical antipodes are identical. Such isomers differ from one another only in the symmetry (or asymmetry, to be more exact) of their crystals and *in the direction of rotation of the plane of polarized light.*

If polarized light [1] is passed through an optical isomer in the crystalline, liquid, gaseous or dissolved state, the plane of polarization is rotated through a certain angle, depending on the number of molecules of the substance in the path of the light beam. Substances which rotate the plane of polarization are said to be *optically active.* When polarized light is passed through the other isomer, the plane of polarization is rotated through the same angle, but in the opposite direction. One of the isomers is *dextrorotatory* (+) and the other, *laevorotatory* (−).

The configuration of optically active organic compounds is distinguished by the prefix *D-* or *L-* (from the Latin words *dexter*, right, and *laevus*, left). Thus, the *D-* and *L*-forms of amino-acids are considered as derivatives of the *D-* and *L*-isomers of the amino-acids of alanine (Fig. 10.4).

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[1] The polarization of light is discussed in Appendix IV.

In chemical reactions in which optically active compounds are not involved the end product, if it contains an asymmetric carbon atom, will always be a mixture of equal quantities of the two stereo-isomers. Three methods of dividing optical isomers are known, all of which were first proposed by Pasteur.

1. When a mixture of optical isomers is crystallized they form crystals of different asymmetry; by carefully examining these crystals it is possible to separate the crystals of one isomer from those of the other isomer.

2. Microorganisms for which the given substance is a nutrient, usually decompose only one of the optical isomers, leaving the other untouched. The explanation is that only certain forms of optically active compounds can serve as building material for living organisms.
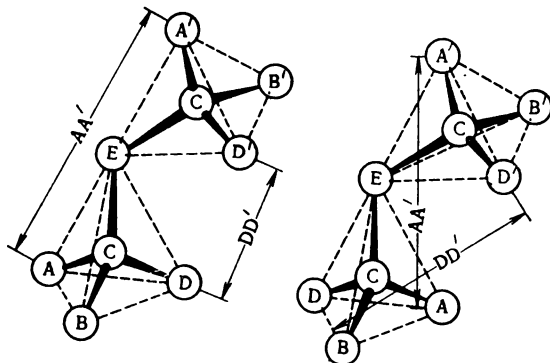
Fig. 10.5. Structure of addition products of optical isomers with another optically active compound

3. When optical isomers are made to combine with another optically active compound the products will not be identical in properties. This is due to the fact that in this case the distances between the atoms are different. As can be seen in Fig. 10.5, when two particles with asymmetric atoms are combined in a molecule, the interatomic distances, e.g. the distance DD', cannot be identical for the different isomers. Compounds thus prepared can be separated, and after that the optical isomers can be isolated.

It is noteworthy that the proteins of all living organisms consist only of the *L*-isomers of amino-acids, but the causes of this phenomenon are unknown. Since only certain forms of optically active substances are utilised by organisms, the other forms are useless for them. This explains the fact that microorganisms decompose only one from a pair of optical isomers, the other being left untouched.

Another form of spatial isomerism not associated with the presence of mirror-like arrangements of the atoms in the molecules, which cannot be superimposed, is *geometric isomerism*. It is caused by unlike arrangement of the atoms and is characteristic of unsaturated and cyclic organic compounds. It is the different arrangement of the substituents attached to the carbon atoms in relation to the double bond in unsaturated compounds, or in relation to the plane of the ring in cyclic compounds that gives rise to this form of isomerism. In the first case the isomers are compounds containing a like substituent combined with both of the carbon atoms joined by a double

bond. The substance in which the like substituents are on one side of a plane drawn through the double bond is called the *cis isomer*. In the *trans isomer* the substituents are on different sides of the plane. In cyclic compounds the difference consists in whether the like substituents are arranged on the same side of the plane of the ring (*cis* form) or on different sides (*trans* form). Thus in the *cis* form the like substituents are closer together than in the *trans* form. This is illustrated by the following molecules

Cis-1,2-dichloro-
ethylene

Trans-1,2-di-
chloroethylene

Cis-1,2-dichlorocyclo-
pentane

Trans-1,2-dichlorocyclo-
pentane
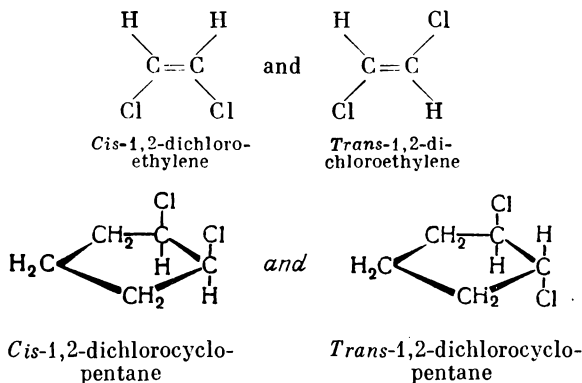
It should be emphasized that *cis—trans* isomerism is not found in acyclic compounds in which the carbon atoms are joined by single bonds because of the possibility of rotation round the single bond (for example, the CH_3 group in ethane).

Unlike optical isomers, geometric isomers differ in their physical and chemical properties. Thus melting points of the *cis-* and *trans*-dichloroethylenes differ by over 30 °C.

It follows that often it is not enough to know the sequence of the atomic bonds—one must also know their spatial arrangement, i.e., the *configuration* of the molecules.

It should be noted that spatial isomerism, like structural isomerism-is also characteristic of inorganic compounds, such as complex com, pounds (see pp 235-236).

CHAPTER ELEVEN

BASIC CHARACTERISTICS
OF THE CHEMICAL BOND—LENGTH, DIRECTION, STRENGTH

The basic parameters of molecules are the *length of the bonds* between the atoms (the internuclear distance), the angles formed in the molecules by the lines connecting the centres of the atoms in the direction of action of the chemical bonds between them (*valence angles*), and also the *energies of the bonds*, which determine their

strength[1]. For a complete characterization of a molecule it is neces-
sary to know the distribution of electron density and the electronic
energy levels.

11.1. Length of Bonds[2]

Bond length d can be estimated approximately on the basis of the
atomic or ionic radii or from a rough determination of the size
of the molecules by means of the Avogadro number (see p. 15).
Thus, the volume of the water molecule

$$v_{H_2O} = \frac{18}{6.023 \cdot 10^{-23}} = 29.7 \cdot 10^{-24} \text{ cm}^3$$

from which

$$d_{H_2O} \approx \sqrt[3]{29.7 \cdot 10^{-24}} \approx 3 \cdot 10^{-8} \text{ cm} = 3 \text{ Å}$$

Actually the length of the bonds is of the order of 1 Å. For an
approximate estimation of d one can also use the formula

$$d_{A-B} = \frac{d_{A-A} + d_{B-B}}{2}$$

based on the assumption that each atom makes a constant contri-
bution to the interatomic distance.

Methods to be taken up later enable a precise determination of
bond lengths. Thus, the following values of d were found by means
of these methods: for H_2, 0.74; N_2, 1.09; O_2, 1.21 Å. The regular
change in the atomic (ionic) radii in the periodic system entails
a regular change in internuclear distances d. Thus, for the molecu-
les HX we find

H—F	0.92 Å	H—Br	1.42 Å
H—Cl	1.28 Å	H—I	1.62 Å

If the hydrogen in this series is replaced by a different element,
say carbon, the character of changes in d for the same X remains the
same.

The parallelism of changes in d in diatomic molecules makes it
possible to employ the method of comparative calculation for their
quantitative estimation (see p. 75)[3].

An analysis of experimental data shows that for a constant valent
state the internuclear distance for a given type of bond remains

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[1] The strength of the bond can be characterized by energy or by the force
required to break the bond, but these characteristics are not equivalent. The
term strength is used here as a synonym of energy.

[2] Here and below, what is meant is the internuclear distance corresponding
to the stable state of the molecules where the forces of attraction are balanced
by the forces of repulsion, and potential energy is minimum (see p. 167).

[3] In this way it has been possible to determine the value of d for over 100 bonds
for which there is no experimental data.

practically constant in different compounds. Thus, in all aliphatic compounds d_{C-C} lies within the range from 1.54 to 1.58 Å, and in aromatic compounds, from 1.39 to 1.42 Å.

Transition from the single bond to a multiple bond is marked by a shortening of internuclear distances which can be associated with strengthening of the bond. Whereas $d_{C-C} \approx 1.54$, $d_{C=C} \approx 1.34$ and $d_{C \equiv C} \approx 1.20$ Å.

11.2. Valence Angles

The values of valence angles depend on the nature of the atoms involved and the character of the bond. Whereas all diatomic molecules of the A_2 or AB types can be represented as

various configurations are possible for triatomic, tetratomic and more complicated molecules.

A triatomic molecule can be linear or nonlinear

$\angle BAB = 180°$ $\angle BAB < 180°$

The first type is found in molecules containing some elements of Group II, for example, $BeCl_2$, $ZnBr_2$, CdI_2, and in a number of

$\angle BAB = 120°$ $\angle BAB < 120°$
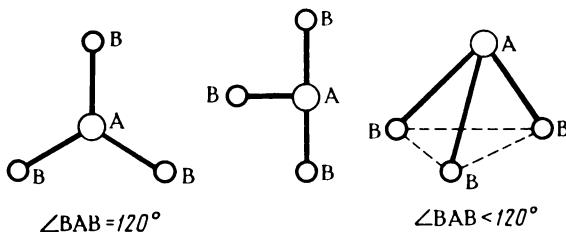
Fig. 11.1. Structural variants of molecule AB_3

other molecules (CO_2, CS_2). Some molecules with unlike internuclear distances, HCN for one, also have this configuration. The second type includes many compounds of *p*-elements of Group VI (SO_2, H_2O, etc.).

In series of similar molecules, $\angle$ BAB changes regularly, an example being the series H_2O (104°28′), H_2S (92°), H_2Se (91°), and H_2Te (89°30′).

A tetratomic molecule, AB_3, can be of planar or pyramidal configuration (Fig. 11.1). The first type of molecule is characteristic of some compounds of elements of Group III (BCl_3, $AlBr_3$); some ions also have a planar configuration (NO_3^-, CO_3^{2-}). ClF_3 is an example of a T-shaped molecule.
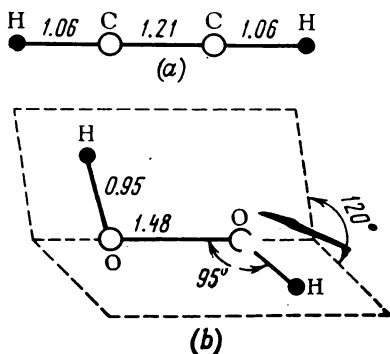
Fig. 11.2. Structure of molecules of (a) acetylene; (b) hydrogen peroxide (interatomic distances are shown over the bonds)

A three-dimensional arrangement of the atoms in molecules is encountered more often. NH_3, PCl_3 and other compounds of p-elements of Group V have a pyramidal configuration. Here too there is a regular change in the angles, as seen in the series NH_3 (107°20′),
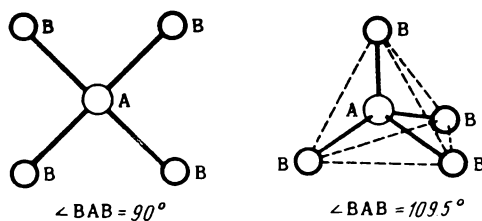
Fig. 11.3. Structural variants of molecule AB_4

PH_3 (93°20′), AsH_3 (91°50′) and SbH_3 (91°20′); PCl_3 (101°), $AsCl_3$ (97°), $SbCl_3$ (96°) and $BiCl_3$ (94°); PF_3 (104°), PCl_3 (101°) and PI_3 (98°).

Valence angles in tetratomic molecules can also have other values. Acetylene and hydrogen peroxide are examples (Fig. 11.2).

AB_4 molecules may have the configurations shown in Fig. 11.3. The first type is found comparatively rarely. An example of such a square, planar particle is the $(PdCl_4)^{2-}$ ion. A tetrahedral arrangement of the atoms is more frequent, and is typical of compounds of carbon (see p. 123) and its analogues of Group IV. The $(SO_4)^{2-}$ ion likewise has a tetrahedral structure.

$TeCl_4$ is an example of a molecule of the type
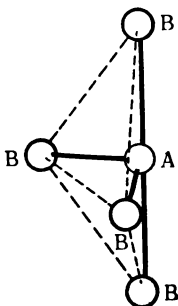
The following structures are characteristic of AB_5 molecules:
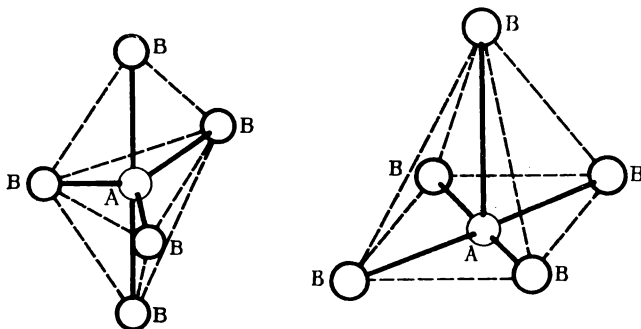
PCl_5 is an example of the first structure (trigonal bipyramid), and IF_5, an example of the second.

Diagrammatic representations of AB_6 and AB_7 molecules (octahedron and pentagonal bipyramid, respectively) are as follows
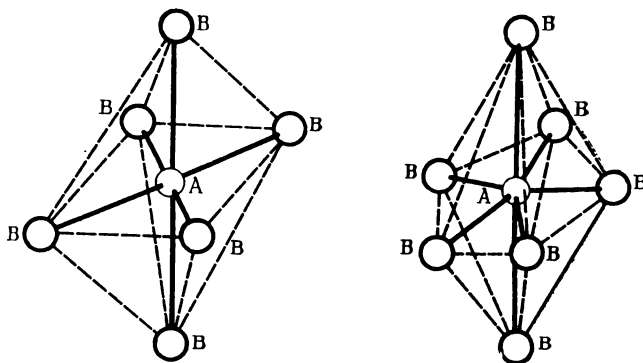
SF_6 is an example of the first structure, and IF_7, an example of the second.

In aliphatic organic compounds the length of the C—C bonds is ~1.54 Å, and the valence angles between the C—C bonds are
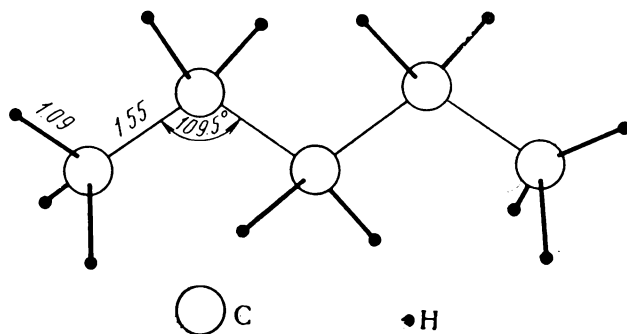
Fig. 11.4. Structure of normal pentane molecule
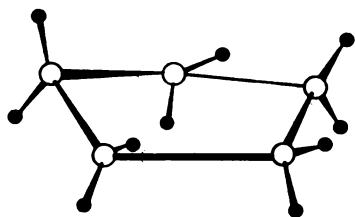
Fig. 11.5. Structure of cyclopen-
tane molecule
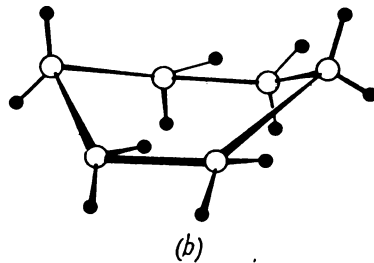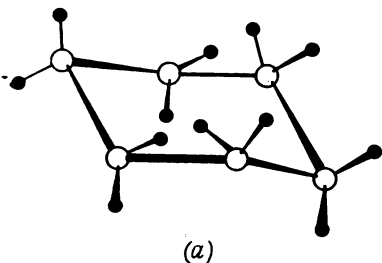
Fig. 11.6 Structural variants of cyclohexane molecule

109.5°. Hydrocarbons of the methane series have the structure of a zigzag chain. A representation of the normal pentane molecule is given in Fig. 11.4.

In saturated cyclic hydrocarbons the length of C—C and C—H bonds is the same as in the paraffin hydrocarbons but the valence angles are distorted, which produces tension in the cycle. The cyclo-

pentane molecule has tetrahedral angles—four carbon atoms are in one plane, while the fifth lies by approximately 0.5 Å higher (Fig. 11.5).

The cyclohexane molecule also has a non-planar structure with tetrahedral valence angles. In this case two configurations are possible—'armchair' and 'bath' (Fig. 11.6), of which the former has been considered the more probable. Recent investigations have demonstrated that in ordinary conditions the cyclohexane molecule does have the shape of an armchair.

It is evident from the carbon compounds cited above that the valence angles of an element can be different in different compounds.

Methods employed in determining the values of valence angles are the electron-diffraction (see p. 138-145), the X-ray diffraction (see p. 273-277) and the spectral (see p. 145-149), as well as measurement of dipole moments (see p. 153-157).

11.3. Strength of the Bond

The strength of the chemical bond can be expressed as the amount of energy expended in breaking it, or the value which when summed up for all the bonds gives the energy of formation of the molecule from atoms (mean bond energy). The *bond-breaking energy* (bond-dissociation energy) is always positive; the *bond-forming energy* is the same in magnitude but is negative.

For diatomic molecules the bond energy is equal in magnitude to the dissociation energy. For polyatomic molecules with a single type of bonds, e.g. for AB_n molecules, the mean bond energy is equal to one-nth of the total energy of formation of the compound from the atoms. Thus, the energy absorbed in the process

$$CH_4 \longrightarrow C + 4H$$
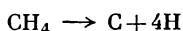
is equal to 397 kcal/mole. But in the methane molecule all four C—H bonds are equivalent. Hence the mean energy of this bond

$$E_{C-H} = \frac{397}{4} = 99 \text{ kcal/mole}$$

This calculation has been employed to determine the scale of the value of E for other atoms: 104 kcal/mole for hydrogen, and 118 kcal/mole for oxygen. Applying each of these values of E to a single molecule, we would obtain a quantity of the order of $\sim$ $\sim 10^{-19}$ cal.

But let us assume a process of *consecutive* removal of B atoms from the AB_n molecule. Such dissociation of the molecule will cause a change in the nuclear and electron configuration of the system and consequently a change in the energy of interaction of the atoms forming the molecule. Whereas the H—C—H angles in CH_4 are equal

to 109.5°, they are approximately 120° in CH_3—the tetrahedral CH_3 group in methane is converted into the almost planar methyl radical.

For this reason the energy involved in the consecutive removal of B atoms from the AB_n molecule will be different for each B atom. Different cases are possible. If breaking one bond requires a certain weakening of another bond, the energy required for consecutive removal of the B atoms will decrease. The H_2O molecule is an example. Removal of the first hydrogen atom requires 118 kcal/mole but removal of the second atom requires only 102 kcal/mole, a quantity characterizing the strength of the OH radical. If breaking one bond involves strengthening of another, the sequence will be reversed. Thus removal of the chlorine atoms from $AlCl_3$ requires 91, 95 and 119 kcal/mole. More complicated cases are also possible. The consecutive removal of the four hydrogen atoms from methane involves a loss of energy equal to 102, 88, 124 and 80 kcal/mole, respectively. Nevertheless, for any substance the mean arithmetical quantity coincides with the mean bond energy. Thus, for CH_4 we have

$$E_{C-H} = \frac{102 + 88 + 124 + 80}{4} = 99 \text{ kcal/mole}$$

The atom-removal energy is known for few molecules, and consequently such a calculation can only be carried out in isolated cases.

If a molecule contains more than two different atoms, the conception of the mean bond energy does not coincide with the conception of the bond dissociation energy. If there are different types of bonds in a molecule, each of them can be assigned, to a first approximation, a definite value of E. This makes it possible to calculate the energy of formation of the molecule from the atoms. Thus the energy of formation of the pentane molecule from carbon and hydrogen atoms is determined from the equation[1]

$$E_{C_5H_{12}} = 4E_{C-C} + 12E_{C-H}$$

Table 11.1 gives the energy of certain bonds. An examination of these quantities reveals a regular change in accordance with the periodic system of elements. Diminution of the bond energy in the series C—X (X=F, Cl, Br, I) is due to weakening of the bond as the internuclear distance of carbon—halogen increases. The great strength of the C—F bond is one of the causes of the chemical inertness of fluorine derivatives of hydrocarbons, among them the perfluoroalkanes, C_nF_{2n+2}. Augmentation of the bond energy in a series is indicative of a strengthening of the bond and, as a consequence, reduction of interatomic distances (see p. 129). Transition from a

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[1] Naturally this method yields only approximate results. Contrary to experimental findings it gives the same atomic energies of formation for all the isomers of a given compound.

Table 11.1

Lengths and Dissociation Energy of Chemical Bonds

Bond	Compound	Bond length, Å	E, kcal/mole
C—H	Saturated hydrocarbons	1.095	98.7
C—F	CH_3F	1.381	116.3
C—Cl	CCl_4, $CHCl_3$	1.767	75.8
C—Br	Bromine-substituted saturated hydro-carbons	1.94	63.3
C—I	Iodine-substituted saturated hydro-carbons	2.14	47.2
C—C	Saturated hydrocarbons	1.54	79.3
C∴C	Benzene	1.40	116.4
C=C	Ethylene and its derivatives	1.34	140.5
C≡C	Acetylene hydrocarbons	1.20	196.7
C=O	CO_2	1.160	191.1
O—H	H_2O	0.958	109.4
O—H	Alcohols	0.96	104.7
O—O	H_2O_2	1.48	33.3
S—H	H_2S.	1.346	86.8
S=O	SO_2	1.432	125.9
N—H	NH_3, amines	1.008	92.0
N∴O	NO	1.151	149.4
As—H	AsH_3	1.519	47.5

single bond to a double or triple bond between the same atoms brings an increase in the bond energy but this is not proportional to the increase in the multiplicity of the bond.

The regular change in E in bonds of the same type makes it possible to employ methods of comparative calculation for their estimation. Thus it is possible to compare the values of the mean bond energy in two series of single-type compounds, for example, in the series R_2 and HR, where R = Cl, Br and I. Fig. 11.7 gives an example of such a comparison: the values of the mean bond energy of elements of the main subgroup of Group VI are compared with carbon and silicon, and by graphic extrapolation the unknown value of E_{C-Te} can be estimated as approx. 132 kcal/mole.

Let us now consider an example of the comparison of the values of E with the values of another property in a series of compounds. We have already seen that the bond energy diminishes as the length of the bond increases. Let us assume that to a first approximation this diminution of the energy of the given element's bond with a series of analogues is linear—for example, for the bond C—R,

where R $=$ F, Cl, Br and I. The correctness of this assumption is illustrated in Fig. 11.8. This example could be extended by comparing the internuclear distances and the energies of the carbon—carbon bond, depending on the multiplicity of the bond, and so on.

The values of E for organic compounds are more reliable than for inorganic compounds, since the former are characterized by great
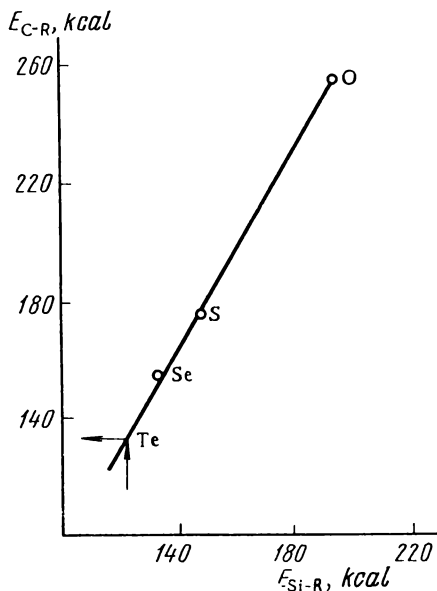
Fig. 11.7. Correlation diagram of bond energies of silicon and carbon compounds
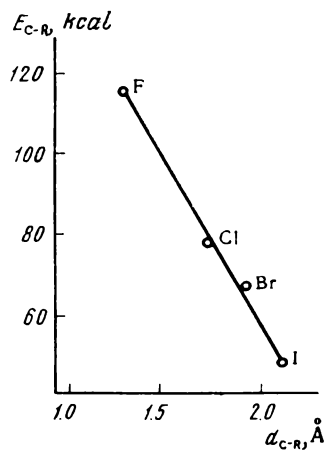
Fig. 11.8. Correlation diagram of bond energies and lengths in carbon halides

diversity of the molecules studied, along with a small number of types of bonds; the latter, on the contrary, present a very great number of bond types, with relatively scanty experimental material.

Without taking up methods of determining bond energies (by measuring the energy changes of various processes, molecular spectroscopy, etc.), it can be stated that if the energy change of a certain process is known and also the energies of all the bonds except a given bond, the latter can be calculated. Thus when hydrogen burns according to the reaction

$$2H_2 + O_2 = 2H_2O$$
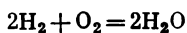
116 kcal are evolved. It can be assumed that in the process the H—H and O—O bonds are broken, and the free atoms combine to

form H_2O molecules, each of which contains two O—H bonds:
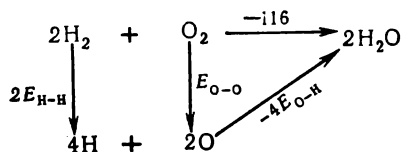
From the law of the conservation of energy it follows that

$$2E_{H-H} + E_{O-O} - 4E_{O-H} = -116$$

whence, if the energy of any two bonds is known, the energy of the third bond can be calculated

$$E_{O-H} = \frac{2E_{H-H} + E_{O-O} + 116}{4}$$

Substituting the values $E_{H-H} = 104$ and $E_{O-O} = 118$ kcal/mole in the above equation, we find $E_{O-H} = 110$ kcal/mole.

The energy of the formation of a compound from atoms is equal in magnitude and opposite in sign to the sum of the bond energies. It is to be understood that both the initial molecule and the products of its dissociation are at absolute zero and have the properties of an ideal gas (see p. 262), and, furthermore, that the dissociation products are in the ground state. Nevertheless, the chemist should bear in mind that many reactions take place between excited atoms at high temperatures and pressures.

Although temperature and pressure have little effect on bond energies (for which reason all values of E_{bnd} cited above are for $P = 1$ atm and $t = 25$ °C)[1], the transition to an excited state is accompanied by a great energy change.

CHAPTER TWELVE

PHYSICAL METHODS OF DETERMINING MOLECULAR STRUCTURE

It was pointed out above that the Butlerov theory of chemical structure established the fact that every organic molecule has a definite structure, and indicated chemical methods for determining molecular structure. Chemical methods of studying structure have also been developed for determining the structure of complex compounds which are an important class of inorganic substances (see p. 235-236). The structures of an immense number of compounds have been determined by chemical methods. This information, together with the results of investigations into the properties of com-

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[1] The difference in the value of E_{bnd} at $T = 0$ and $T = 298°K$ does not, as a rule, exceed 1 kcal/mole.

pounds and the principles underlying their changes, revealed through the discovery and elaboration of the Periodic Law, have determined the lines along which the science of chemistry has developed.

Chemical methods of studying molecular structure are still widely employed, but along with them there are a number *of physical methods* which make it possible to study features of molecular structure which cannot be determined by chemical methods, such as the precise values of interatomic distances and the angles between bonds, the distribution of electric charges in a molecule, etc.

One of the methods of studying molecular structure extensively used is *electron-diffraction examination.*

12.1. Electron-Diffraction Examination

The electron-diffraction examination method makes use of the diffraction of electrons on molecules. Electrons like all other micro-particles possess wave properties. Therefore, when a beam of elect-rons characterized by a de Broglie wavelength λ impinges on an
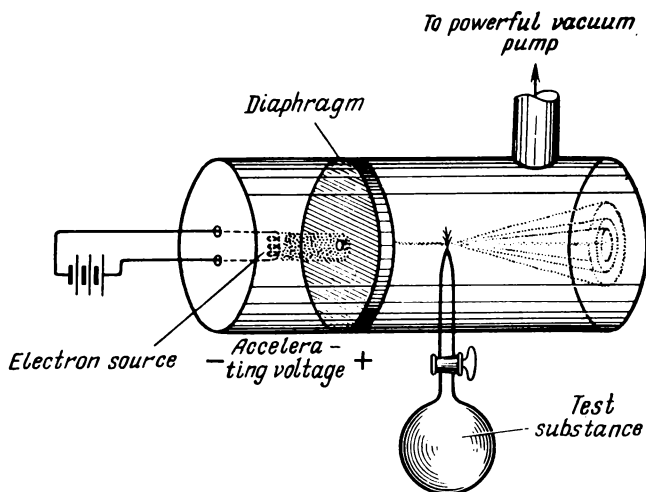
Fig. 12.1. Diagram of electron diffraction camera

obstacle whose size is of the same order as λ, a diffraction pattern is produced corresponding to this wavelength.

Electron-diffraction is examined by means of an instrument called an *electron-diffraction camera.* A diagram showing its principle of operation is given in Fig. 12.1.

The electron source in the electron-diffraction cameras is usually a hot metal filament, since metals when strongly heated begin

to emit electrons. The electrons escaping from the filament are accelerated by a potential difference of tens of thousands of volts—usually 30-60 thousand volts when studying molecular structure. This gives electrons of great velocity—*fast electrons*. The value of λ for electrons accelerated by a potential difference, *V*, can be found by substituting in de Broglie's equation (3.18) the value of the electron velocity, *v*, calculated from the ratio

$$eV = \frac{m_e v^2}{2}$$ (12.1)

where *e* and m_e are the charge and mass of the electron, respectively. Thus for *V* = 10,000 volts, λ = 0.12 Å.

A diaphragm is used to obtain a narrow beam from the stream of accelerated electrons, the usual thickness in the electron-diffraction cameras being about 0.1 mm. To study molecular structure, molecules of the test substance are introduced into the electron beam. If the given substance is a gas or volatile liquid, it is placed in a glass bulb having a delivery tube which ends in a narrow jet tip (see Fig. 12.1). A stream of the test gas is supplied for an instant (about 0.1 s) by turning a cock. If the substance has a high boiling point, a small electric heater is mounted in the instrument to vaporize it. When the beam of electrons passes through the stream of molecules from the test substance, electron-diffraction takes place, and the diffraction pattern is recorded on a photographic plate positioned a short distance (usually 10-25 cm) from the stream.

A very high vacuum must be maintained in the instrument when studying electron diffraction. Therefore, the camera is connected to a powerful vacuum pump which constantly evacuates the gas being introduced. This must be done because the electrons would be quickly decelerated by the substance. Moreover, fast electrons must be used. Slow electrons with energy of the order of 100 eV are completely retarded if they collide with only five or six molecules of a substance.

The diffraction pattern obtained on the photographic plate—the electron-diffraction photograph—consists of a central spot formed by electrons which were not deflected, and rings of varying intensities due to impingement on the plate of electrons scattered through different angles, θ, to the original direction of the beam. The change in intensity in the electron-diffraction photograph depending on angle θ is strictly definite and depends on the molecular structure of the test substance. Fig. 12.2 presents, by way of example, diffraction patterns of CCl_4 and CS_2. Deciphering the photographs makes it possible to determine the structure of a given molecule.

The electron-diffraction photograph is deciphered by using an expression which determined the intensity *I* of a beam of electrons scattered by molecules through an angle θ to the original direction

of the electron beam. It has the form[1]

$$I \sim \sum_{1}^{n} l \sum_{1}^{n} m Z_l Z_m \frac{\sin sr}{sr} .$$ (12.2)

in which

$$s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$ (12.3)

and r is the internuclear distance; $\sim$ is the proportionality sign.
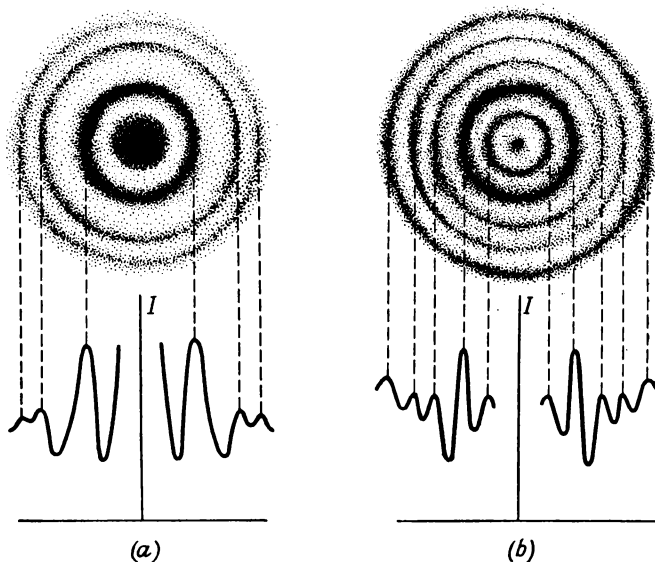
Fig. 12.2. Electron diffraction patterns
(a) CCl$_4$; (b) CS$_2$

When calculating with equation (12.2) summation of the values

$$Z_l Z_m \frac{\sin sr}{sr}$$

is performed for each of the atoms in the molecule. Z_l is understood to be the nuclear charge of the atom under consideration, and Z_m, the nuclear charge of the neighbouring atom, while r is the distance between the given atom and its neighbour. By the first neighbour of the atom under consideration is meant the atom itself; in this case $Z_l = Z_m$, $r = 0$ and $(\sin sr)/sr = 1$, from which it follows that the given member of the sum is simply Z^2.

---

[1] Derivation of the relationship (12.2) is given in Appendix V.

We shall now consider some examples of the use of expression (12.2).

For diatomic molecules consisting of like atoms, for example, Cl_2, Br_2, N_2, etc., with charge Z, expression (12.2) acquires the form

$$I \sim Z^2 + Z^2 \frac{\sin sr}{sr} \sim Z^2 \left(1 + \frac{\sin sr}{sr} \right) \tag{12.4}$$

The expression obtained has the member $(\sin sr)/sr$ which includes internuclear distance r; from (12.3) it can be seen that s has the dimen-
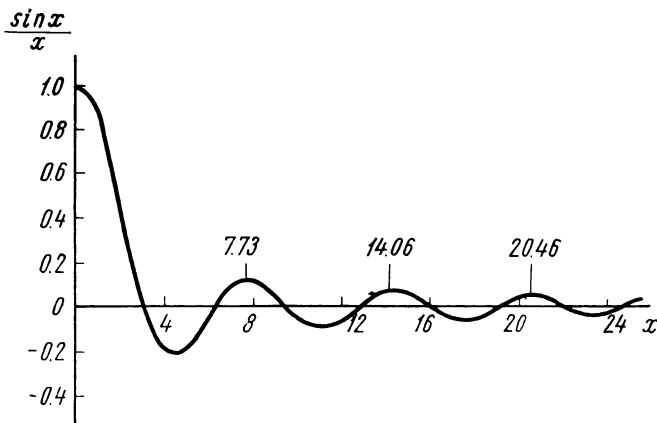
Fig. 12.3. Graph of function $y = \dfrac{\sin x}{x}$

sion cm^{-1}; therefore, sr is a dimensionless quantity. A graph of the function

$$y = \frac{\sin x}{x} \tag{12.5}$$

is shown in Fig. 12.3. This is a periodic function with maxima and minima, but these become less and less noticeable as x increases. The first four maxima are found at values of x equal to 7.73, 14.06, 20.46 and 26.66. It is evident that multiplying the function $(\sin x)/x$ by a constant quantity will change only the amplitude of the oscillations, without affecting the position of the maxima. Nor will their position be changed by adding some constant quantity to the given function, this will only raise the entire curve with respect to the x axis. Thus the intensity of electron scattering by diatomic molecules described by expression (12.4) is a periodic function of the quantity sr; this function has maxima at values of sr equal to 7.73, 14.06, 20.46, 26.66 and so on. It can be seen from Fig. 12.3 that the first maximum is the sharpest.

To decipher the electron-diffraction picture of a diatomic molecule one must find the value of angles θ for which the intensity of the stream of scattered electrons is maximum. These angles can be determined by measuring the radii of the rings in the diffraction picture, from which, knowing the distance from the molecule source to the photographic plate, it is easy to calculate the angle sought. Substituting the values of θ in ratio (12.3) makes it possible to calculate the values of s corresponding to the intensity maxima. On the other hand, as was pointed out above, the values of the product sr at which the intensity of electron scattering has a maximum are known, from which the value of the internuclear distance r can be determined.

The experimentally determined values of s for the first three maxima in the chlorine electron-diffraction picture are 3.87, 6.93 and 10.29 Å^{-1}, from which calculation of r gives the following results

$$r = \frac{7.73}{3.87} = 2.00 \text{ Å}; \quad r = \frac{14.06}{6.93} = 2.03 \text{ Å}; \quad r = \frac{20.46}{10.29} = 1.99 \text{ Å}$$

Thus the internuclear distance in the chlorine molecule can be considered equal to 2.01 $\mp$ 0.02 Å.

When determining the internuclear distance in diatomic molecules it is sufficient to calculate the value of s corresponding to the first intensity maximum in the diffraction picture, since this maximum is the most intense and affords greater precision in calculations than the following maxima.

When deciphering electron-diffraction pictures of more complicated molecules, the *trial-and-error method* is used. This consists in assigning a definite structure to the molecule being studied, and then calculating by means of expression (12.2) the dependence of the intensity of blackening in the picture on the value of s, comparing this dependence with experimental findings. If the maxima of the theoretical and experimental curves coincide, it can be considered that the molecule has the suggested structure. If the maxima do not coincide, other possible structures must be tried, until the calculated and experimental curves coincide.

As an example, we shall now consider calculation of the curves of electron-scattering intensity for carbon tetrachloride, CCl_4, and benzene, C_6H_6. Let us assume, in accordance with the teachings of organic chemistry, that the CCl_4 molecule is of tetrahedral structure (Fig. 12.4). It follows from an examination of the model shown in Fig. 12.4 that if the distance C — Cl is designated as R, the distance Cl — Cl will be $2\sqrt{2/3}\,R = 1.63\,R$. We now set up the function of electron-scattering intensity for the given model. Let us first consider the carbon atom. This atom's first neighbour is itself, which gives the member Z_C^2; its other neighbours are four chlorine atoms, each of them at a distance R. Thus in the sum there appears the component

$$4Z_C Z_{Cl} \frac{\sin sR}{sR}$$

Next let us consider the chlorine atoms. Each of the four chlorine atoms has as its neighbours itself, one carbon atom at a distance R, and three other chlori-

ne atoms at a distance of 1.63 R. This gives the following members in the sum

$$4Z_{Cl}^{2}+4Z_{C}Z_{Cl}\ \frac{\sin sR}{sR}+(4)\ 3Z_{Cl}^{2}\ \frac{\sin 1.63sR}{1.63sR}$$

Adding all the members we obtain

$$I \sim Z_{C}^{2}+4Z_{Cl}^{2}+8Z_{C}Z_{Cl}\ \frac{\sin sR}{sR}+12Z_{Cl}^{2}\ \frac{\sin 1.63sR}{1.63sR}$$

If R is taken to be 1.75 Å, an intensity curve is obtained in which all the maxima coincide with those found experimentally. Thus the electron-diffraction

Fig. 12.4. Diagram for calculating the CCl_4 electron diffraction pattern
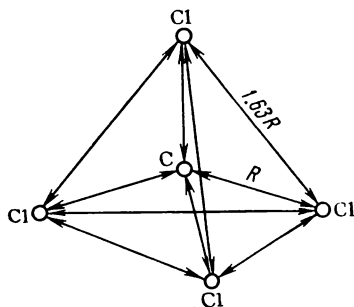
technique shows that the CCl_4 molecule is of tetrahedral configuration and that the distances, C — Cl and Cl — Cl, are 1.75 and $1.63 \times 1.75 = 2.85$ Å, respectively.

When calculating the intensity curve for benzene it must be borne in mind that it is difficult to establish the position of the hydrogen atoms in the molecu-
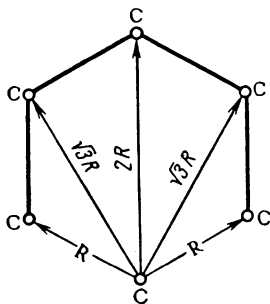
Fig. 12.5. Diagram for calculating the C_6H_6 electron diffraction pattern

le by the electron-diffraction technique. This is because the charge on the nucleus of the hydrogen atom — the proton, equal to unity, is very small compared to the charges on other atomic nuclei. For that reason the scattering of electrons by protons is negligible and has little effect on intensity curves. Therefore, when calculating the electron-diffraction pictures for benzene, it is possible, to a first approximation, to take into account only the structure of the carbon skeleton.

Let us assume that the six carbon atoms of benzene lie in a single plane, thus forming a regular hexagon with a distance R between adjacent atoms. In that

case, as can be seen from Fig. 12.5, each carbon atom has, in addition to itself, five neighbours — two at a distance R; two others at a distance $\sqrt{3}\,R = 1.74\,R$ and one at a distance $2R$. From this we find for the electron-scattering intensity, the expression

$$I \sim 6Z_C^2 + 12Z_C^2 \frac{\sin sR}{sR} + 12Z_C^2 \frac{\sin 1.74sR}{1.74sR} + 6Z_C^2 \frac{\sin 2sR}{2sR}$$

If R is taken to be 1.40 Å the position of all the maxima on the theoretical and experimental curves coincide. Thus the electron-diffraction technique confirms the assumption that the benzene molecule has a cyclic structure and makes it possible to determine the dimensions of the benzene ring. Electron-diffraction examination also shows that all the bonds in the benzene ring are of the same length — something of extremely great importance. For an explanation of this fact on the basis of the modern theory of the chemical bond see pp 192-194.
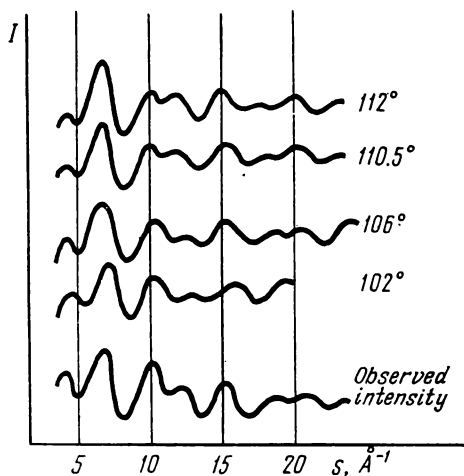
Figure 12.6 shows the observed and calculated electron-

Fig. 12.6. Observed and calculated electron-scattering intensity curves for CHF_3

scattering intensity curves for CHF_3. Calculations were made for different values of the angle between the F — C — F bonds. From a comparison of the curves the conclusion can be drawn that the value of the given angle in the CHF_3 molecule lies between 106 and 110.5°.

The disadvantage of the trial-and-error method is the necessity of assigning some configuration to a molecule beforehand. In the case of complicated molecules where many structures seem possible it is difficult to single out a model corresponding to the actual configuration of the molecule. There are other methods of deciphering electron-diffraction pictures which are free from this uncertainty but discussion of the same is beyond the scope of this book. It should be noted, however, that a great amount of information of fundamental importance for the science of chemistry has been obtained through the deciphering of electron-diffraction pictures by the trial-and-error method.

Table 12.1 gives some results of electron-diffraction investigations into molecular structure.

The electron-diffraction technique is not always applicable for establishing the structure of molecules. As already noted it is difficult to determine the position of hydrogen atoms by this method. Great difficulties are also encountered when employing the electron-diffraction technique in the case of complicated molecules containing many different groups of atoms.

Table 12.1

Results of Electron-Diffraction Determination of Molecular Structure

Molecule	Interatomic distance, Å		Configuration of molecule
Br_2	Br — Br	2.28	Dumbbell
Cl_2	Cl — Cl	2.01	Same
CO_2	C — O	1.13	Linear
CS_2	C — S	1.54	Same
SO_2	S — O	1.43	Bent; angle O — S — O equal to 120±5°
CCl_4	C — Cl	1.75	Tetrahedron
PCl_3	P — Cl	2.00	Pyramid; angle Cl — P — Cl equal to 101±2°
C_6H_6	C — C	1.40	Flat ring
C_6H_{12}	C — C	1.52	Ring with zigzag arrangement of atoms
C_2H_6	C — C	1.55	
C_2H_4	C = C	1.34	
C_2H_2	C ≡ C	1.22	
BF_3	B — F	1.30	Flat; angle F — B — F equal to 120°
SiF_4	Si — F	1.54	Tetrahedron
$N(CH_3)_3$	N — C	1.47	Pyramid; angle C — N — C equal to 108°
P_4	P — P	2.21	Tetrahedron
$(HF)_n$	F — F	2.25	Zigzag chain
cis-$C_2H_2Cl_2$	Cl — Cl	3.22	
trans-$C_2H_2Cl_2$	Cl — Cl	4.27	

12.2. Molecular Spectra

When discussing atomic spectra (see p. 57) it was shown that spectral lines originate as the result of the transition of electrons in the atom from one energy level to another. The existence of discrete energy levels in the atom is due to the quantum-mechanical character of electron motion. When it comes to molecules there is possible, in addition to the movement of electrons, displacement of the nuclei in respect to one another—the *oscillation* and *rotation* of atoms round the centre of mass may appear. These motions are also quantized, but because of the substantially greater mass of the particles, the energy levels here are very close to one another, the least distinct being the levels of molecular rotation.

It is usually the *absorption spectra* of molecules that are studied. This is done by passing light through the test substance and finding

by means of a spectrograph the wavelengths of the radiations absorbed. When a molecule absorbs a quantum of radiation it passes from one energy state to another. The only quanta absorbed are those whose energy is equal to the energy of these transitions—thus the absorption spectrum like the emission spectrum makes it possible to judge of the energy levels in the molecule.

In accordance with the foregoing principles, there are three types of molecular spectra—*spectra of electron transitions, vibrational spectra* and *rotational spectra*. Fig. II.2 (Appendix II) shows the energies and radiation wavelengths corresponding to different changes in the state of the molecule.

The lowest energies are those of rotational transitions; they correspond to radiation in the *far infrared region*. Rotational spectra can be observed unhampered without the superimposition of changes in other forms of motion—vibrational and electron transitions.

The energy of vibrational transitions is approximately ten times that of rotational transitions, and the corresponding radiation lies in the *near infrared region*. Changes in vibrational motion of the molecule are always accompanied by changes in rotation, and for that reason the vibrational spectrum, unlike the rotational spectrum, cannot be observed in the 'pure form'—these spectra are always superimposed on one another, thus forming a *vibrational-rotational spectrum*.

Transitions of electrons in molecules, as in atoms, correspond to energies of several electron-volts; in this case the radiation is in the *visible* or *ultraviolet* region. Transitions of electrons are accompanied by changes in vibrational and rotational motion; this is reflected in the spectrum, which in this case shows the aggregate of all forms of energy changes in the molecules.

Study of molecular spectra provides much valuable inrormation about molecules, including their structure.

Examination of rotational spectra makes it possible to determine molecular *moments of inertia* (the physical meaning of the concept 'moment of inertia' is taken up in Appendix VI), knowing which, definite conclusions can be drawn about the structure of the molecules concerned.

We shall now set up an equation describing the frequency of the lines of the rotational spectrum of a diatomic molecule consisting of atoms A and B. To do this we express the energy of rotational motion through the molecule's angular momentum M and moment of inertia I (see Appendix VI).

$$E_{rot} = \frac{M^2}{2I} \tag{12.6}$$

To find an expression defining the angular momentum M it is necessary to solve the Schrödinger equation for a particle rotating uni-

formly at a constant distance from a centre; such a system is termed a *rigid rotator*. The solution cannot be gone through here but it shows that the angular momentum of a rigid rotator is defined by the relationship

$$M = \hbar \sqrt{J(J+1)} \tag{12.7}$$

where J is the quantum number, which can have the values 0, 1, 2, . . . As can be seen we have a familiar expression—such a formula defines the angular momentum of the electron in the atom [see equation (4.18)]. Substituting (12.7) in (12.6) we have

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1) \tag{12.8}$$

Equation (12.8) determines the energy levels of the rotating molecule.

We now find the energy difference ΔE_{rot} for two levels in which J differs by one. Let the quantum number for one level be J, and for the other $J + 1$. Then

$$\Delta E_{rot} = \frac{\hbar^2}{2I} [(J+1)(J+2) - J(J+1)] = \frac{\hbar^2}{I}(J+1) \tag{12.9}$$

The wave number of a spectral line corresponding to the transition of a molecule from one rotational state to another is determined by the relationship

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\Delta E_{rot}}{hc}$$

from which, taking into account (12.9), we obtain

$$\bar{\nu} = \frac{h}{4\pi^2 I c}(J+1) \tag{12.10}$$

Employing equation (12.10), the moment of inertia is found from the wavelengths of the lines of the rotational spectrum, from the moment of inertia the distance between the nuclei of atoms A and B can be determined (see Appendix VI). Relationships making it possible to determine interatomic distances can also be drawn up for molecules consisting of more than two atoms.

When atoms in a molecule are displaced relative to the equilibrium position, a restoring force f is set up. The assumption that it is proportional to the displacement Δr, that is,

$$f = k\Delta r \tag{12.11}$$

corresponds to the condition of harmonic vibration. The proportionality coefficient k is called the *force constant*. This quantity is determined on the basis of an analysis of the vibrational spectrum from the equation

$$\Delta E_{vib} = \hbar \sqrt{\frac{k}{m^*}} \tag{12.12}$$

expressing the difference of two energy levels for a harmonic vibrator; m^* is the reduced mass (see Appendix VI). The value of k depends on the nature of the atoms and on the multiplicity of the bond. Thus whereas $k_{Cl_2} = 3.21 \times 10^5$ and $k_{HCl} = 4.74 \times 10^5$ (single bond), $k_{O_2} = 11.3 \times 10^5$ (double bond) and $k_{N_2} = 22.2 \times 10^5$ (triple bond) dynes/cm. In the series of analogues HF — — HCl — HBr — HI it diminishes from 8.65×10^5 (HF) to 2.89×10^5 (HI) dynes/cm.

For large values of Δr, vibrations become nonharmonic; as the interatomic distance increases the restoring force progressively diminishes and equation (12.11) no longer holds true.

It is obvious that if the energy of radiation acting on a molecule is increased, it will finally be possible to bring about its disintegration—its *dissociation*. Further increase in the energy will only increase the translational velocity of the atoms formed through molecular dissociation, and this is not quantized. Therefore, at a definite wavelength the spectrum will become continuous. Just as it is possible to calculate the energy of the detachment of the electron from the atom—the energy of ionization (see p. 60)—from the short-wavelength limit of the atomic spectrum, the short-wavelength

Table 12.2

Results of Spectral Study of Di- and Triatomic Molecules for Substances in the Gaseous State

Molecule	r, Å	E_{bnd}, eV
H_2	0.74116	4.4763
Li_2	2.6725	1.03
Na_2	3.0786	0.73
Cl_2	1.988	2.475
HF	0.9175	5.8
HCl	1.2744	4.430
KCl	2.6666	4.97
CsI	3.315	3.37

Molecule	Interatomic distance, Å		Valence angle, deg
(1) (3) (2)	r_{1-3}	r_{2-3}	
$O = C = O$	1.160	1.160	180
$H - O - H$	0.958	0.958	104.5
$O = S = O$	1.432	1.432	122
O_3	1.278	1.278	117
$O = C = S$	1.160	1.560	180
$H - C \equiv N$	1.059	1.157	180

limit of the electron spectrum of the molecule gives the energy of dissociation of the molecule, from which it is possible to find the energy of the bond.

Table 12.2 gives data on the structure of molecules and the energy of bonds obtained through the study of spectra. A comparison with the data in Table 12.1 shows that for Cl_2, CO_2 and SO_2 the results of electron-diffraction and spectral determination of molecular structure agree well.

Besides the electron-diffraction and spectral methods, the *X-ray diffraction analysis of crystals* is of great importance in determining molecular structure (see pp 273-277).

It should be noted that the configuration of the molecule in a crystal may differ markedly from the configuration of the isolated molecule.

CHAPTER THIRTEEN

BASIC TYPES OF THE CHEMICAL BOND—IONIC AND COVALENT BOND

13.1. Electronegativity of the Elements

Let us assume that atoms A and B interact, producing a chemical bond by the transfer of an electron from one atom to another. The question then is which of these atoms draws an electron onto its shell. Let us assume that an electron is transferred from A to B. This involves the liberation of energy $(E_B - I_A)$, where E_B is the electron affinity of B, and I_A the ionization energy of A. In the reverse process, the energy $(E_A - I_B)$ would be liberated. The direction of the process is determined by the maximum liberation of energy, since this stabilizes the system. Let us assume that the actual electron transfer is from atom A to atom B. This means that

$$(E_B - I_A) > (E_A - I_B)$$

or

$$(I_B + E_B) > (I_A + E_A)$$

The quantity $1/2\ (I + E)$ is termed *electronegativity*. Let it be designed x. Then

$$x = \frac{1}{2}\ (I + E) \tag{13.1}$$

Thus the electron is transferred to the atom of the element which has greater electronegativity. *Electronegativity characterizes an atom's power to add electrons, thus forming a chemical bond*. The method cited for calculating electronegativity was proposed by Mulliken (USA). The disadvantage of this method is that the electron affinity is known for only a few atoms.

Figure 13.1 shows the electronegativity values of various elements according to Pauling, who has recommended another method for their determination (see p. 232). In Pauling's system the electronegativity of fluorine is arbitrarily taken as 4. The somewhat unusual form of the diagram was dictated by the desire to give the graph the appearance of the periodic system. As might be expected the
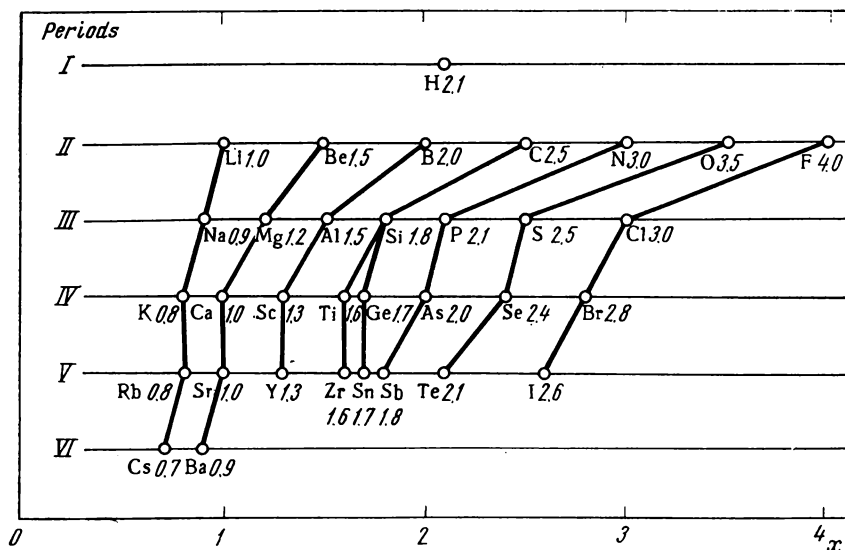
Fig. 13.1. Electronegativity of the elements (according to Pauling)

value of x is greatest for fluorine and least for caesium. Hydrogen occupies an intermediate position—when it reacts with some elements, for example, with F, it gives up an electron; when it reacts with other elements, such as Rb, it acquires an electron.

Some 20 electronegativity scales have been proposed, different properties being taken as a basis (internuclear distances, bond energies, etc.). They give dissimilar values for x, but it is the differences between these values that are of great importance. The relative values of x are close. The qualitative coincidence of results in the different scales indicates coincidence in the arrangement of elements in the electronegativity series.

What is more important is to bear in mind that, when using electronegativity as a quantity characterizing an atom's power to attract ·valence electrons, it is impossible, strictly speaking, to ascribe a constant electronegativity to an element. This depends on the composition of the compound which contains the atom being studied, on the elements whose atoms surround the atom under

consideration. Thus the free chlorine atom and that in the molecules Cl_2, NaCl, CCl_4 and $PdCl_2$ have different properties. It follows that what must be borne in mind, strictly speaking, is not the electronegativity of an element in general but its electronegativity when forming specific chemical bonds in specific surroundings and in a specific valent state. But in spite of this, the conception of electronegativity is useful in explaining many properties of chemical bonds.

13.2. Ionic and Covalent Bond

If atoms A and B have greatly differing electronegativity, the transition of an electron during their interaction converts them onto oppositely charged ions

$$A = A^+ + e + I_A \qquad (13.2)$$

$$B + e = \quad^- - E_B \qquad (13.3)$$

where I_A and E_B are the ionization energy of atom A and the electron affinity of atom B, respectively. The electrostatic attraction set up between A and B causes the formation of a molecule

$$A^+ + B^- = A^+B^- + E \qquad (13.4)$$

where E is the energy change. As a result the ions in the molecule must be at such a distance that the attraction balances the repulsion of the like-charged electron shells of the ions and nuclei. It is in this way that the *ionic bond* is formed (called also the *heteropolar* or *electrovalent* bond). Consequently the ionic bond corresponds to the equation

$$A + B = A^+B^- + I_A - E_B + E \qquad (13.5)$$

obtained by summing (13.2), (13.3) and (13.4).

When atoms of the main subgroups of the periodic system are converted into ions their electron shells are converted into the stable electron shells of the corresponding noble gases. Thus when KF is formed, the K^+ ion acquires the electronic configuration of argon, and the F^- ion, that of Ne. These views were developed by Kossel in 1916. As we shall see in Chapter Fifteen (p. 233), complete transition of the electrons from one atom to another never takes place—there is never a 100% ionic bond.

Chemical interaction is not limited to the formation of an ionic bond. If, for example, it is assumed that in ClF, as in CsF, the valence electron is drawn to the fluorine atom, calculation gives a negative value for the Cl—F bond-dissociation energy. This would mean that the ClF molecule cannot exist—something that is contrary to fact. Although chlorine fluoride is very reactive, it is stable, the experimental value of the bond energy being 2.6 eV. The obvious conclusion is that the bond in this molecule is not ionic.

Let us now consider a molecule consisting of atoms which have the same electronegativity. H_2 can be taken as an example. In this case the two atoms are equal in their power to attract an electron. In 1916-1918 Lewis and Langmuir (USA) suggested that the chemical bond is formed by a pair of electrons held jointly by two atoms. Such a bond is termed *covalent* or *homeopolar*. If the valence line is replaced by two dots representing the Lewis and Langmuir electron pair, one can write H : H in place of H—H. Using this symbolism for the outer layer (the valence electrons) of atoms, the structure of the chlorine and nitrogen molecules can be represented as follows

$$:\overset{..}{\underset{..}{Cl}} : \overset{..}{\underset{..}{Cl}}: \qquad :N:::N:$$

Extending this system to molecules consisting of atoms of different elements we obtain

$$\begin{matrix} H & & H & & H & H \\ H :\overset{..}{C}: H & & H :\overset{..}{C}: \overset{..}{\underset{..}{Cl}}: & & \overset{..}{C}: : \overset{..}{C} \\ \overset{..}{H} & & \overset{..}{H} & & \overset{..}{H} & \overset{..}{H} \end{matrix}$$
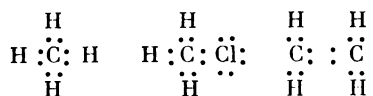
Obviously the number of such examples can easily be increased, taking into consideration the enormous number of organic compounds in which the covalent bond is typical. Here, as in the case of the ionic bond, there is a tendency to form electron octets (or dublets).

Attention must be called to the fact that if molecules consisting of like atoms are left out of consideration (and they are comparatively few in number), all the other covalent molecules are characterized by a greater or less displacement of the electron pair to one of the atoms, since they are composed of atoms which differ in their electronegativity. Such a bond is *polar covalent*. CF_4 and CH_3Cl are examples of molecules with a polar bond. It is more convenient to represent a polar covalent bond by an arrow rather than by a shift of the relevant pair of dots: Cl → F. The polarity of the O ← H bond explains many properties of water, among them the electrolytic dissociation of substances dissolved in it.

In the light of what has been said, the ionic bond can be considered the limiting case of the polar bond, where the electron pair (or electron pairs) is practically completely displaced, i.e., becomes a constituent part of the electron shell of one of the atoms.

The number of covalent molecules A_2 is limited by the number of elements in the periodic system, but there are few symmetrical molecules A_n, where $n > 2$; there are practically no molecules with a purely ionic bond (see p. 233). Therefore, the chemical bond in the majority of known compounds (now more than three million) is polar covalent.

13.3. The Dipole Moment and Molecular Structure

Let us assume that we have found the 'centres of gravity of the negative and positive parts of a molecule. We must then discover that all compounds can be divided into two groups. One group would consist of compounds in whose molecules the two centres of gravity coincide. These are called *non-polar* molecules. They include all covalent diatomic molecules of the A_2 type, as well as tri- and polyatomic molecules of high symmetry, such as CO_2, CS_2, CCl_4, C_6H_6 and the like (see p. 145). The other group would include all compounds whose molecules are electrically asymmetric, i.e., molecules in which the centres of gravity of the charges do not coincide. Such molecules are said to be *polar*. They include compounds with an ionic type of bond, such as CsF, and any AB compounds since their atoms have unlike electronegativity, as well as $A_n B_m$ compounds whose structure is asymmetric.

A molecule's polarity is characterized by the *dipole moment*

$$\mu = el \qquad (13.6)$$

where e is the charge of the electron and l is the distance between the centres of gravity of the positive and negative charges. The greater the polarity and the greater the displacement of the electron pairs to one of the atoms, the greater the value of μ. On the contrary, if the electrical asymmetry of a molecule is slight, the value of μ is small.

Dipole moments are determined experimentally by measuring the *dielectric constant* at different temperatures.

If a substance is placed in an external electric field produced by a capacitor, the capacitance of the latter will be increased ε times, that is

$$\varepsilon = \frac{c}{c_0} \qquad (13.7)$$

where c_0 and c are the capacitance in a vacuum and with the substance, respectively, and ε, the dielectric constant.

The increase in capacitance as a result of the reduction of the strength of the electric field is caused not only by the presence of the constant dipole moment μ which is characteristic of the molecules of the given compound, but also by their deformation by the field. In other words the electric field not only causes orientation of the molecules of the polar compound in the direction of the field but produces an *induced dipole moment* μ_{ind} through displacement of the electrons and, to some extent, the nuclei.

If fields are not very strong the induced dipole moment can be considered proportional to the field strength E

$$\mu_{ind} = \alpha E \qquad (13.8)$$

Proportionality factor α is called the *polarizability* (or *deformation polarizability*); the more the molecule is subject to deformation (i.e., the weaker its electron shells), the greater the polarizability. The induced dipole moment disappears as soon as the field is removed—in accordance with (13.8), when E is zero, μ_{ind} is also zero.

It can be shown that for gases and for polar substances dissolved in non-polar solvents, there is a relationship between ε and μ, expressed by the equation

$$\frac{\varepsilon-1}{\varepsilon+2}\frac{M}{\rho}=\frac{4}{3}\pi N_0\left(\alpha+\frac{N_0\mu^2}{3RT}\right) \tag{13.9}$$

where M is the molecular weight of the compound; ρ is the density; N_0 is Avogadro's number; R is the universal gas constant and T is the absolute temperature. The first component in parentheses corresponds to the deformation effect; the second, to the orientation effect. Obviously the latter should be the greater, the more polar the molecule, i.e., the greater μ and the lower the temperature, since heating increases the thermal motion of the molecules, thereby impeding their orientation[1]. In accordance with equation (13.9), the orientation effect is predominant at low temperatures, and the deformation effect, at high temperatures.

We now substitute symbols for the members of (13.9)

$$\frac{\varepsilon-1}{\varepsilon+2}\frac{M}{\rho}=y \tag{13.10}$$

$$\frac{4\pi N_0\alpha}{3}=A \tag{13.11}$$

$$\frac{4\pi N_0^2\mu^2}{9R}=B \tag{13.12}$$

$$\frac{1}{T}=x \tag{13.13}$$

Then equation (13.9) can be written as

$$y = A + Bx \tag{13.14}$$

Therefore, if the reciprocals of the absolute temperatures are laid off as abscissae, and the values of $\dfrac{\varepsilon-1}{\varepsilon+2}\dfrac{M}{\rho}$ are used as ordinates, a straight line is produced, and the dipole moment can easily be found from its slope (B). Actually, in accordance with equations (13.12) and (13.14)

$$\mu=\sqrt{\frac{9RB}{4\pi N_0^2}}=0.01282\cdot10^{-13}\sqrt{B} \tag{13.15}$$

---

[1] α and therefore μ_{ind} do not depend on the temperature since the difference between the normal and excited levels of the electrons in the molecules is very great, i.e., much energy is required for altering the structure of the electron shell, which corresponds to a very high temperature.

In order to construct this straight line, the capacitance of a capacitor with the test compound must be measured at least at two temperatures, and the density of the compound at these temperatures must be known.

$$y = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho}, cm^3$$
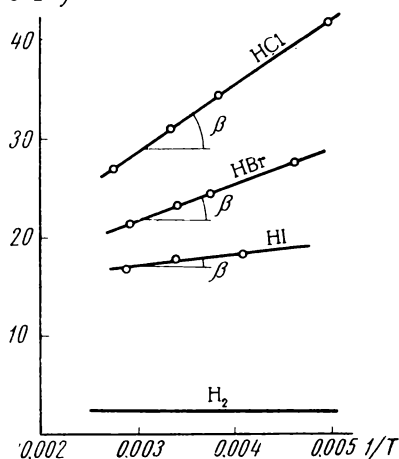
Fig. 13.2. Graph for determining the dipole moment ($\mu = 0.01282 \times 10^{-18} \sqrt{\tan\beta}$)
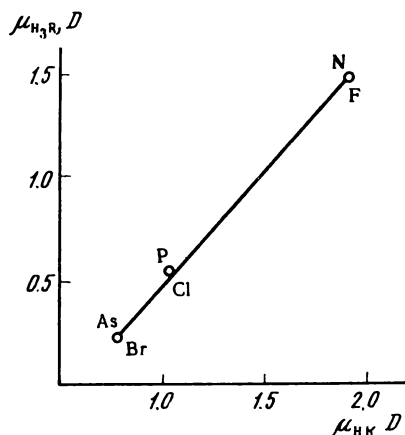
Fig. 13.3. Comparison of dipole moments of hydrogen compounds of elements of Groups VII and V of the periodic system
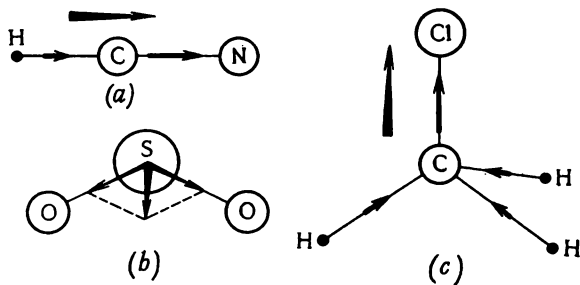
Fig. 13.4. Addition of dipole moments of molecular bonds
(a) HCN; (b) SO₂; (c) CH₃Cl

The method of calculation is illustrated in Fig. 13.2 ($B = \tan\beta$). It can be seen from the graph that $\mu_{HCl} > \mu_{HBr} > \mu_{HI}$ and that $\mu_{H_2} = 0$. By using equation (13.9) it is also easy to determine α from Fig. 13.2.

Let us consider the scale of μ. Since $e = 4.802 \cdot 10^{-10}$ and l is comparable with the size of molecules (10^{-8} cm), μ is a quantity of the order 10^{-18}. This unit of dipole moments has been named the debye (D) after Peter Debye, the Dutch physicist.

We begin as before with the way in which this property changes in a group of similar compounds. For HCl, HBr and HI the dipole moments are 1.04, 0.79 and 0.38 D, respectively. The fall in the value of μ in this series is explained by the diminution of the polarity of the bond due to diminution of the difference in electronegativity.

The parallelism in the distribution of μ values in two similar series is illustrated in Fig. 13.3.

When considering the dipole moments of complex molecules it is advisable to assign a definite value of μ to each bond, taking into account not only the quantity but also the sign, depending on the direction of displacement of the electrons, i.e., considering the dipole moment of a bond as a vector. The contribution of unshared electron pairs to the dipole moment must be taken into account (see p. 199).

The dipole moment of a polyatomic molecule can be considered equal to the vector sum of the dipole moments of all the bonds, neglecting their mutual effect. The vector addition of the dipole moments of bonds is shown in Fig. 13.4, it being understood that in all cases the vector is directed from $+$ to $-$.

From what has been said it follows that determination of the dipole moment can reveal the character of the chemical bond (ionic, polar or covalent) and indicates the geometrical structure of the molecule. Thus in order to determine the structure of a compound, μ is calculated for different models according to the rule for adding vectors, and the model for which the calculated value is closest to that found by experiment is taken to be the correct one.

We shall consider some simple examples. Of two possible structures of ammonia (a and b, Fig. 13.5), we choose b, since measurements show that the molecule is polar (see also p. 199). Say we have synthesized dichlorobenzene, $C_6H_4Cl_2$. Which of the three isomers have we obtained?

ortho-   para-   meta-
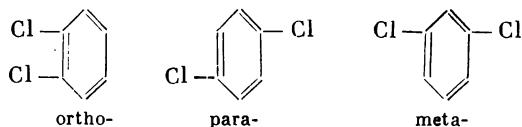
Let us assume that the dipole moment of the compound obtained is found to be equal to the dipole moment of chlorobenzene, C_6H_5Cl. Then by constructing the parallelograms of the dipole moments of the bonds (Fig. 13.6), we see that it was the *meta*-isomer that was

synthesized, since for *para*-dichlorobenzene $\mu = 0$, and for *ortho*-dichlorobenzene $\mu = \mu_{C-Cl} \sqrt{3}$[1].

By means of the dipole moment it is also possible to distinguish *cis* and *trans* isomers. Thus in *trans*-dichloroethylene, unlike *cis*-dichloroethylene, the dipole moment is equal to zero.
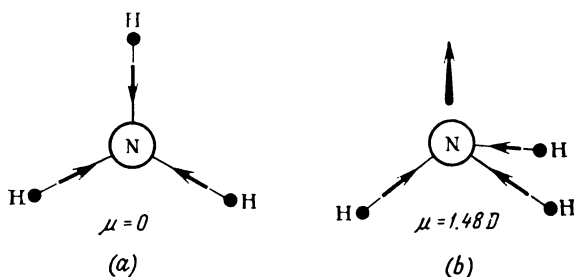
Fig. 13.5. Dipole moments of two conceivable structural variants of the NH_3 molecule (a) planar; (b) pyramidal
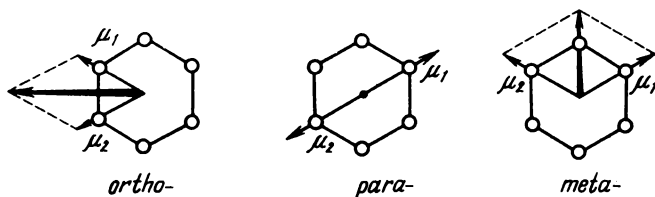
Fig. 13.6. Dipole moments of dichlorobenzene isomers (arrows are scaled to the value of μ_{C-Cl})

If there are polyatomic substituents in a molecule, their nature must be taken into account. As an example take the case of nitrobenzene and toluene
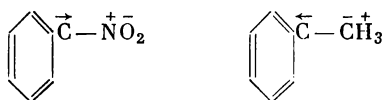
The NO_2 and CH_3 groups make contributions to the molecular dipole moment differing not only in magnitude but also in sign.

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[1] When measuring μ for *ortho*-dichlorobenzene, we would find that the experimental value was lower than that calculated as the repulsion of the closely situated negatively charged chlorine atoms would make itself felt.

13.4. Effective Charges

When an atom forms a chemical bond, its electron density changes. This change can be assessed by assigning to the atom a certain *effective charge* δ in units of the electron charge. Effective charges express the asymmetry of the electron cloud and are conventional in character, since the electron cloud is delocalized and cannot be divided between the nuclei.

For atoms forming a covalent molecule, $\delta = 0$, while in the ionic molecule the effective charge of the atoms is equal to the charge of the ion. For all other (polar) molecules it has intermediate values.

Under the influence of an external field δ increases up to a value corresponding to the ionic bond. This increase is the greater, the greater the polarizability, which in turn increases with the electronegativity.

The value of δ is determined from optical absorption spectra, X-ray spectra, nuclear resonance, etc.

The effective charge can be considered a measure of the polarity of the covalent bond. Thus the calculation for HCl on the basis of X-ray absorption spectra gave the following values

$$H^{+0.2}Cl^{-0.2}$$
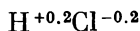
This result can be interpreted thus: in the HCl molecule the zone of maximum overlapping of the bonding electron clouds is shifted toward the more electronegative chlorine atom, which results in the hydrogen atom being polarized positively ($\delta_H = 0.2$) and the chlorine atom being polarized negatively ($\delta_{Cl} = -0.2$). It can also be said that the bond in the HCl molecule is approximately 20% ionic, and is thus close to covalent. On the other hand, the NaCl molecule, for which the values $Na^{+0.8}Cl^{-0.8}$ are found, is a compound in which the chemical bond is close to ionic. This is borne out by the following figures: $\mu_{HCl} = 1.0D$; $\mu_{NaCl} = 10D$.

The values of δ for analogous atoms in compounds of the same type change regularly. In the HHal series we find: $\delta_F = 0.45$; $\delta_{Cl} = 0.2$; $\delta_{Br} = 0.12$; $\delta_I = 0.05$. Evidently in such series of molecules there is a quantitative parallelism between the values of δ and the values of μ (α).

Table 13.1 gives the values of the effective charges of the atoms of compounds as found from X-ray absorption spectra. Although these values of δ are approximate they provide a basis for definite conclusions: it is noteworthy that there is no compound in which the effective charge of an atom is greater than 2; in compounds of the same atom, its effective charge falls as the degree of oxidation increases ($Cr^{+2}Cl_2$—$Cr^{+3}Cl_3$—$K_2Cr^{+6}O_4$), i.e., the greater the formal valence, the greater the proportion of the covalent bond, which is due to diminution of the polarity of the bonds as their number increases.

Table 13.1

Effective Charges of the Atoms in Compounds

Compound	Atom	δ	Compound	Atom	δ
HCl	Cl	−0.2	GeBr$_4$	Ge	+1.1
SO$_2$Cl$_2$	Cl	−0.1		Br	−0.3
C$_2$H$_4$Cl$_2$	Cl	0	ZnBr$_2$	Zn	+0.5
KClO$_3$	Cl	+0.7		Br	−0.25
LiClO$_4$	Cl	+0.8	IBr	Br	−0.1
H$_2$S	S	−0.2	GeH$_4$	Ge	+0.2
SO$_2$	S	−0.1	GeO$_2$	Ge	+1.0
SCl$_2$	S	+0.2	K$_2$Cr$_2$O$_7$	Cr	+0.1
CaSO$_4$	S	+0.4	K$_2$CrO$_4$	Cr	+0.2
KMnO$_4$	Mn	+0.3	CrCl$_3$	Cr	+1.3
CaTiO$_3$	Ca	+1.5	CrCl$_2$	Cr	+1.9

CHAPTER FOURTEEN

QUANTUM-MECHANICAL EXPLANATION OF THE COVALENT BOND

It was only after the laws governing the motion of microparticles became known and quantum mechanics was formulated that it was possible to establish the physical causes of a bond between atoms. In 1927, a year after the publication of Schrödinger's article in which he proposed the equation which now bears his name, the work of Heitler and London (Germany) appeared which contained the quantum-mechanical calculation of the hydrogen molecule. This marked the beginning of the use of quantum mechanics for the solution of chemical problems.

It should be noted that the exact solution of Schrödinger's equation for concrete problems encountered in atomic and molecular theory involves extremely great mathematical difficulties which it has been possible to overcome in only a few cases[1].

Up to now the exact solution has only been found for single-electron systems—the hydrogen atom and hydrogen-like ions, as well

[1] Here and below, what is meant by the exact solution of Schrödinger's equation is the exact mathematical solution, i.e., finding analytical expressions for ψ and E, which when substituted in Schrödinger's equation for the problem considered will give identity. An approximate solution is not necessarily less exact in the practical sense. For example, as we shall see below, the energy of the bond in the hydrogen molecule can be calculated by approximate methods with as great precision as that achieved experimentally.

as the ionized hydrogen molecule, II_2^+. For other atoms and molecules only *approximate solutions* of Schrödinger's equation are possible at present. These solutions are of great importance for chemistry since they explain the nature and properties of chemical bonds. For that reason it would be advantageous to take up some of the mathematical techniques employed for obtaining approximate solutions of Schrödinger's equation before considering the quantum-mechanical interpretation of the chemical bond.

14.1. Solution of the Schrödinger Equation Using Approximate Functions

The Schrödinger equation for a simple imaginary model—the movement of a particle in a potential well—as well as its solution have been considered in Chapter Three (see pp 35-45). In the potential well problem it was possible to find a function ψ and an expression for energy E which satisfied the Schrödinger equation for the given case. The solution was not difficult because the potential energy of the particle U could be considered equal to zero. The problem then consisted in finding a function whose second derivative was expressed by the same function with the opposite sign. This condition is satisfied by the function of the sine.

As we shall see below when considering the hydrogen molecule, the potential energy of the electrons is defined by a six-membered expression. For other molecules the potential energy of the electrons is described by still more complicated relationships. In such cases it proves impossible to find a function ψ which would satisfy the Schrödinger equation, and consequently a function ψ and a value of E are sought, which are close to the unknown ψ and E that would be a solution of the equation.

For the motion of a single particle the Schrödinger equation has the form

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+U\,(x,\ y,\ z)\,\psi=E\psi \qquad (14.1)$$

This can be written in a more compact form which is convenient for finding approximate solutions. We introduce symbols making it possible to give the equation such a form that for a certain function of the potential energy $U\,(x,\ y,\ z)$ the value of E can be found by means of a function which can be considered a sufficiently close approximation to the unknown function ψ which would be a solution of the Schrödinger equation.

We use the symbol

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \qquad (14.2)$$

The symbol ∇^2 (nabla square) is called the *Laplacian operator*[1]. It is an abbreviated conventional expression for denoting the summation of the second derivatives of a function with respect to coordinates. When this symbol is introduced the Schrödinger equation becomes

$$- \frac{h^2}{8\pi^2 m}\, \nabla^2 \psi + U\psi = E\psi \qquad (14.3)$$

it being understood that U is a function of the coordinates x, y and z.

For still greater simplification we introduce the *Hamiltonian operator*

$$\boldsymbol{H} = - \frac{h^2}{8\pi^2 m}\, \nabla^2 + U \qquad (14.4)$$

When the Hamiltonian is introduced, the Schrödinger equation assumes a very simple form

$$\boldsymbol{H}\psi = E\psi \qquad (14.5)$$

It should be emphasized that in (14.5) it is only the notation that has been changed. Equations (14.5) and (14.1) are the same.

We now multiply both sides of (14.5) by function ψ. We then obtain

$$\psi\boldsymbol{H}\psi = \psi E\psi \qquad (14.6)$$

or

$$\psi\boldsymbol{H}\psi = E\psi^2 \qquad (14.7)$$

from which

$$E = \frac{\psi\boldsymbol{H}\psi}{\psi^2} \qquad (14.8)$$

If an expression were known for function ψ, which is a solution of the Schrödinger equation, equation (14.8) would give a value of E for any point in space if the values of $\psi\boldsymbol{H}\psi$ and ψ^2 were substituted[2].

Obviously if an approximate function ψ is used, substituting the values of this function will give approximate values of E. Since the function is approximate, employing some of its values can give a value of E greatly differing from the true value. Uncertainty in the choice of values of $\psi\boldsymbol{H}\psi$ and ψ^2 can be obviated if these functions are integrated over all space (from the value $-\infty$ to $+\infty$ for each coordinate). The equation for calculating the energy will then take

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[1] *An operator is a symbol of mathematical operations which transforms one function into another.* For example, in the expression tan α, $\log_{10} \alpha$ and dy/dx, [tan], [$\log_{10}$] and [d/dx] are operators.

[2] The expression $\psi\boldsymbol{H}\psi$ cannot be replaced by $\psi^2\boldsymbol{H}$ or $\boldsymbol{H}\psi^2$, or $\nabla^2\psi$ by $\psi\nabla^2$, just as it is impossible to replace

$$y\, dy/dx \text{ by } dy^2/dx$$

the form

$$E = \frac{\int \psi H \psi \, dv}{\int \psi^2 \, dv} \qquad (14.9)$$

where dv is the volume element. If the function ψ is normalized (for the operation of normalization see p. 43), the integral in the denominator is equal to unity and equation (14.9) takes the form

$$E = \int \psi H \psi \, dv \qquad (14.10)$$

Equations (14.9) and (14.10) can likewise be employed for calculating the energy in systems containing several electrons. In that case the Hamiltonian is written in the following form:

$$H = -\frac{h^2}{8\pi^2 m_e} \sum \nabla_i^2 + U \qquad (14.11)$$

where ∇_i^2 is the Laplacian operator containing the coordinates of electron i, summation being carried out to cover all the electrons.

Using equation (14.9), the energy of a system (atom or molecule), its basic characteristic, can be calculated approximately, providing that a function ψ is found which is sufficiently close to the system's correct wave function. The choice of the best form of the approximate function is made by the *variational method*.

The variational method is based on the fact that *the smaller the value of E obtained through equation* (14.9) *or* (14.10), *using the selected function ψ, the closer it is to the value of the energy of the system in the ground state, and the closer the selected wave function is to the correct function*. This can be rigorously proved. Without going into this proof, the principle of the variational method can be explained by the following reasoning. As we know, the wave function describes the distribution of the density of the electron cloud. The ground state of the molecule, the state of the lowest energy, corresponds to a certain distribution of the electron density, which is expressed by the correct wave function which is unknown. The approximate wave function corresponds to some other distribution of the electron density for which the energy will be greater. The closer the selected function is to the correct function, the lower the energy calculated with this function will be, and the closer it will be to the actual value of E for the ground state of the system.

The solution of quantum-mechanical problems in molecular theory comes down to testing various functions with equation (14.9), coordinating these functions with the physical pattern of electron motion in the molecule. The function which gives the minimum value of E can be considered the best for describing the state of the system.

When using the variational methods, the approximate function ψ is usually taken as the sum of the products of independent functions

φ_1, φ_2, φ_3, . . . and the coefficients c_1, c_2, c_3, . . ., that is

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + \ldots + c_n\varphi_n \qquad (14.12)$$

Functions φ_1, φ_2, . . . must meet the same requirements as the wave functions; they must be finite, continuous and single-valued, and must become zero at an infinitely great distance from the molecule (see p. 36). It goes without saying that the functions must correspond to the problem being considered, namely they must depend on the charge of the nucleus and the coordinates. It is desirable that they should take into account all the features of the system as precisely as possible, in particular the mutual repulsion of the electrons.

Obviously, when function (14.12) is substituted in equation (14.9) the value of E depends on the values of the coefficients c_1, c_2, c_3, ... In accordance with the principle of the variational method these coefficients must be so selected that the value of E is minimum. This is conveniently done by considering the coefficients as variables on which the value of E depends. In that case the condition of the minimum E is expressed by a system of equations

$$\frac{\partial E}{\partial c_1} = 0; \quad \frac{\partial E}{\partial c_2} = 0; \quad \ldots \frac{\partial E}{\partial c_n} = 0 \qquad (14.13)$$

Solution of this system of equations makes it possible to find such values of c_1, c_2, c_3, . . ., at which the value of the system's energy is minimum. In this case function ψ represented by the sum (14.12) will be as close as possible to the correct wave function which is a solution of the Schrödinger equation.

We can see how this is done by considering the example of a wave function containing two coefficients c_1 and c_2

$$\psi = c_1\varphi_1 + c_2\varphi_2 \qquad (14.14)$$

and then extending the result to a function containing any number of coefficients.

Substituting the expression (14.14) into equation (14.9) and taking into account that the Hamiltonian of the sum can be represented as the sum of the Hamiltonians of the components we have

$$E = \frac{c_1^2 \int \varphi_1 H\varphi_1 \, dv + c_1c_2 \int \varphi_1 H\varphi_2 \, dv + c_1c_2 \int \varphi_2 H\varphi_1 \, dv + c_2^2 \int \varphi_2 H\varphi_2 \, dv}{c_1^2 \int \varphi_1^2 \, dv + 2c_1c_2 \int \varphi_1\varphi_2 \, dv + c_2^2 \int \varphi_2^2 \, dv} \qquad (14.15)$$

For the sake of brevity it is convenient to denote the integrals in equation (14.15) with letters. We denote the integrals containing the Hamiltonian with the letter H, and those not containing the Hamiltonian, with the letter S. The subscripts show what functions stand under the integral sign. Thus H_{11} (to be read H one—one)

corresponds to the integral $\int \varphi_1 H \varphi_1 \, dv$. Similarly

$$H_{12} = \int \varphi_1 H \varphi_2 \, dv$$

$$H_{21} = \int \varphi_2 H \varphi_1 \, dv$$

$$H_{22} = \int \varphi_2 H \varphi_2 \, dv$$

$$S_{11} = \int \varphi_1 \varphi_1 \, dv = \int \varphi_1^2 \, dv$$

$$S_{12} = S_{21} = \int \varphi_1 \varphi_2 \, dv$$

$$S_{22} = \int \varphi_2 \varphi_2 \, dv = \int \varphi_2^2 \, dv$$

It can be demonstrated that

$$H_{12} = H_{21} \tag{14.16}$$

Using this notation equation (14.15) is written in a more compact form

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} - c_2^2 S_{22}} \tag{14.17}$$

In accordance with conditions (14.13) the expression for E must be differentiated with respect to c_1 and c_2 and the derivatives obtained equated to zero. For this purpose the formula expressing the derivative of a fraction should be used

$$\left(\frac{u}{v} \right)' = \frac{vu' - uv'}{v^2}$$

Here, u and v represent the expressions in the numerator and denominator of (14.17). In this case

$$\left(\frac{u}{v} \right)' = \frac{vu' - uv'}{v^2} = 0$$

from which

$$u' - \left(\frac{u}{v} \right) v' = 0$$

or

$$u' - Ev' = 0$$

Differentiating with respect to c_1, we obtain

$$2c_1 H_{11} + 2c_2 H_{12} - E \left(2c_1 S_{11} + 2c_2 S_{12} \right) = 0$$

or

$$\left(H_{11} - E S_{11} \right) c_1 + \left(H_{12} - E S_{12} \right) c_2 = 0$$

Differentiating with respect to c_2 and taking account of (14.16) gives an analogous expression

$$(H_{21} - ES_{21}) c_1 + (H_{22} - ES_{22}) c_2 = 0$$

Thus in order to determine the necessary coefficients c_1 and c_2 we must solve the system of equations

$$\left.\begin{array}{l} (H_{11} - ES_{11}) c_1 + (H_{12} - ES_{12}) c_2 = 0 \\ (H_{21} - ES_{21}) c_1 + (H_{22} - ES_{22}) c_2 = 0 \end{array}\right\} \quad (14.18)$$

These equations are called *secular equations*, a term borrowed from celestial mechanics. Using similar systems astronomers determine changes in the movement of planets taking place over the ages. On inspection of the above system of equations we see that the first index in the symbols for the integrals coincides with the number of the equation and the second, with the number of the term in the equation. In the general case, when the wave function is given by expression (14.12) containing n coefficients, the system of secular equations becomes

$$\left.\begin{array}{l} (H_{11}-ES_{11}) c_1+(H_{12}-ES_{12}) c_2 + \ldots + (H_{1n}-ES_{1n}) c_n = 0 \\ (H_{21}-ES_{21}) c_1+(H_{22}-ES_{22}) c_2 + \ldots + (H_{2n}-ES_{2n}) c_n = 0 \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ (H_{n1}-ES_{n1}) c_1+(H_{n2}-ES_{n2}) c_2 + \ldots + (H_{nn}-ES_{nn}) c_n = 0 \end{array}\right\}$$

$$(14.19)$$

The above equations can be written in a shorter form

$$\sum (H_{ij} - ES_{ij}) c_j = 0$$

where i and j are the numbers of the equations and of their terms, respectively, passing through all the values from 1 to n.

The solutions of such systems of equations differ from zero when the determinant composed of the coefficients of the unknowns in the system is equal to zero (see Appendix X), i.e.,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \ldots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \ldots & H_{2n} - ES_{2n} \\ \cdot \quad \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot \quad \cdot & \cdot \quad \cdot \quad \cdot \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} \ldots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

This is called a secular determinant. The given condition can be written more compactly in the general form

$$|H_{ij} - ES_{ij}| = 0$$

Having solved the secular determinant we find the expression for energy E, and substituting it into the system of secular equations determine coefficients $c_1, c_2 \ldots$.

If the sum (14.12) contains a large number of terms, the form of functions φ_1, φ_2, . . . has comparatively little effect on the result. If coefficients c_1, c_2, . . . are properly selected, a sufficiently close approximation of the correct wave function can be obtained. If there is an infinitely large number of terms in equation (14.12) with any functions corresponding to the problem under consideration, and if appropriate coefficients are found, the value of E calculated from equation (14.9) will coincide with the actual value. Naturally, if there is a large number of terms in equation (14.12), the calculation becomes very difficult.

On the contrary, if a sum is taken which consists of a small number of terms, the choice of functions making up the sum is of great importance. Obviously, a satisfactory result can only be obtained if the function taken reflects the actual condition of the system, and if there is a small number of terms, this can only be achieved if there is a good choice of functions.

14.2. Potential Energy Curves for Molecules

Before taking up the results of the quantum-mechanical treatment of molecules we must examine the relationship between the potential energy of the molecule and the interatomic distance.

Let us consider two atoms whose nuclei are at a distance r from one another, and ascertain how the potential energy of such a system changes when there are changes in r. It is convenient to consider zero potential energy to be that of a state in which the atoms are at an infinitely great distance apart and do not interact. If atoms are capable of uniting to form a molecule, the *attractive force* begins to act as the distance between them decreases, whereupon the potential energy of the system falls. This continues up to a certain distance r_0. As r continues to decrease, the potential energy begins to rise due to action of the *repulsive force* which is of considerable magnitude at small interatomic distances. It follows that the relationship between the potential energy and r is expressed by a curve having a minimum. The potential energy curve for the hydrogen molecule is shown in Fig. 14.1.

We now consider the potential energy curve for two atoms which cannot combine to form a molecule. In that case the repulsive force (for repulsion of the electron shells) predominates at all values of r, and the potential energy curve has the shape shown in Fig. 14.2; as r decreases, the curve continuosly rises[1].

The above potential energy curves for molecules are a formal description of the sum of energy changes taking place in atoms as the

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[1] A weak attractive force also acts between atoms which do not form molecules. This is due to the so-called *dispersion interaction* (see p. 265), but it is very slight and can be neglected here.

internuclear distance decreases. Deducting the slight *zero-point oscillation energy of the nuclei* (see below) which appears as the atoms approach one another, the change in the energy of the system E expressed by the potential energy curve (*the depth of the potential curve*) is the sum of changes in the total energy of the electrons and the potential energy of the nuclei in the molecule. Therefore, the quantum-mechanical calculation of the energy in a molecule with equation (14.9) for different values of r makes it possible to find
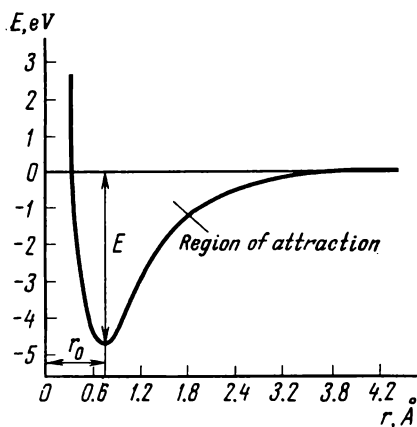
Fig. 14.1. Potential energy curve for the hydrogen molecule
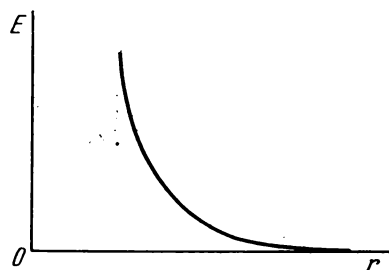
Fig. 14.2. Potential energy curve for two atoms which do not form a chemical bond

the theoretical potential energy curve of the molecule. The correctness of the calculation can be judged by the degree to which the theoretical and experimental curves coincide.

If a molecule is in an unexcited state its energy is minimum. Accordingly, the atomic nuclei are at the *equilibrium distance* r_0. It is also evident that the minimum in the potential energy curve corresponds to the bond-dissociation energy E_{bnd} taken with the opposite sign, since according to the definition (see p. 133) this quantity represents the energy required to separate the atoms making up the molecule, and displace them beyond the space within which they interact (theoretically, until they are at an infinitely great distance apart).

The parameters of the potential energy curve can be determined experimentally. The internuclear distance is found by the methods discussed in Chapter Twelve. The value of E_{bnd} can be calculated from spectroscopic data (see p. 146) or by *thermochemical* methods which are taken up in courses of inorganic chemistry.

According to the results of spectral investigations of the hydrogen molecule, $r_0 = 0.74116$ Å and $E_{bnd} = 4.4763$ eV (see Table 12.2). It has been pointed out that even in the unexcited state every molecule has a certain nuclear zero-point oscillation energy (for a discussion of zero energy see p. 91). For the hydrogen molecule which contains the lightest nuclei this energy is comparatively high, it amounts to 0.2703 eV. When the molecule is ruptured this energy is liberated (the hydrogen atom, unlike the molecule, has only one nucleus, and oscillation is therefore impossible). Thus in order to find the depth of the potential curve on formation of the bond, 0.2703 eV must be subtracted from the bond energy taken with the minus sign. This gives the value $E = -4.7466$ eV.

There are also experimental methods for determining the other parameters of the potential energy curves of molecules.

14.3. Results of Quantum-Mechanical Treatment of the Hydrogen Molecule by Heitler and London

In the hydrogen molecule there are two electrons moving in the field of two nuclei. If the distances between the particles are desig-
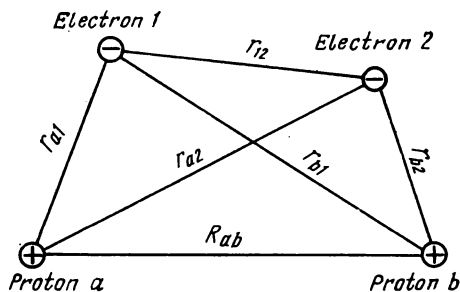
Fig. 14.3. Distances between particles in the hydrogen molecule

nated as in Fig. 14.3, the expression for the potential energy is written in the form

$$U = \frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b2}} - \frac{e^2}{r_{b1}} \qquad (14.20)$$

Heitler and London based the wave function for the electrons in the hydrogen molecule on the wave function of the electron in the hydrogen atom in the normal, $1s$-state. This wave function is determined by the relationship

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r} \qquad (14.21)$$

(see Table 4.1), in which r is the distance of the electron from the nucleus expressed in atomic units.

It is evident that if the atoms are a great distance apart, the movement of their electrons will not undergo significant changes and the wave function of the system can be expressed by the product of the wave functions of two hydrogen atoms

$$\psi = \psi_a (1) \psi_b (2) \qquad (14.22)$$

This form of the general wave function depends on the fact that ψ^2 expresses the probability of the electron being found in the volume element under consideration, while the probability of finding electrons simultaneously in the relevant volume elements is determined by the product of the probabilities, since, according to the law of probability, the probability of two events taking place simultaneously is equal to the product of their probabilities. The quantity r in expression (14.21) is equal to r_{a1} for function $\psi_a(1)$, and to r_{b2} for function $\psi_b(2)$.

Since electrons are absolutely indistinguishable, it can be considered, conversely, that electron 1 moves about nucleus b, while electron 2 moves about nucleus a. Therefore, similarly to (14.22) we can write

$$\psi = \psi_b (1) \psi_a (2) \qquad (14.23)$$

Because of the indistinguishability of the electrons, expressions (14.22) and (14.23) are equivalent, both, however, are poor approximations of the correct form of the wave function in the hydrogen molecule because the movement of electrons in a molecule is greatly different from their movement in free atoms.

Heitler and London assumed that an expression which took into account the possibility of electron movement expressed by both relationships would be a sufficiently close approximation of the correct wave function in the hydrogen molecule. Thus a wave function for the electrons in the hydrogen molecule was 'constructed' by *linearly combining functions* (14.22) and (14.23)

$$\psi = c_1\psi_a (1) \psi_b (2) + c_2\psi_b (1) \psi_a (2) \qquad (14.24)$$

It is evident from relationship (14.21) that the wave function proposed by Heitler and London for the electrons in the hydrogen molecule takes account of their interaction with the nuclei (the value of ψ falls as r increases), but neglects the mutual repulsion of the electrons.

Using function (14.24) the energy of the electrons was calculated for different values of the distance between the nuclei R_{ab}.

It can be shown by the variational method[1] that in this case two

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[1] Heitler and London carried out their calculation by the so-called *perturbation technique*, but the variational method discussed previously gives the same results. The latter method is simpler and was employed by other investigators in later, more exact quantum-mechanical calculations of the hydrogen molecule.

solutions of the system of equations (14.13) are possible

$$c_1 = c_2$$

and

$$c_2 = -c_1$$

Therefore, two forms of wave function (14.24) are possible

$$\psi_S = c_S \left[\psi_a (1) \, \psi_b (2) + \psi_b (1) \, \psi_a (2) \right] \qquad (14.25)$$

and

$$\psi_A = c_A \left[\psi_a (1) \, \psi_b (2) - \psi_b (1) \, \psi_a (2) \right] \qquad (14.26)$$

In these equations the coefficients c_S and c_A are normalization factors and are so selected that the summarized probability of the electrons being found in space is equal to unity (see p. 43).

Equation (14.25) shows that if the nuclei or electrons are interchanged (i.e., if indices (1) and (2) or a and b are interchanged), function ψ_S remains the same. It is therefore said to be *symmetric* with respect to the coordinates of both nuclei and electrons. On the contrary, if there is such an interchange in (14.26) the sign will be reversed. Accordingly, function ψ_A is said to be *antisymmetric*.

How are symmetric and antisymmetric functions to be interpreted physically? Recall Pauli's exclusion principle. According to that principle there cannot be two electrons in an atomic or a molecular system in which all four quantum numbers are identical (see p. 55). The quantum numbers determine the form of the wave function characterizing the state of the electron. Since the symmetric function remains the same when the electrons are interchanged it might seem that these electrons are in the same state, which is contrary to the Pauli principle. However, the wave functions of the hydrogen atom (14.21) from which function (14.24) is derived neglect the spin of the electron. Therefore, the *electrons in the molecule whose state is expressed by the symmetric ψ-function must have different spin quantum numbers*, i.e. these electrons have oppositely directed or antiparallel spins.

Conversely, the antisymmetric function corresponds to a state in which the electrons have undirectional or *parallel spins*.

When wave functions (14.25) and (14.26) are substituted into equation (14.9) and the mathematical operations indicated in the latter carried out, expressions for the energy are obtained which can be written in the general form as follows:

For the symmetric function

$$E_S = \frac{J + K}{1 + S^2} \qquad (14.27)$$

For the antisymmetric function

$$E_A = \frac{J - K}{1 - S^2} \qquad (14.28)$$

The quantities in the above equations denoted by the letters J, K and S are determined by integrals whose value depends on the distance between the atomic nuclei. In general form these integrals may be written

$$J = \int \psi_I H \psi_I \, dv$$

$$K = \int \psi_I H \psi_{II} \, dv$$

Here

$$\psi_I = \psi_a(1)\,\psi_b(2)$$

$$\psi_{II} = \psi_a(2)\,\psi_b(1)$$

$$S = \int \psi_a(1)\,\psi_b(1)\,dv = \int \psi_a(2)\,\psi_b(2)\,dv$$

The integral denoted by the letter J is termed the *Coulomb integral* since it characterizes the electrostatic interaction of electrons with nuclei, as well as electron and nuclear interaction. Integral K is the *exchange integral* [1]. It determines the reduction in the energy of the system due to the movement of each electron about both nuclei (this movement may conventionally be called the exchange of electrons). The physical meaning of this principle will be discussed below. The exchange integral has a negative sign; it makes the principal contribution to the energy of the chemical bond. Integral S is the *overlap integral*. It shows to what

Fig. 14.4. Comparison of hydrogen molecule calculation with experimental findings

1—experimental curve; *2*—calculation by means of symmetrical wave function (14.25); *3*—calculation with antisymmetrical function (14.26)
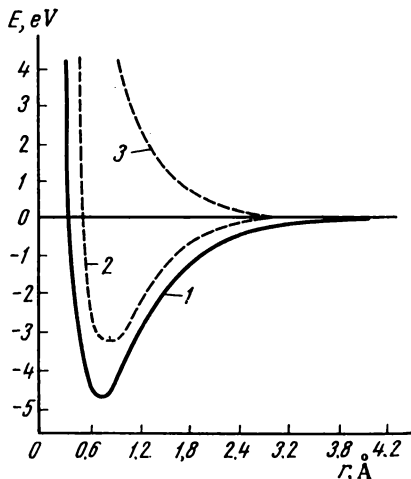
extent the wave functions of the electrons of the hydrogen atoms overlap. The integral varies from 1 at $R_{ab} = 0$ to 0 at $R_{ab} = \infty$; at $R_{ab} = r_0$ it is equal to 0.75.

The results of calculation of the electron energy in the H_2 molecule are shown in Fig. 14.4. Two curves are obtained corresponding to expressions (14.27) and (14.28), respectively. In the case of the symmetric wave function the curve has the form characteristic of

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[1] Relationship (14.27) is sometimes given the form $E_S = 2E_H + \dfrac{J+K}{1+S^2}$, wherein the first term ($2E_H$) expresses the energy of the two hydrogen atoms in the normal state, and the second term, the energy changes taking place as the atoms approach one another. When relationship (14.27) is written in this form the Coulomb and exchange integrals acquire a somewhat different appearance.

the molecule, it shows the formation of the chemical bond. The equilibrium interatomic distance, r_0, as calculated by Heitler and London is 0.869 Å, and the depth of the potential curve comes to 3.14 eV (72.3 kcal/mole). As noted previously the most precise experiment gives $r_0 = 0.74116$ Å and $E = 4.7466$ eV. Taking account of the very approximate character of the wave function employed, composed of the unaltered wave functions of the atoms and allowing but indirectly for the mutual repulsion of the electrons, such a coincidence can be considered quite satisfactory.

Thus Heitler and London's calculation provided a quantitative explanation of the chemical bond on the basis of quantum mechanics. It showed that if the electrons of the hydrogen atoms have antiparallel spins there is a substantial diminution of the energy of the system as the atoms approach one another, and a chemical bond is formed. The formation of the chemical bond is due to the fact that if the electrons have antiparallel spins their movement about both nuclei becomes possible, something that at times is termed, not too aptly, the 'exchange of electrons'. The possibility of the electrons' movement about both nuclei brings about a considerable increase in the density of the electron cloud in the space between the nuclei. A region with a high density of the negative charge appears between the positively charged nuclei which draws them together. The attraction reduces the potential energy of the electrons and consequently the potential energy of the system, and a chemical bond results[1]. It follows that the *formation of the chemical bond is explained by the lowering of the potential energy of the electrons, resulting from the increased density of the electron cloud in the internuclear space.*

Figure 14.5 shows the distribution of electron density in a system consisting of two nuclei and two electrons as calculated with wave functions (14.25) and (14.26) (recall that the density of the electron cloud is determined by the square of the wave function). Areas with a higher density of the electron cloud are made darker in Fig. 14.5. The wave functions of electrons with antiparallel spins are added together, and therefore the density of the electron cloud between the nuclei increases. In this case it is said that the *electron clouds, or to be more exact, the wave functions, overlap.*

Overlapping of the electron clouds cannot be regarded simply as the superimposition of the electron cloud of one isolated atom on the electron cloud of another isolated atom. Since the wave functions are added, the electron density between the atoms determined by the quantity ψ^2 is greater than the sum of the densities of the electron clouds of isolated atoms for the same distances from the

---

[1] Precise calculations show that there is a slight increase in the kinetic energy of the electrons when the bond is formed but it is small in comparison to the fall in the potential energy.

nuclei. When a chemical bond is formed the electron clouds stretch out toward one another as it were.

On the contrary, in the case of the antisymmetric wave function which is characteristic of electrons with parallel spins, the density of the electron cloud between the atoms falls to zero because the electrons are forced out of the space between the nuclei and a chemical bond is not formed.

The quantum-mechanical calculation of the hydrogen molecule was first carried out by Heitler and London who used the approximate function (14.24). The calculation was later repeated by other investigators using more complicate
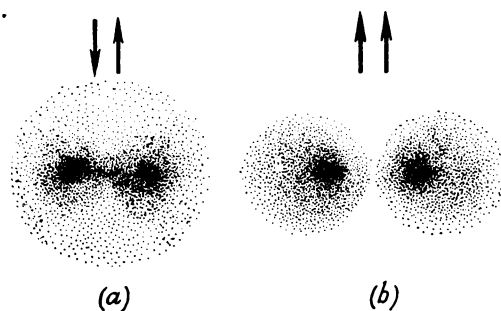
Fig. 14.5. Electron clouds of hydrogen atoms with different relative orientation of electron spins

(a) antiparallel spins—atoms combine to form a molecule; *(b)* parallel spins—atoms are repulsed

expressions for the wave function which took into consideration the deformation of the electron shells, the mutual repulsion of the electrons, etc. In 1935 James and Coolidge (USA) employed a 13-termed expression for the approximate wave function, and obtained the values of r_0 and E which were very close to those found experimentally (see Table 14.1). In 1960 Kolos and Roothan (USA) used a still more complicate expression consisting of 50 terms, and differences between the results obtained and the experimental values were infinitesimal.

Table 14.1

Quantum-Mechanical Calculations of the Hydrogen Molecule

Investigators	Number of terms in wave function equation	r_0, Å	E, eV
Heitler and London (1927)	2	0.869	3.14
James and Coolidge (1935)	13	0.740	4.72
Kolos and Roothan (1960)	50	0.74127	4.7467
Experimental values		0.74116	4.7466± ±0.0007

Performing the calculations in this case was only possible thanks to the use of an electronic computer.

It follows that in spite of it being impossible to find the exact solution of the Schrödinger wave equation for the hydrogen molecule, the use of approximate methods makes it possible to calculate the system with a very high degree of accuracy.

Heitler and London also carried out the quantum-mechanical calculation of the interaction energy of the hydrogen molecule and a third atom of hydrogen. The calculation showed that the third atom would not be attracted, which means that formation of the H_3 molecule is impossible[1]. This was theoretical substantiation of a most important quality of the covalent bond, *saturability*.

Without going into the calculation, the result can be explained on the basis of what was said above about the calculation of the H_2 molecule. The addition of a third atom to the H_2 molecule is impossible because the condition for overlapping of the electron clouds and formation of the chemical bond, namely the presence of electrons with antiparallel spins, is not fulfilled. The spin of the third electron would inevitably coincide in direction with the spin of one of the electrons in the H_2 molecule and a repulsive force would act between them, just as a repulsive force appears on the approach of two hydrogen atoms with parallel spins.

14.4. Valence of the Elements on the Basis of the Heitler and London Theory

The possibility of interaction between the He atom and the H atom can be treated in the same way as the possibility of interaction of the H_2 molecule with a third H atom.

The electronic structure of the helium atom in the normal state is expressed by the formula $1s^2$. This means that the helium atom has two electrons in which $n = 1$, $l = 0$, and $m = 0$. According to Pauli's exclusion principle these electrons must have antiparallel spins. It is evident that the electron of the hydrogen atom would have a spin coinciding in direction with one of the electrons of the helium atom. Consequently, there can be no common electron cloud joining the He and H atoms, and no chemical bond can be formed.

Heilter and London likewise treated the interaction of two He atoms. Here, too, the formation of a chemical bond is impossible because each of the electrons of an He atom would have a spin which coincided in direction with the spin of one of the electrons in another He atom.

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[1] Although the addition of a third atom of hydrogen to the hydrogen molecule is impossible, the hydrogen ion H^+ deprived of its electrons can be added, the ionized molecule H_2^+ exists.

The electronic configuration of the He atom can be represented by the diagram

$$\text{He} \quad \boxed{\uparrow\downarrow}$$
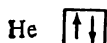
which shows that two electrons are contained in a single quantum cell (see p. 57). Two electrons with opposite spins occupying the same quantum cell are said to be *paired*. Using this terminology it can be said that according to the Heitler—London theory hydrogen can form an H_2 molecule because it contains an unpaired electron, but helium cannot form an He_2 molecule because the electrons in the He atom are paired.

We next consider the interaction of two Li atoms. The electronic configuration of the Li atom ($1s^2 2s$) is represented by the diagram

$$\text{Li} \quad \begin{array}{c} 2 \\ 1 \end{array} \boxed{\begin{array}{c} \uparrow \\ \uparrow\downarrow \end{array}}$$
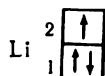
This atom contains one unpaired 2s-electron. Therefore, one can expect the formation of an Li_2 molecule by the pairing of the lone s-electrons, in the same way as the H_2 molecule is formed. Actually, the Li_2 molecule exists. The bond energy of the Li_2 molecule (1.13 eV) is roughly one-fourth that of the H_2 molecule (4.48 eV). This is because of the first electron shell around the Li nucleus, the Li—Li bond, is considerably longer than the H—H bond (2.67 Å as compared to 0.74 Å). Moreover, the two pairs of first-shell electrons strongly screen the charges of the nuclei and repulse one another. All this causes a substantial weakening of the bond.

Extending this principle to other systems it can be said that a chemical bond is formed when two atoms having unpaired electrons come into contact. Overlapping of the electron clouds of the unpaired electrons, or more exactly their wave functions, then becomes possible, and a zone of high electron density appears between the atoms, resulting in the formation of a chemical bond. It follows that if an atom has n unpaired electrons it can form chemical bonds with n other atoms, each of which has a single unpaired electron. Therefore, according to the Heitler—London theory, the *valence of an element is equal to the number of unpaired electrons in its atom*. Thus Heitler and London's quantum-mechanical calculations provided theoretical substantiation for Lewis's assumption that the chemical bond is formed by a pair of electrons.

On the basis of the foregoing discussion we now consider the valence of the elements of the second period of the periodic system.

Lithium. As we have seen, lithium has one unpaired electron and its valence is therefore one.

Beryllium. The beryllium atom has the electronic configuration $1s^2 2s^2$; distribution of the electrons in quantum cells is represented by the diagram
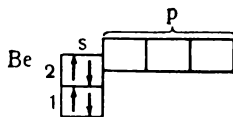
Thus in the normal state the beryllium atom has no unpaired electrons and its valence is therefore zero. However, imparting a certain amount of energy to the beryllium atom (62 kcal/g-at) brings it into an excited state

$$Be \ (1s^2 \ 2s^2) \xrightarrow{\ 62kcal\ } Be^* \ (1s^2 \ 2s \ 2p)$$
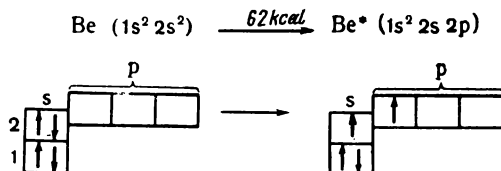
In this state there are two unpaired electrons, i.e., the beryllium atom now has a valence of two. The energy expended in bringing the atom into an excited state is more than compensated by the energy liberated on formation of the chemical bond (recall that the energy of the single bond is of the order of 100 kcal (see p. 134)).

Boron. The electronic configuration of the unexcited atom is $1s^2 2s^2 2p$. Distribution of the electrons in the quantum cells is represented by the diagram
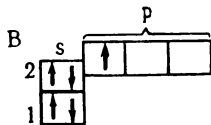
The presence of an unpaired $2p$-electron in the normal state would indicate a valence of one. Univalence, however, is not characteristic of boron, since it is converted into the excited state by a relatively small amount of energy.

$$B \ (1s^2 2s^2 2p) \xrightarrow{\ 127.3 \ kcal\ } B^* \ (1s^2 \ 2s \ 2p^2)$$
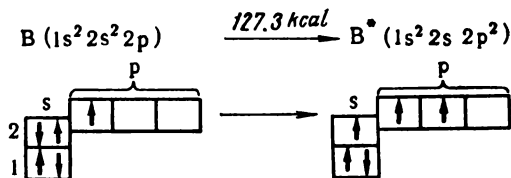
In this state it has a valence of three.

Carbon. The electronic configuration of the carbon atom, $1s^2 2s^2 2p^2$, corresponds to a distribution of the electrons in the cells in which, in accordance with Hund's rule, there are two unpaired electrons. Bivalence is not characteristic of carbon[1] as it is comparatively easily converted into the excited state, in which it has a valence of four.

$$C(1s^2 2s^2 2p^2) \xrightarrow{\quad 96\, kcal \quad} C^*(1s^2 2s\, 2p^3)$$
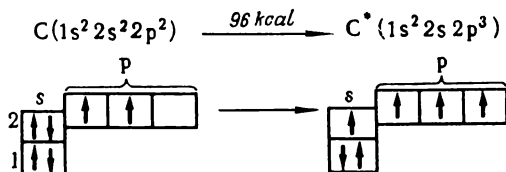
As in the case of Be and B, the excitation energy of the carbon atom is compensated by the formation of a large number of chemical bonds.

Nitrogen. The electronic configuration of the nitrogen atom corresponds to the following diagram of the electrons in the quantum cells

$$N\,(1s^2 2s^2 2p^3)$$
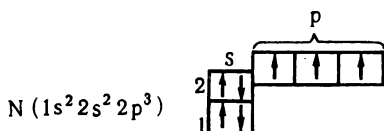
In accordance with Hund's rule, the nitrogen atom has three lone *p*-electrons, and the valence is therefore three. It should be noted that nitrogen does not exhibit a valence of five. This would require the transfer of electrons to a new shell (the third), which would require such a great expenditure of energy that it could not be compensated by any chemical bond with some other atom. For that reason nitrogen, unlike other elements of Group V, does not form such compounds as NCl_5, NBr_5, etc. The configuration of the nitric acid molecule in which the degree of oxidation of nitrogen is $+5$, will be considered later (see p. 199); it will only be noted here that nitrogen in HNO_3 and N_2O_5 is not pentavalent.

Oxygen. The electronic configuration of the oxygen atom and the distribution of the electrons in the quantum cells are as follows:

$$O\,(1s^2 2s^2 2p^4)$$
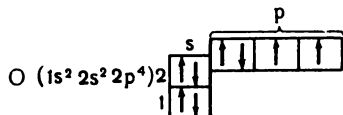
Accordingly, oxygen has a valence of two.

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[1] As we shall see later, carbon in the CO molecule is not bivalent (see p. 197).

   Fluorine. The electronic configuration of the atom and the arrange-
ment of the electrons in the quantum cells

$$F (1s^2 \, 2s^2 \, 2p^5)$$
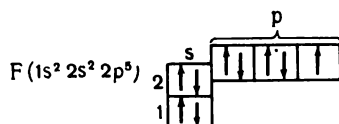
show that there is only one unpaired electron; therefore, fluorine
is monovalent.
   Neon. The electronic configuration of the atom and the arrangement
of the electrons in the quantum cells

$$Ne \; (1s^2 \, 2s^2 \, 2p^6)$$
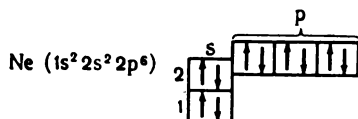
are such that there are no unpaired electrons. Neon, like helium,
does not form molecules with other atoms, and its valence is zero.
A very great amount of energy would be required to excite the Ne
atom since the electrons would have to be forced to a new electron
shell.
   The foregoing consideration of the valence of the elements of the
second period of the periodic system makes it clear why there is such
a great difference between these elements and all the other elements
of the periodic system, a distinction which was pointed out earlier
(see p. 84). It is particularly striking in three elements—nitrogen,
oxygen and fluorine. Besides the peculiar features of these elements
due to the small radius of their atoms and ions, there are also dif-
ferences arising from the fact that the external electrons are in the
second shell in which there are only four quantum cells. For that
reason these elements do not have the high valences of their analogues.
   Heitler and London's concept of the formation of the chemical
bond proved to be very fruitful and was the basis for the explanation
and approximate calculation of the bond in more complicate mole-
cules. Their ideas were developed into the theory of the chemical
bond which has come to be called the *valence bond method* or *the
electron pair method*. Slater and Pauling (USA) contributed largely
to the formulation and development of the valence bond me'.hod.
   The basic principles of the valence bond method are as follows:
   1. The single chemical bond is formed by two electrons with
opposite spins, belonging to different atoms. The wave functions
of the two electrons overlap and a zone of high electronic density
is produced between the atoms; this lowers the system's potential
energy and a chemical bond is formed.

2. The bond lies in the direction in which the possibility of the overlapping of the wave functions of the electrons forming the bond is the greatest.

3. Of the two orbitals of any atom, the strongest bond is formed by the orbital on which the orbital of another atom is more strongly superimposed.

Proceeding from these principles, the method of valence bonds provides theoretical substantiation of the orientation of the chemical bond.

14.5. Explanation of the Orientation of Valence

The atoms of elements of the second and following periods can be considered as consisting of a *core* containing the inner shells and of the *outer, valence electrons*. Approximate expressions for the wave functions of the valence electrons in different atoms are now known, and are extensively used in quantum-mechanical calculations of molecules. However, for a qualitative, graphic examination it is more convenient to simplify and consider the wave functions of the 2s-, 2p- and 3d-electrons, etc., the same in form for all the atoms, as for the hydrogen atom. This simplification will be consistently employed henceforth.

Data concerning the wave functions of the electron in the hydrogen atom were previously cited (see pp. 47-49). We shall now supplement them with a graphic representation.

Figure 14.6 shows the curves of the radial components of the wave functions $R(r)$ for the 1s-, 2s- and 2p-states of the electron (see Table 4.1). The diagrams under the curves give a clear idea of the dependence of the wave function on the direction in space, determined by its angular component $\Theta(\theta)\,\Phi(\varphi)$. These diagrams show the dependence of ψ on the angles θ and φ when r is fixed. They are constructed in such a way that the radius vector connecting any point on their surface with the origin of the coordinates is proportional to the value of ψ at a point lying in the given direction at a definite distance, for example 1 Å, from the nucleus.

It can be seen that the wave functions of the s-electrons have a spherical symmetry; the sign of the wave function of the 2s-electrons reverses—at short distance from the nucleus it is negative; at long distances, positive. The ψ function for the 2p-electrons has a cylindrical symmetry (in case of $2p_z$-electrons, the axis of symmetry being the z axis); it consists of two halves having different signs.

We shall now consider examples to illustrate the general principles concerning the orientation of the chemical bond.

We shall first discuss the chemical bond in the water molecule. The H_2O molecule is formed from an atom of oxygen and two atoms
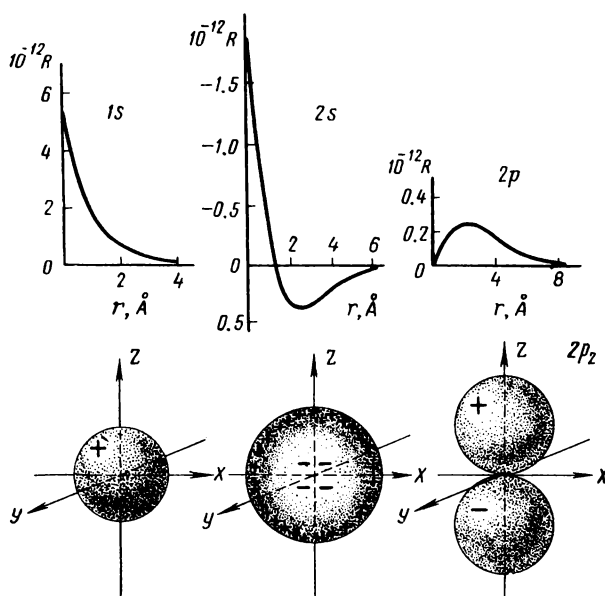
Fig. 14.6. Wave functions of $1s$-, $2s$- and $2p_z$-electrons ('+' and '—' are signs of
wave function)

Values $R(r)$ correspond to charge on nucleus $Z = 1$
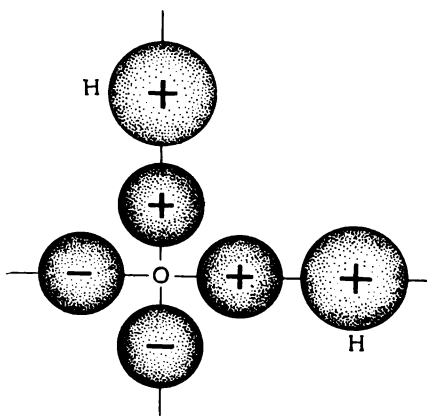
Fig. 14.7. Wave functions of hydrogen and oxygen atoms (diagrammatic rep-
resentation)

of hydrogen. The oxygen atom has two unpaired p-electrons (see p. 177), which occupy two orbitals at an angle of 90° to one another. The hydrogen atoms have $1s$-electrons. The wave functions of the unpaired electrons in the oxygen and hydrogen atoms are shown in Fig. 14.7. It is evident that on the approach of a hydrogen atom having an electron whose spin is directed opposite to the spin of one of the unpaired p-electrons of an oxygen atom, these electrons will form a common electron cloud linking the oxygen and hydrogen atoms. The angle between the bonds should be close to 90°, i.e. the angle between the p-electron clouds.

The deviation of the actual angle between the bonds in the H_2O molecule (104.5°) from the value of 90° which might be expected on the basis of the diagram can be explained by two causes:

1. The O—H bond is of the polar covalent type, that is the electrons are drawn more strongly to the oxygen atom (see the electronegativity graph, Fig. 13.1). As a result the hydrogen atoms have a certain positive charge, and the repulsion of these charges tends to increase the angle between the bonds.

2. Electrons of the two O—H bonds in the H_2O molecule have like-directed spins, which causes a repulsive force to act between them. (There is a similar effect during the interaction of two He atoms.)

A diagrammatic representation of the overlapping of the electron wave functions in the H_2O molecule is shown in Fig. 14.8.

The effect of the above factors is less in hydrogen sulphide (H_2S), an analogue of water. In this compound the bond is less polar (see the electronegativity graph), and the distance between the atoms greater. In H_2S the angle between the bonds is 92°, and in H_2Se, 91° (see p. 129).

The configuration of the ammonia molecule can be found in a similar way. The nitrogen atom has three unpaired p-electrons whose orbitals are arranged in three mutually perpendicular directions. It is evident that in accordance with the requirements of the method of electron pairs, the three N—H bonds must be situated at angles of about 90° to one another. The NH_3 molecule should have the shape of a pyramid with the nitrogen atom at the vertex (Fig. 14.9). The value of the angle between the bonds in the NH_3 molecule, as found experimentally, is 107.3°. The causes of the discrepancy between the experimental value and that to be expected from the diagram are the same as in the case of the H_2O molecule, and as in the preceding example the effect of side factors diminishes as the size of the atom increases. In the compounds PH_3, AsH_3 and SbH_3 the angles between the bonds are 93.3, 91.8 and 91.3°, respectively.

The conclusion can be drawn on the basis of the foregoing discussion that, *neglecting the effect of secondary factors, the bonds formed by p-orbitals are situated at an angle of 90° to one another.*

The picture is more complicate whén it comes to the formation of bonds by the carbon atom. As already noted, this atom has four unpaired electrons when in the excited state—one *s*-electron and three *p*-electrons.

By analogy one might expect the carbon atom to have three bonds directed at an angle of 90° to one another (the *p*-electrons), and one bond formed by the *s*-electron, which could be directed at any angle since the *s*-orbital has a spherical symmetry.

The bonds formed by the *p*-electrons should be stronger, since the *p*-orbitals extend further from the nucleus than the *s*-orbital, and
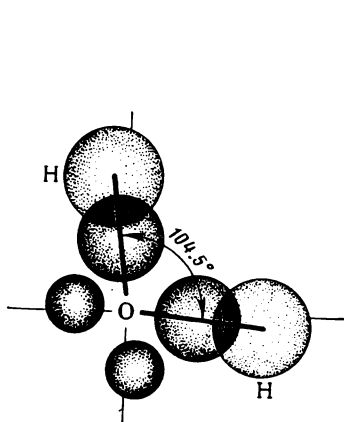
Fig. 14.8. Overlapping of electron wave functions when H_2O molecule is formed
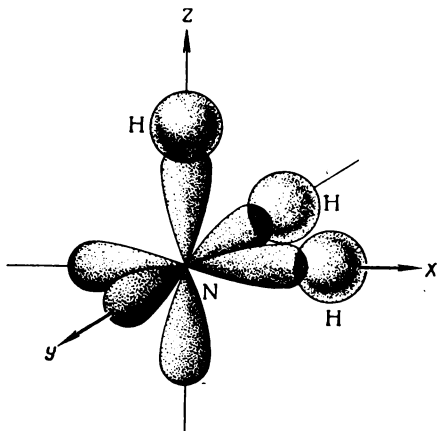
Fig. 14.9. Diagram of overlapping of electron clouds when NH_3 molecule is formed

should overlap to a greater extent the orbitals of other atoms forming bonds with carbon. But as we know, all the bonds of the carbon atom are equivalent and are directed toward the vertices of a tetrahedron, the angle between them being 109.5°.

A theoretical explanation of this fact was suggested by Slater and Pauling. They demonstrated that in the interpretation and calculation of the chemical bond, several orbitals which do not differ greatly in energy could be replaced by the same number of like orbitals called *hybrids*. The wave function of the hybrid orbital is formed by the wave functions of the electrons involved multiplied by certain coefficients. Thus, as regards the formation of four bonds by the carbon atom, the hybrid wave functions of the carbon electrons are expressed by relationships in the form

$$\psi_{hyb} = a\psi_s + b\psi_{p_x} + c\psi_{p_y} + d\psi_{p_z} \qquad (14.29)$$

The values of the coefficients a, b, c and d are found from the normalization and some other mathematical requirements which the wave

functions must meet. The coefficients may be either positive or negative. The operation of finding hybrid orbitals is similar to replacing a vector by the sum of its projections on the axes of the coordinates.

: From Fig. 14.6 it can be seen that the 2s wave function is negative at small distances from the nucleus, and positive at long distances. However, the negative part is close to the nucleus and corresponds to only a small part of the electron cloud; practically speaking it takes no part in the overlapping of the orbitals. The 2p-orbital is positive to one side of the origin of the coordinates, and negative to the other. When the 2s-orbital is added to the 2p-orbital, the positive part of the 2p-orbital is augmented,
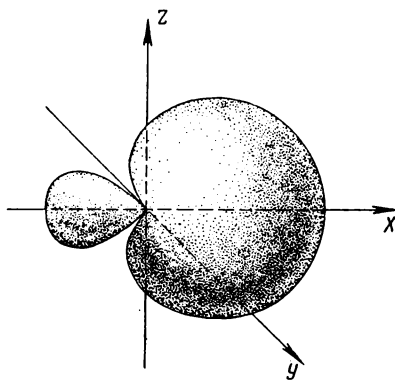
Fig. 14.10. Surface of hybrid wave function

and the negative part diminished. On the contrary, when the 2p-orbital is subtracted from the 2s-orbital, the negative part increases, and the positive part decreases. Therefore, the hybrid wave functions have a small value on one side of the nucleus, and a large value on the other. The surface representing the hybrid function is shown in Fig. 14.10.

The four hybrid orbitals of the carbon atom are arranged at an angle of 109.5° to one another, they are directed toward the vertices of a tetrahedron, the carbon atom being at its centre. The shape of the electron clouds for the hybrid orbitals of the carbon atom is shown in Fig. 14.11. From Figs 14.10 and 14.11 it can be seen that the hybrid orbital is extended strongly to one side of the nucleus. This causes a much greater overlapping of these orbitals with the orbitals of electrons belonging to other atoms than the overlapping of the orbitals of s- and p-electrons. In accordance with the third principle of the method of valence bonds, this produces a stronger bond, and for that reason hybridization causes the formation of more stable molecules. Hybridization is also furthered by the fact that the electrons in many-electron atoms are mutually repellent and tend to move in such a way as to be as far distant from one another as possible. Hybrid orbitals correspond to this tendency better than non-hybrid orbitals.

Regrouping of the electron clouds of the carbon atom to form hybrid orbitals is shown diagrammatically in Fig. 14.12.

It follows that when carbon compounds are formed, the different orbitals of the valence electrons of the carbon atom—one s-orbital and three p-orbitals—are transformed into four equivalent hybrid sp^3-orbitals. This explains the equivalence of the four bonds of the carbon atom in the compounds CH_4, CCl_4, $C(CH_3)_4$, etc., and their being oriented at equal (tetrahedral) angles to one another.

Hybridization of the orbitals of the valence electrons is not limited to carbon compounds. *The necessity of employing the hybridization*
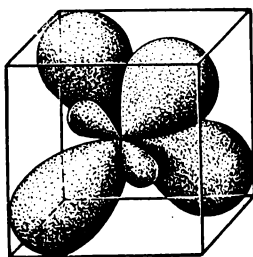
Fig. 14.11. Spatial arrangement of hybrid electron clouds of carbon atom
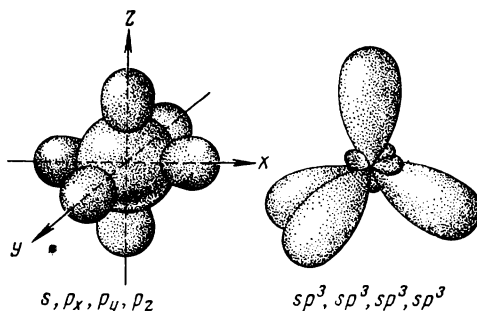
Fig. 14.12. Diagram showing redistribution of electron density when hybrid orbitals are formed

concept arises whenever several bonds are formed by electrons belonging to different subshells which do not differ greatly in energy (a substantial difference in energy prevents hybridization).

We now consider examples of different types of hybridization involving s- and p-orbitals (the expressions for their wave functions are given in Appendix VII).

Hybridization of one s- and one p-orbital (sp-hybridization) takes place during the formation of beryllium, zinc, cadmium and mercury halides. In the normal state the atoms of these elements have two paired s-electrons in their outer shell. When excited, one of the s-electrons is promoted to become a p-electron, resulting in two unpaired electrons—one of them an s-electron, the other a p-electron. When a chemical bond is formed, these unlike orbitals are transformed into equivalent hybrid sp-orbitals oriented at an angle of 180° to one another because the two bonds are opposite in direction (Fig. 14.13). Experimental determination of the configuration of the molecules BeX_2, ZnX_2, CdX_2 and HgX_2, where X is a halogen, has demonstrated that they are linear and that the two metal-halogen bonds are of equal length.

Hybridization of one *s*- and two *p*-orbitals (*sp²*-hybridization) takes place when boron compounds are formed. As stated above (see p. 176), the excited boron atom has three unpaired electrons, one *s*-electron and two *p*-electrons. From their orbitals there are formed three equivalent *sp²*-hybrid orbitals located in a single plane at an angle of 120° to one another (Fig. 14.14). Experimental investigations have demonstrated that the molecules of such boron compounds

Fig. 14.13. Arrangement of electron clouds following *sp*-hybridization
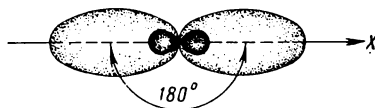
as BX₃ (X—halogen), B(CH₃)₃ (trimethylboron), and B(OH)₃ (boric acid) do have a planar configuration, all three bonds being of the same length and arranged at an angle of 120° to one another.
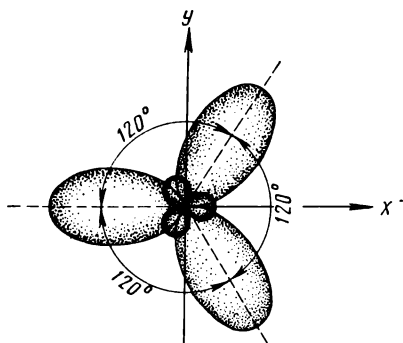
Fig. 14.14. Arrangement of electron clouds following *sp²*—hybridization

This shows the advantage of quantum-mechanical conceptions over the old structural theory. From the standpoint of the old theory there is no difference between the bonds in the compounds

$$\begin{array}{ccc} \text{Cl} & & \text{Cl} \\ | & & | \\ \text{B} & \text{and} & \text{N} \\ \diagup \ \diagdown & & \diagup \ \diagdown \\ \text{Cl} \ \ \text{Cl} & & \text{Cl} \ \ \text{Cl} \end{array}$$
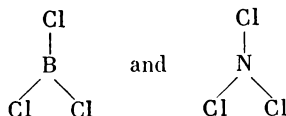
Actually the former compound is flat while the latter is in the form of a pyramid with the nitrogen atom at the vertex. This results, for one thing, in a difference in polarity $\mu_{BCl_3} = 0$, $\mu_{NCl_3} \neq 0$. From what has been said it can be seen that the present-day theory of the chemical bond gives a precise explanation of this fact and enables one to foresee other similar principles. Thus quantum chemistry, besides making it possible to calculate the properties of molecules, creates a new system of concepts; it provides a new chemical langua-

ge which supplements and develops the principles of A. Butlerov's theory of chemical structure.

Hybridization of one s- and three p-orbitals (sp³-hybridization), as noted above, explains the valence of the carbon atom. The formation of sp³-hybrid bonds is likewise characteristic of the carbon analogues, silicon and germanium. Their valences also have a tetrahedral orientation.

Since hybrid orbitals provide greater concentration of the electron clouds between nuclei and, consequently, a stronger bond, one may wonder why such hybridization does not occur in H_2O and NH_3. Actually the orientation of the bonds in these compounds can also be explained by sp³-hybridization. Such an approach is even more exact than that set forth on pp. 179 and 181. It should not be forgotten, however, that both approaches are approximate. When the H_2O molecule is formed the outer shell of the oxygen atom can assume the configuration ψ_1^2, ψ_2^2, ψ_3, ψ_4, where ψ_1, ψ_2, ψ_3, and ψ_4 are sp³-hybrid wave functions, the upper index showing the number of electrons occupying the given orbital. Thus two of the four hybrid orbitals are occupied by unpaired electrons and can form chemical bonds. The angle between these bonds should be 109.5° which is closer to the experimental value, 104.5°, than the 90° given in the diagram on p. 180. But whereas on pp. 179 and 181 it was necessary to account for the deviation of the theoretical value from the experimental in the H_2O molecule, it is now necessary to explain why the angles between the bonds in the analogues of water, H_2S, H_2Se and H_2Te, differ markedly from 109.5°. This is explained by a number of factors, in particular by the fact that in compounds containing large atoms the bond is weaker and the gain in energy resulting from the formation of the bond by hybrid orbitals would not compensate for a certain increase in the energy of the s-electrons that would be caused by their transition to sp³ hybrid orbitals. This hampers hybridization. Moreover, recent precise calculations have demonstrated that when R—H bonds are formed, the 2s-orbitals of oxygen and nitrogen overlap to a greater extent with the 1s-orbitals of hydrogen than do the 2p-orbitals. When it comes to the analogues of oxygen, on the contrary, the p-orbitals overlap to a greater extent. This brings about the greater contribution of the s-state (hybridization) in the formation of the chemical bond in the H_2O molecule than in its analogues. Therefore, the valence angles in H_2S, H_2Se and H_2Te are close to 90°.

Similarly, the structure of the NH_3 molecule is explained by sp³-hybridization. The electronic configuration of this molecule can be represented by the diagram

$$\begin{matrix} & H \\ & \cdot\cdot \\ :\!\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\!\!:\!H \\ & H \end{matrix}$$

The valence electrons of the nitrogen atom occupy four sp^3 hybrid orbitals. One electron is found in each of three orbitals and the latter form bonds with hydrogen atoms. The fourth orbital is oc-cupied by two electrons which do not form chemical bonds. Investi-gations have demonstrated that ammonia's dipole moment is chiefly due to this *unshared* pair of electrons.

The unshared pair contribution to the dipole moment is shown by comparison of the values of μ for NH_3 and NF_3, molecules which have a similar configuration. Since the N—F bond is more polar than the N—H bond (see the electronegativity graph, Fig. 13.1) it might be expected that μ_{NF_3} would be greater than μ_{NH_3}. Actual-ly the reverse is the case: $\mu_{NH_3} = 1.48$ *D*, and $\mu_{NF_3} = 0.24$ *D*. This is explained by the fact that the direction of the dipole moments of the N—H and N—F bonds is different; in the NH_3 molecule the nitrogen atom is charged negatively, and in the NF_3 molecule, posi-tively. In the NH_3 molecule the total moment of the bonds and the moment of the unshared pair of electrons have the same direction and are added; in the NF_3 molecule these moments have opposite directions and are subtracted. Consequently NF_3 has a small dipole moment.

From what has been said it follows that the H—N—H valence angles in the NH_3 molecule should be equal to 109.5° which is close to the value found experimentally, 107.3°. The deviation from this value in the NH_3 analogues, PH_3, AsH_3 and SbH_3, is due to the same factors as in the case of H_2O analogues.

Hybridization is not limited to the cases considered, other types are possible, among them hybridization involving *d*-orbitals (see p. 239).

14.6. Single, Double and Triple Bonds

Discussion of this problem can conveniently begin with the bonds in the N_2 molecule.

The electronic configuration of the nitrogen atom is $1s^2$, $2s^2$, $2p^3$ with three orbitals oriented perpendicular to one another along the *x*, *y* and *z* axes. Assume that two nitrogen atoms approach one another, moving in the direction of the *x* axis. When they are suf-ficiently close, two $2p_x$-orbitals overlap, forming a common electron cloud along the axis connecting the atomic nuclei. *The bond formed by an electron cloud having maximum density on the line connecting the centres of atoms is called a σ bond.*

We shall now consider the other unpaired electrons of the nitrogen atoms. The diagram in Fig. 14.15 presents the surfaces of the wave functions of the $2p_z$ nitrogen electrons. It can be seen that the wave functions overlap but the overlapping is different than that which produces the σ bond. There are now two areas of overlapping, one on each side of the line connecting the atomic nuclei, the plane of

symmetry being that which passes through the coordinates x and z. *The bond formed by electrons whose orbitals have maximum overlapping on both sides of the line connecting the centres of the atoms is called a π bond.*

It is evident that the two $2p_y$-electrons of the nitrogen atoms form a second π bond located about the plane passing through the coordinates x and y.

Thus there are three chemical bonds in the nitrogen molecule but these bonds are not the same—one of them is a σ bond, the other
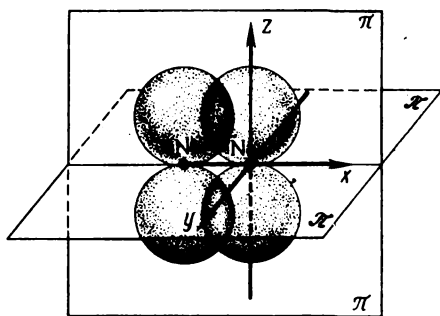
Fig. 14.15. Diagram showing formation of chemical bonds in N_2 molecule

two are π bonds. The three lines used to designate the bonds in the nitrogen molecule in accordance with the old structural theory are not equivalent.

We next examine the chemical bonds in some carbon compounds.

Figure 14.16 is a diagram representing the structure of the ethane molecule, C_2H_6. In this compound the four bonds of the carbon atoms are formed by hybrid sp^3-orbitals, which are arranged at an angle of 109.5° to one another. All the bonds are single, σ bonds.

The electron cloud of the σ bond located along the axis connecting the centres of the carbon atoms has a cylindrical symmetry in respect to the axis. Revolution of one of the atoms round this axis does not change the distribution of the electron density in the σ bond; consequently this can be done without breaking or deforming the bond. This explains the possibility of the revolution of the atoms round the C—C bond, thus preventing *cis—trans* isomerism in ethane derivatives and other organic compounds having a single bond between the carbon atoms—something that chemists have long known.

We now take up the bond in the ethylene molecule, C_2H_4. Consideration of the various possibilities of bond formation in this molecule shows that the greatest overlapping of the orbitals takes place, and consequently the system with the least potential energy is formed, when one s-orbital and two p-orbitals of the carbon atoms form three sp^2-hybrid orbitals, while the third p-orbital remains

a simple p-orbital. A diagram of the bonds forming in this case is shown in Fig. 14.17.

As we already know, the electron clouds in the case of sp^2-hybridization are found in a single plane at an angle of 120° to one another (see p. 185). In the ethylene molecule the hybrid orbitals form three σ bonds, one C—C bond and two C—H bonds which lie in the same plane at angles of 120° to one another. Experimental investigation
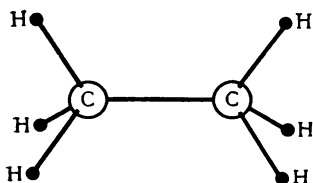
Fig. 14.16. Structure of C_2H_6 molecule
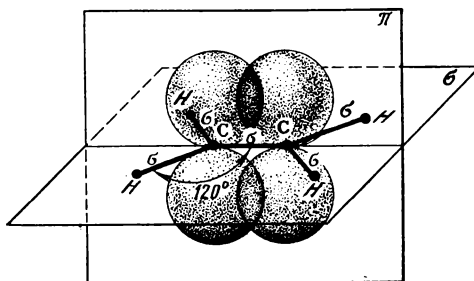
Fig. 14.17. Diagram showing formation of chemical bonds in C_2H_4 molecule

has demonstrated that the C_2H_4 molecule does have a planar configuration. It is evident that the p-orbitals of the carbon atoms remaining non-hybrid form a π bond. Because of the mutual repulsion of the electrons of different bonds (see p. 181), the π bond is in a plane perpendicular to that in which the σ bonds lie (see Fig. 14.17). When the bonds are so arranged, the molecule has the least potential energy, i.e., this state is the most stable.

Thus the two carbon—carbon bonds in the ethylene molecule are not equivalent—one of them is a σ bond, and the other, a π bond. This explains the peculiarities of the double bond in organic compounds. Overlapping of the orbitals is less in the π bond than in the σ bond, and the zones of high electron density lie further from the nuclei. For that reason the π bond is weaker than the σ bond, and because of the lower strength of the π bond, the energy of the C=C double bond is less than twice the energy of the C—C single bond (see Table 11.1); formation of two single σ bonds from a double bond results in a gain of energy, which accounts for the unsaturated character of organic compounds having a double bond.

Unlike the σ bond, the π bond has no cylindrical symmetry with respect to the axis connecting the centres of the atoms. Therefore, rotating one of the atoms round this axis changes the configuration of the electron clouds. From Fig. 14.17 it is readily seen that the π bond is broken if the atom is rotated through 90°, while the σ bond remains unchanged. Since considerable energy is required to break

the π bond, free rotation round the C—C bond in the C_2H_4 molecule is impossible. This gives rise to *cis—trans* isomerism in ethylene derivatives. On the other hand, if the molecule is subjected to the action of considerable energy, for instance, if the substance is heated the π bond may be ruptured and one of the carbon atoms may rotate through 180° about the σ bond, after which the π bond may form again; as a result a *cis* isomer is transformed into a *trans* isomer
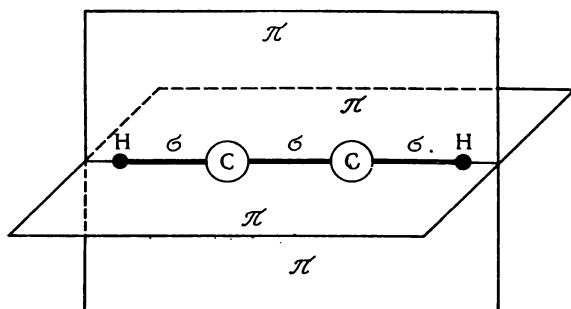
Fig. 14.18. Diagram showing formation of chemical bonds in C_2H_2 molecule

Such transformations are well known. For example, when maleic acid which has a *cis* configuration is heated, it is converted into fumaric acid, the *trans* isomer

Maleic acid → Fumaric acid
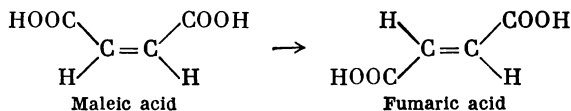
sp^2-Hybridization which determines the orientation of the chemical bond in ethylene also occurs in other molecules in which the carbon atom is joined to three other atoms or groups, for example, in the compounds

Carbonyl chloride (phosgene)   Formaldehyde   Formic acid
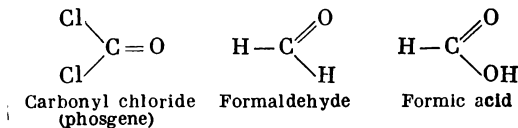
the bonds of the carbon atoms are in a single plane, and the angle between them is close to 120°.

Figure 14.18 is a diagrammatic representation of the arrangement of the bonds in the acetylene molecule, HC≡CH. In this case only two electrons of the carbon atom form hybrid orbitals through sp-hybridization. The two sp-hybrid orbitals are arranged at an angle of 180° to one another, forming a σ bond between the carbon

atoms, and also forming the C—H bonds. The C_2H_2 molecule has a linear configuration. The remaining two non-hybrid p-orbitals of the carbon atom are arranged at an angle of 90° to one another. They form two π bonds whose electron clouds lie about two mutually perpendicular planes.

Since the valence electrons of the carbon atom which are not involved in the formation of the triple bond are oriented at an angle of 180° to one another, such compounds, unlike carbon compounds containing a double bond, cannot exhibit *cis—trans* isomerism.
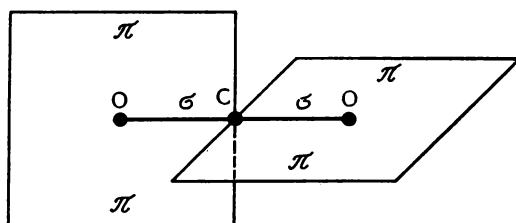
Fig. 14.19. Diagram showing formation of chemical bonds in CO_2 molecule

It should not be thought, however, that *cis—trans* isomerism is impossible in principle for compounds of the general formula A_2B_2. Thus the recently prepared difluorodiazine, N_2F_2, exists in two isomeric forms
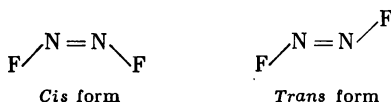
In this case the molecule is not linear, while the nitrogen atoms are joined by a double bond. Free rotation about such a bond is impossible. These factors bring about *cis—trans* isomerism.

The C—H bonds in acetylene formed by sp-hybrid orbitals are different in properties from the C—H bonds in saturated hydrocarbons formed from sp^3-orbitals. Thus, for example, the hydrogen in acetylene is rather easily replaced by metal, an instance being the precipitation of copper acetylide, Cu_2C_2, when acetylene is passed into solutions containing Cu^+.

sp-Hybridization likewise occurs in the molecule of carbon dioxide CO_2 (Fig. 14.19). Two sp-hybrid orbitals of the carbon atom form two σ bonds with the oxygen atoms, while the remaining, non-hybrid carbon orbitals form mutually perpendicular π bonds with the two p-orbitals of the oxygen atoms. This explains the linear structure of the CO_2 molecule.

A particular form of the chemical bond is found in the benzene molecule

$$\begin{array}{ccc} & CH & \\ HC & & CH \\ HC & & CH \\ & CH & \end{array}$$
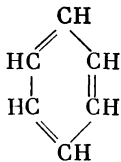
In this molecule each carbon atom is joined to two other carbon atoms and one hydrogen atom. As in the formation of ethylene and the other molecules considered above in which the carbon atoms are
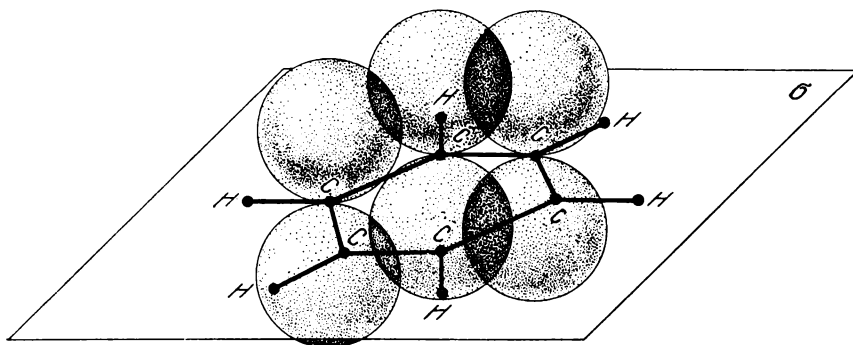
Fig. 14.20. Diagram showing formation of chemical bonds in C_6H_6 molecule (for the sake of simplicity only three p-orbitals are shown)

joined to three other atoms, sp^2-hybridization takes place in benzene. Three hybrid orbitals form three σ bonds, two with carbon atoms, and one with hydrogen, which are located in a single plane at angles of 120° to one another. This explains the flat configuration of the C_6H_6 molecule which has the form of a regular hexagon. The orbitals of the unhybridized p-electrons in C_6H_6, as in C_2H_4, are arranged perpendicular to the plane of the molecule. The diagram in Fig. 14.20 represents the surfaces of the wave functions of the p-electrons of the carbon atoms in the benzene molecule. It is evident that each p-orbital overlaps other p-orbitals on two sides. We know that overlapping of the orbitals of two atoms makes it possible for the electrons to be about both atoms. Since all the p-orbitals in the C_6H_6 molecule overlap one another, each p-electron can be about any of the carbon atoms. The π bonds in the benzene molecule bind all the carbon atoms in the same way, and it is impossible to say to which atoms each of the three pairs of electrons forming the π bonds belongs. In the C_6H_6 molecule the π bonds are *delocalized*. The p-electrons in the C_6H_6 molecule move along the ring of carbon atoms without meeting

resistance in the way, this takes place in some metals at very low temperatures, giving rise to the phenomenon of *superconductivity*.

The possibility of the electrons moving about all the carbon atoms in the C_6H_6 molecule lowers their kinetic energy, and consequently strengthens the bonds. This explains the chemical properties of benzene, particularly its diminished tendency to react by addition, as compared to ethylene and other unsaturated hydrocarbons.

Delocalization of the electrons also explains the properties of benzene derivatives. When one of the hydrogen atoms in the C_6H_6 molecule is replaced by some other atom or group, the latter strongly influences the probability of a second substituent occupying one of the possible positions—*ortho-*, *meta-* or *para-*. The mutual action of several functional groups in aromatic compounds is also great. These facts are explained by the extension of the perturbation of the electron cloud about one of the carbon atoms to the entire benzene ring. Thanks to the delocalization of the valence electrons, free radicals such as triphenyl-methyl are comparatively stable (see p. 116).

Since the π bonds in the C_6H_6 molecule are delocalized, it is evident that the structural formulae with double bonds employed in elementary discussions do not illustrate the actual electronic configuration of this molecule. The true structure of the C_6H_6 molecule is intermediate between the two variants represented by the following structural formulae:

(1)   (2)
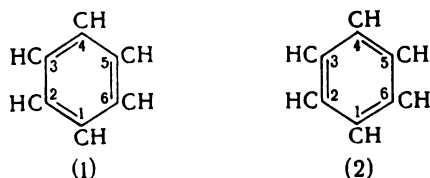
Since the three pairs of π-electrons shown by lines to indicate a double bond are distributed evenly among all the carbon atoms, the following representation of the C_6H_6 molecule corresponds more closely to the actual configuration
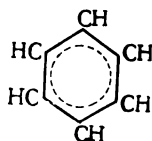
Here the dotted line indicates the delocalized π bonds. It is noteworthy that on the basis of an analysis of the behaviour of benzene in different reactions, the German chemist Thiele came to the con-

clusion that the double bonds in the C_6H_6 molecule were not localized and suggested the above formula as being the best representation of the molecule's structure. That was in 1899, long before the development of the quantum-mechanical theory of the chemical bond.

The conclusion that the bonds in the C_6H_6 molecule are intermediate in character between single and double bonds is borne out by the fact that their length (1.40 Å) lies between the lengths of the single and the double bond (1.54 ± 0.02 Å and 1.32 ± 0.02 Å, respectively) (Fig. 14.21).

The formation of delocalized electron pairs is characteristic not only of
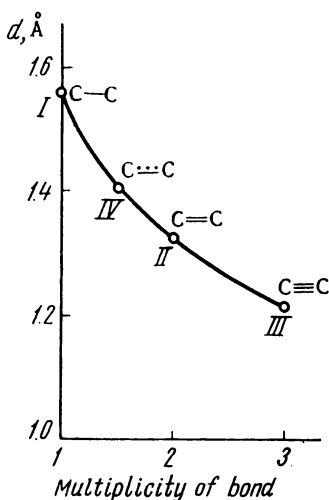
Fig. 14.21. Relationship between bond length and bond multiplicity

I—ethane; *II*—ethylene; *III*—acetylene; *IV*—benzene

the benzene molecule but also of many other organic molecules in which a carbon chain contains several carbon atoms near one another, each of which is joined to three other atoms. Examples of such molecules are

$$CH_2 = CH - CH = CH_2$$

$$CH_2 = CH - C {\diagup}^{CH_3}_{\diagdown CH_2}$$

$$CH_2 = CH - CH = CH - CH = CH_2$$
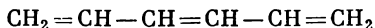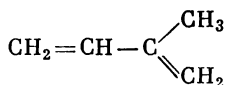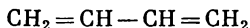
In these molecules, represented here in the traditional form, double bonds alternate with single bonds, forming what is called a *system of conjugated double bonds*. In such a system, as in the C_6H_6 molecule, the clouds of unhybridized *p*-electrons of all the carbon atoms overlap and the electrons can move freely along the chain of carbon atoms.

As was pointed out earlier (see p. 39), the movement of π-electrons in a system of conjugated bonds is similar to the movement of particles in a one-dimensional potential well. In many cases the spectra of compounds containing conjugated double bonds can be calculated with sufficient precision with the aid of this simple quantum-mechanical model. Examples of such calculations are given in Appendix IX.

It was noted above (p. 193) that neither the first nor the second structural ormula (valence diagram) of benzene reflects the properties of the latter, i.e., loes not correspond to the actual structure of its molecule. Let wave functions ψ_1 and ψ_2 correspond to these structures. What was said above signifies that ieither ψ_1 nor ψ_2 (each of which represents localized bonds) describes the benzene nolecule which is characterized by the presence of unlocalized π bonds. A linear :ombination of ψ_1 and ψ_2 would be a better approximation

$$\psi = c_1\psi_1 + c_2\psi_2 \tag{14.30}$$

which assumes equality of the length of all bonds. Each of the components of the mixed wave function ψ corresponds to the ultimate (unperturbed) structu-re (1) or (2).

Since the ultimate structures (1) and (2) differ only in the arrangement of the single and double bonds, it follows that $c_1 = c_2$; function ψ will correspond to the smaller value of energy, i.e., we approach the results of the correct solution of the Schrödinger equation.

The result is still more exact if five valence diagrams are introduced into the calculation, adding to (1) and (2) the following three structural formulae suggested by Dewar:

3   4   5
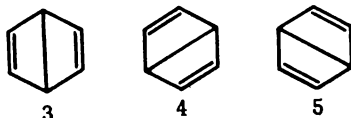
In that case the mixed wave function will have the form

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 + c_5\psi_5 \tag{14.31}$$

where ψ_3, ψ_4 and ψ_5 are wave functions for diagrams with diagonal bonds. Obviously, $c_3 = c_4 = c_5$, i.e., there are only two coefficients in (14.31). True, the energy of the electron states corresponding to structures (3), (4) and (5) is higher than for structures (1) and (2) since one of the π bonds in the Dewar structures is weaker than the others. Therefore, their contribution to the value of ψ will be less than that of the first two structures. This means that when calculating to a first approximation, one can limit oneself to ψ_1 and ψ_2 while ψ_3, ψ_4 and ψ_5 can be neglected.

The method of calculating the chemical bond in molecules considered above in its application to benzene is called the *method of valence diagram superposition (of resonance theory)*. The wave functions employed have the form

$$\psi = \sum c_i\psi_i \tag{14.32}$$

in which ψ_i in each of the components corresponds to a certain arrangement of the bonds in the molecule. The less the energy of the structure to which each ψ_i entering (14.32) corresponds, the greater its coefficient c_i (or as it is said, the greater its weight).

It goes without saying that the method of superimposing valence diagrams, which employs different variants of the representation of the wave function of electrons in the molecule (the C_6H_6 molecule, for example), which is less exact in (14.30) and more exact in (14.31), is only a mathematical technique. The true distribution of electron density in a molecule is absolutely definite, unique and unchanging in a given energy state. Therefore, it would be incorrect to think that benzene consists of a mixture of molecules in five different states, or that the molecular structure determining the properties of this compound is the superposition (resonance) of five actually existing structures. The super-position of valence diagrams cannot be considered a physical phenomenon. It is a method of quantum-mechanical treatment of the state of electrons whose

movement is not localized about a definite pair of electrons. This technique is only used in the method of electron pairs and has no place in the method of molecular orbitals, another extensively applied quantum-mechanical theory which we shall consider later.

It would, therefore, be a mistake to gather the idea from the method of superimposing valence diagrams that these structures actually exist, continually changing from one to another, a mistake to think that the superposition of structures stabilizes a molecule and accounts for its properties and even its existence, and that certain ultimate structures are responsible for certain properties of the molecule.

For complicate molecules, carrying out calculations when valence diagrams are superimposed involves great mathematical and computing difficulties. If n is the number of unlocalized electrons in a molecule, the number of independent valence diagrams which must be taken into account in the calculation will be

$$\frac{n!}{\frac{n}{2}!\left(\frac{n}{2}+1\right)!}$$

Accordingly, for naphthalene

it will be 42, while for anthracene
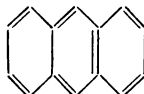
it will come to 429. In such cases calculations are very difficult and cannot be performed without a large number of assumptions, which greatly lowers the reliability of results.

During the 'forties and 'fifties when the resonance theory was the vogue, many chemists, acting without any quantum-mechanical substantiation, chose from a collection of valence diagrams those which it seemed to them were more in line with the properties of the compound in question, maintaining that its chemical behaviour was determined by the given structure. Naturally, it was necessary to use certain valence diagrams to explain some reactions of a compound, and other diagrams to explain other reactions. This often led to confusion and misunderstanding.

The sharp increase in the difficulty of calculating by the method of valence diagrams as the number of atoms in the molecule increased was one of the reasons prompting rapid development of other quantum-mechanical interpretations of the chemical bond.

14.7. The Donor-Acceptor Bond

We shall now examine the chemical bond in the carbon monoxide molecule CO. The distribution of electrons in the quantum cells in the excited carbon atom
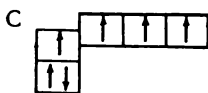
and in the oxygen atom
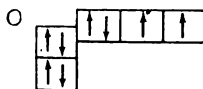
is such that the formation of two chemical bonds is possible since there are two unpaired electrons in the oxygen atom. However, when an electron is transferred from oxygen to carbon there will be·three unpaired electrons in each of the C^- and O^+ ions formed
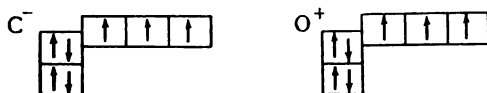
These ions have the same electronic configuration as the nitrogen atom (see p. 177). When the C^- and O^+ ions combine, a triple bond appears, similar to the bond in the N_2 molecule. It is evident that the triple bond is stronger than the double bond; its formation leads to a state having lower potential energy. Therefore it can be assumed that this bond is formed in the CO molecule. Actually, as is readily seen from Table 14.2, the physical properties of carbon monoxide and nitrogen are very close. This bears out the above assumption regarding the character of the bond in the CO molecule.

Table 14.2

The Properties of Carbon Monoxide and Nitrogen

Property	CO	N_2
Internuclear distance, Å	1.13	1.09
Ionization energy, eV	14.1	15.6
Bond-dissociation energy, kcal/mole	256	225
Melting point, °K	66	63
Boiling point, °K	83	78
Density in liquid state, g/cm³	0.793	0.796

A somewhat different course of reasoning which leads to the same result is also possible. The unexcited carbon atom has two unpaired
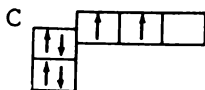
electrons which can form two shared electron pairs with the two un‑
paired electrons of the oxygen atom. But the two paired p-electrons
in the oxygen atom can form a third chemical bond since there is
an unfilled quantum cell in the carbon atom which can receive this
pair of electrons. *A chemical bond formed by a pair of electrons pre‑
viously belonging to one of the atoms is called a donor-acceptor bond.*
The terms *semipolar* and *coordinative* are also used for designating
this type of bond. The atom contributing to the electron pair is
called the *donor*, and the atom to which the pair is transferred is
called the *acceptor*. Shifting of the electron pair makes the bond
polar, which explains the origin of the term 'semipolar'.

In formulae the donor-acceptor bond is denoted by the signs $+$
and $-$ after the relevant atoms, which shows that an electron pair
is shifted to one of the atoms, or by an arrow which also indicates
the shift of an electron pair

$$C^- \equiv O^+ \qquad C \leftrightharpoons O$$

It should be noted that the above scheme of the chemical bond
in the CO molecule is only a first approximation. The transition of
an electron pair from the oxygen atom to be shared with the carbon
atom should make the molecule highly polar. Nevertheless the
dipole moment of carbon monoxide is very ·small, only 0.12 D.
On the basis of the above scheme this can be attributed to a certain
shift to the oxygen atom of the electron pair forming the bond.
Below (p. 210) is given a more exact description of the CO molecule
which also leads to the conclusion that the bond in this molecule
is triple.

We shall now consider several more molecules containing a donor-
acceptor bond.

The NH_3 molecule has the following electronic configuration:

$$
\begin{array}{c}
H \\
H \!:\! \overset{\displaystyle ..}{\underset{\displaystyle ..}{N}} \!:\! \\
H
\end{array}
$$

Three electron pairs form N—H bonds, while the fourth pair of outer
electrons belongs to the nitrogen atom alone. It can form a bond
with a hydrogen ion, resulting in the formation of an ammonium ion

$$
\begin{array}{c}
H \\
H\!:\!\overset{..}{\underset{..}{N}}\!:
\end{array}
+ H^+ \longrightarrow
\left[
\begin{array}{c}
H \\
H\!:\!\overset{..}{\underset{..}{N}}\!:\!H \\
H
\end{array}
\right]^+
$$
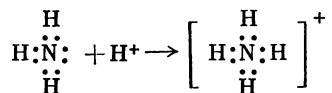
It follows that nitrogen in the NH_4^+ ion is tetravalent. It should
be emphasized that all four bonds in the ammonium ion are equiva‑
lent because of the electron density being evenly distributed among
them.

At this point it would be well to call attention to the fact that because of the free electron pair the dipole moment of ammonia is greater than the calculated value if only the shifting of the electron pairs of the N—H bonds is taken into account (this applies in an even greater degree to the H_2O molecule in which the oxygen atom has two unshared electron pairs). Ignoring the unshared pairs may even lead to an incorrect determination of the direction of the vector μ.

The ammonia molecule can also combine with other particles that can accept an electron pair, for example

$$
\begin{array}{cc}
\text{H} & \text{:F:} \\
\text{H:N:} + & \text{B:F:} \\
\text{H} & \text{:F:}
\end{array}
\rightarrow
\begin{array}{cc}
\text{H} & \text{:F:} \\
\text{H:N} & \text{:B:F:} \\
\text{H} & \text{:F:}
\end{array}
$$

In the compound

$$
\begin{array}{cc}
\text{H} & \text{F} \\
| & | \\
\text{H} - \text{N} \rightarrow \text{B} - \text{F} \\
| & | \\
\text{H} & \text{F}
\end{array}
$$
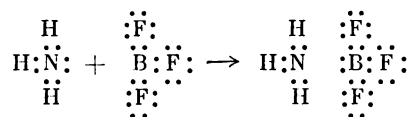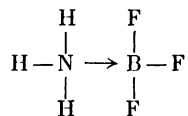
both nitrogen and boron are tetravalent.

Tetravalent nitrogen is also contained in nitric acid, the formula of which can be written

$$
\text{H} - \text{O} - \overset{+}{\text{N}} \overset{\displaystyle \nearrow \text{O}}{\underset{\displaystyle \searrow \text{O}-}{}}
$$
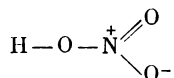
The transfer of one of the nitrogen electrons to oxygen results in the appearance of four unpaired electrons in the nitrogen atom, which can form four chemical bonds. Since the oxygen atoms joined only to nitrogen are the same, there is the same probability of an electron passing to either of them. For that reason the formula

$$
\text{H} - \text{O} - \text{N} \overset{\displaystyle \nearrow \text{O}}{\underset{\displaystyle \searrow \text{O}}{}}
$$
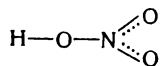
indicating that the fourth bond is divided evenly between the two oxygen atoms, represents the configuration of HNO_3 more exactly than the preceding one. The HNO_3 molecule has the structure shown in Fig. 14.22. It can be seen that the molecular structure corresponds to the foregoing formula: the N⋯O bonds are equal in length and shorter than the N—O bond.

In the isolated (vapour) state, the nitric anhydride molecule, N_2O_5, has the structure

$$O{\Large\diagdown}\!\!{\Large\diagup}N{-}O{-}N{\Large\diagup}\!\!{\Large\diagdown}O$$
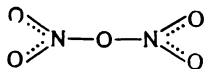
similar to the structure of HNO_3[1].

In $(NO_3)^-$ ion the unlocalized π bonds are uniformly distributed among all the oxygen atoms

$$\left(O{\Large\diagdown}\!{\underset{O}{\overset{N}{\diagup}}}\!{\Large\diagup}O \right)^-$$
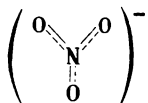
A donor-acceptor bond is likewise formed in H_2SO_4 and H_3PO_4. The electronic configuration of these molecules can be written
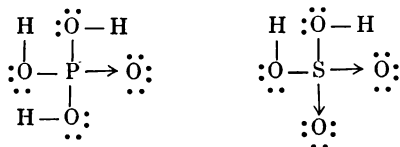
But the sulphur and phosphorus atoms, unlike nitrogen, have free *d*-orbitals in the outer shell, which are filled to a certain degree,
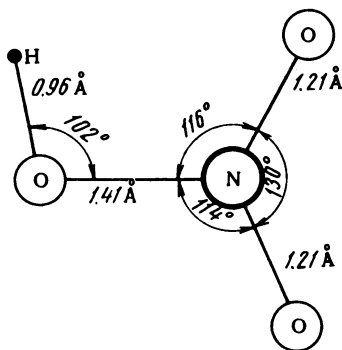
Fig. 14.22. Structure of nitric acid molecule

with the unshared electron pairs of the oxygen atoms. Thus the sulphur and phosphorus bonds with oxygen are intermediate between single and double. Their electronic configuration is better expressed

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[1] Investigations have demonstrated that crystalline nitrogen pentoxide is an ionic compound having the structure $(NO_2)^+ (NO_3)^-$ which is nitronium nitrate. In that case both nitrogen atoms in N_2O_5 are also tetravalent.

by the following formulae:
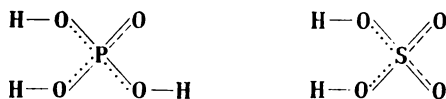
The effective charges on the oxygen atoms and the contribution of these atoms to the formation of π bonds are different depending on whether they are joined to hydrogen or not. This difference is shown by a dotted or a dashed line. In the $(PO_4)^{3-}$ and $(SO_4)^{2-}$ ions having a tetrahedral structure, the π bonds are equivalent; it can be expressed by structural formulae

This also applies to other oxygen-containing acids of elements of the third and following periods. So far as nitrogen is concerned, it cannot be pentavalent. It is evident that the impossibility of exhibiting covalence equal to the number of the group is also characteristic of the elements following nitrogen—oxygen and fluorine—because they have no d cells in their outer electron layer.

We see that the conventional structural representation of molecules, though very useful in giving an idea of the spatial sequence of atomic coupling, is often very inaccurate in portraying electron configuration. In many cases it is impossible in general to denote the features of electronic configuration by means of valence lines. It is urgently necessary to devise convenient and graphic methods of representing the chemical bond which will give more information about electronic configuration than the usual structural formulae.

14.8. The Bond in Electron-Deficient Molecules

There are molecules having fewer electrons than necessary for the formation of two-electron bonds. As an example we shall consider the diborane molecule B_2H_6. It would seem that its structure should be similar to that of ethane, but unlike the latter, diborane has only twelve valence electrons. Experimental findings show that the hydrogen atoms in the B_2H_6 molecule are not equivalent: four of them are easily replaced (e.g., by the CH_3 group), but replacement of the other two groups involves breakup of the molecule, for example, into two $B(CH_3)_3$ molecules. The non-equivalence of the hydrogen atoms in B_2H_6 is borne out by study of its nuclear magnetic

resonance. For that reason there are grounds for ascribing to diborane the following structure:

$$
\begin{array}{ccc}
H & H & H \\
\diagdown & \vdots & \diagup \\
B & & B \\
\diagup & \vdots & \diagdown \\
H & H & H
\end{array}
$$
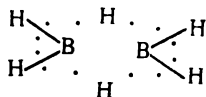
In this structure there are four two-electron terminal B—H bonds; the remaining four electrons unite the BH$_2$ radicals by means of
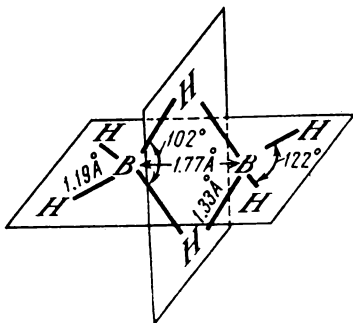
Fig. 14.23. Structure of diborane

hydrogen bridges lying in a plane perpendicular to the plane in which the boron atoms are located, and at a greater distance than the other hydrogen atoms. Thus a distorted tetrahedron is formed round each boron atom (Fig. 14.23).

Each hydrogen bridge atom forms with two boron atoms a common *two-electron three-centre* B—H—B *bond*. As regards energy this bond is more advantageous (by 14 kcal) than the usual two-centre bond, and is formed by the overlapping of two *sp*³-orbitals of the boron atoms and one *s*-orbital of the hydrogen atom
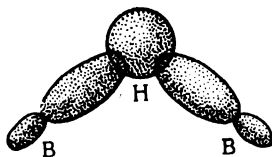
It is in this way that 'banana' bonds are formed:
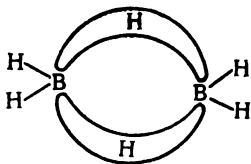
Electron-deficient compounds are electron acceptors. Therefore when B_2H_6 reacts with potassium, acceptance of electrons from the latter produces potassium boronate $K_2B_2H_6$, and as a result all the bonds become two-electron ones.

Other examples of electron-deficient molecules are $Al_2(CH_3)_2$ and $Be_2(CH_3)_4$.

14.9. Molecular Orbital Method

In addition to the difficulties encountered in carrying out calculations when employing the valence bond method discussed above, there are likewise, in a number of cases, difficulties of a fundamental character. Thus, investigations show that in some molecules it is not electron pairs that are involved in the formation of the chemical bond but individual electrons.

The possibility of the formation of a chemical bond by means of a single electron rather than an electron pair is seen most clearly in the case of the ionized hydrogen molecule H_2^+. This particle was discovered at the end of the 19th century by J. Thomson. It is formed when hydrogen molecules are bombarded with electrons. Spectroscopic studies show that the internuclear distance in this particle is 1.06 Å, and its bond energy 2.65 eV. Since there is only one electron in H_2^+, it is evident that in this molecule we have a one-electron bond.

Many polyatomic particles have unpaired electrons. Particular mention should be made of free radicals (see p. 115)., *Free radicals are highly reactive particles containing unpaired electrons.* Unpaired electrons are likewise found in some ordinary molecules, among them NO, NO_2 and ClO_2 which contain an odd number of electrons, and also in the oxygen molecule O_2. The latter is of particular interest for the theory of the chemical bond.

The oxygen atom has two unpaired electrons
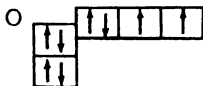
Therefore, on the basis of the valence bond method it could be expected that when two atoms combine, two electron pairs are formed and there are no unpaired electrons in the O_2 molecule. However, study of the magnetic properties of oxygen (see Appendix VIII) shows that there are two unpaired electrons in the O_2 molecule.

From the standpoint of the valence bond method it is not clear what part unpaired electrons play in the formation of the bond in the specified molecules. A number of investigators attempted to

improve the valence bond method and make it more suitable for interpreting these facts. Nevertheless, another approach to the explanation and calculation of the covalent bond, called the *molecular orbital method* (MO), has proved more fruitful. Formulation and development of this method was to a great extent due to the work of R. Mulliken (USA). It is apparently the best approach to the quantum-mechanical interpretation of the chemical bond we now have.

Whereas in the Heitler and London method a wave function (14.24) was set up describing the movement of both electrons in the H_2 molecule, the molecular orbital method proceeds from the wave functions of the individual electrons, the wave functions of the 1st, 2nd, ..., n-th electrons in the molecule being found, i.e.,

$$\psi_1, \ \psi_2, \ \ldots, \ \psi_n$$

It is thus considered that each electron in the molecule is found in a certain molecular orbital described by an appropriate wave function. Each orbital corresponds to a definite energy. In a single orbital there can be two electrons with opposite spins. Wave function ψ characterizing all the electrons in the molecule which are considered, can be found by multiplying the wave functions of the individual electrons

$$\psi = \psi_1\psi_2 \ldots \psi_n \qquad (14.33)$$

Approximate expressions are found for the above one-electron wave functions. As in the valence bond method, the variational principle is employed in selecting expressions which are closest to the correct expressions.

There are several variants of the molecular orbital method. In a method extensively used today, molecular one-electron wave functions are taken as linear combinations of the wave functions of the electrons in the atoms of which the molecule is composed. Since this form of the molecular orbital method is based on the linear combination of atomic orbitals it is known as the MO LCAO.

To make clear the peculiarities of one-electron molecular wave functions it would be well to examine the principle of the quantum-mechanical calculation of the simplest system, the ionized hydrogen molecule H_2^+.

Distances between particles in the H_2^+ molecule are shown in Fig. 14.24. The potential energy of the particles in the system is expressed by the relationship

$$U = \frac{e^2}{R_{ab}} - \frac{e^2}{r_a} - \frac{e^2}{r_b}$$

In accordance with what has been set forth above, the wave function of the electron in H_2^+ can be expressed by the relationship

$$\psi = c_1\psi_a + c_2\psi_b \qquad (14.34)$$

where ψ_a and ψ_b are the wave functions of the electron in the unexcited hydrogen atom determined by equation (14.21). The value of the coefficients in (14.34) can be found by the variational method. Two results are obtained,

$$c_1 = c_2$$

and

$$c_2 = -c_1$$

Consequently, two wave functions describing the movement of an electron in a system containing two nuclei are possible

$$\psi_S = c_S \, (\psi_a + \psi_b) \tag{14.35}$$

and

$$\psi_A = c_A \, (\psi_a - \psi_b) \tag{14.36}$$

The first is symmetric; the second, antisymmetric.

When the calculation of H_2^+ is carried out with the symmetric function, we obtain equilibrium distance $r_0 = 1.3$ Å, and the depth

Fig. 14.24. Distances between particles in the ionized H_2^+ molecule
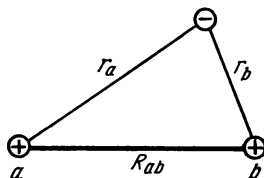
of the potential curve equal to 1.77 eV. According to experimental findings $r_0 = 1.06$ Å and the depth of the potential curve 2.79 eV, i.e., the calculation accords qualitatively with the experimental values. When the calculation is performed with the antisymmetric function (14.36) we find that in this case the H_2^+ molecule is not formed.

We shall now consider the physical meaning of the symmetric and antisymmetric wave functions, which in this case is somewhat different than in the calculation of the H_2 molecule by the Heitler—London method, since here we are concerned with only one electron.

In accordance with (14.21) and the diagram in Fig. 14.24, the expression for the antisymmetric wave function (14.36) has the form

$$\psi_A = \frac{c_A}{\sqrt{\pi}} \, (e^{-r_a} - e^{-r_b})$$

It is evident from the foregoing that when $r_a = r_b$, the wave function is equal to zero. In that case the value of ψ^2 which characterizes the probability of finding the electron also becomes zero. The set of points for which $r_a = r_b$ forms the molecule's *plane of symmetry*. Therefore, if the electron movement is described by the antisymmetric function, the probability of finding the electron in the molecule's plane of symmetry is equal to zero. In that case the electron cloud

will not be concentrated between the nuclei and the latter will be mutually repulsed. Therefore, if the electron movement is described by the antisymmetric function, the H_2^+ molecule will not be formed. Thus we can draw the general conclusion that an orbital described by an antisymmetric wave function will not bring about the formation of a chemical bond; on the contrary it will make a molecule unstable. Such an orbital is said to be *antibinding*.

As regards the symmetrical function, on the other hand, it can be seen from (14.35) that when $r_a = r_b$ the electron density between the nuclei is not equal to zero, its value exceeds the sum of the electron densities of the isolated hydrogen atoms at the same distance from the nucleus, since when (14.35) is squared, the member $2c_S\psi_a\psi_b$ appears in addition to the members $c_S^2\psi_a^2$ and $c_S^2\psi_b^2$. Thus a substantial part of the electron cloud is concentrated in the space between the nuclei, causing them to be drawn together and a chemical bond to be formed. An orbital described by a symmetrical function can accordingly be termed *binding*.

The foregoing conceptions form the basis of the LCAO variant. In this method electrons are added, one at a time, to the system of atomic nuclei 'fixed' in their equilibrium positions. The interaction of the electrons with one another is neglected in this case. When an electron is transferred from an atomic orbital to a molecular binding orbital its energy diminishes. Such an orbital stabilizes the system. Conversely, an antibinding orbital corresponds to a higher energy since it is more advantageous for the electron to be in the atom than in the molecule. The problem of the molecule stability comes down to the energy balance of all the binding and antibinding electrons it contains. As a rough approximation it can be considered that an antibinding electron neutralizes the effect of a binding electron. If a parallel is drawn with the valence bond method, it can conditionally be considered that the formation of a single bond depends on the presence in the molecule of two binding electrons whose effect is not counteracted by antibinding electrons.

We shall first consider qualitatively the results obtained with the molecular orbital method when applied to diatomic molecules formed from atoms of elements of the first and second periods, and then examine in greater detail the variant of the MO LCAO known as the *Hückel method*, which is extensively employed in organic chemistry.

14.10. Molecular Orbitals in Diatomic Molecules

Each electron in a molecule is characterized by a set of quantum numbers, as is the electron in the atom. The electron's energy in the atom depends on the values of the quantum numbers n and l. The magnetic quantum number m, which determines the magnitude

of the projection of the orbital momentum on any axis and characte-
rizes the position of the orbital in space, has no effect on the elect-
ron's energy. This is explained by the fact that in the atom there
is no preferred direction for the orientation of the orbital—all posi-
tions of the orbital are energetically equivalent. In the molecule
the situation is different. In the diatomic molecule there is one
direction which stands out from among all the others, this is the
direction of the line connecting the atomic nuclei. For that reason
the energy of the electron in a molecular orbital depends on the
position of the orbital.

The position of the molecular orbital in space is characterized
by the quantum number λ, which determines the magnitude of the
projection of the orbital momentum on the line connecting the atomic
nuclei in the molecule. It follows that in its physical meaning, the
molecular quantum number λ is analogous to the atomic quantum
number m. Like m, quantum number λ has the values $0, \pm 1, \pm 2, \ldots,$
denoted by the letters $\sigma, \pi, \delta, \ldots$ in the same way as the values of
l are denoted by the letters $s, p, d, \ldots$. Accordingly one speaks of
the σ-, π- and δ-states of the electron in the molecule.

According to the Pauli exclusion principle there can be two elect-
rons with different spins in a σ-orbital. There can be four electrons
in the π- and δ-orbitals; unlike the σ-orbital for which λ can only
be equal to zero, two values of λ are possible here—positive and
negative; for each of them there can be two values of spin.

Making use of the conceptions discussed, we shall now consider
the formation of diatomic molecules from atoms of elements of the
first period.

Formation of the molecule H_2^+ can be represented as follows:

$$H\,[1s] + H^+ \rightarrow H_2^+\,[\sigma 1s]$$
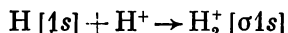
which shows that a binding σ-orbital is formed from a $1s$ atomic
orbital. Similarly we can represent the formation of the H_2 molecule

$$2H\,[1s] \rightarrow H_2\,[(\sigma 1s)^2]$$
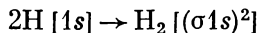
Two electrons in the hydrogen molecule occupy two binding orbitals
formed from $1s$ atomic orbitals. As was pointed out above, it can
conventionally be considered that two binding electrons correspond
to a chemical bond.

We now examine the structure of two unusual molecules He_2^+
and He_2. In the first molecule the three $1s$-electrons of the helium
atoms are to be assigned to molecular orbitals. Evidently two of
them will fill the binding $\sigma 1s$-orbital, while the third electron will
go into the antibinding σ^*1s-orbital (antibinding orbitals are custo-
marily indicated with an asterisk). Thus the He_2^+ molecule will
have the electronic configuration

$$He_2^+\,[(\sigma 1s)^2\,(\sigma^*1s)]$$
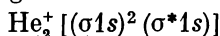
In it there are two binding electrons and one antibinding electron, and according to the above rule such a molecule should be stable. Actually the He_2^+ molecule does exist though less stable than the H_2 molecule since the bond energy in He_2^+ (70 kcal/mole) is less than in H_2 (104 kcal/mole).

If an He_2 molecule is to be formed, the four 1s-electrons of the atoms must be in molecular orbitals. It is evident that two of them would occupy a binding orbital, the other two, an antibinding orbital

$$He_2 \, [(\sigma 1s)^2 \, (\sigma^* 1s)^2]$$
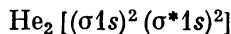
But as was stated above an antibinding electron neutralizes the effect of a binding orbital (actually the antibinding electron is even somewhat stronger than the binding electron), and therefore such a molecule cannot exist. Thus the molecular orbital method, like the valence bond method, demonstrates the impossibility of the formation of the He_2 molecule.

We next consider molecules formed from the atoms of elements of the second period. In these molecules it can be considered that the electrons of the first electron shell (the K-shell) of the atoms are not involved in the formation of the chemical bond but constitute the core, denoted by the letter K in representations of the molecular structure. It must also be borne in mind that since the p-electrons in the atom can have a quantum number m equal either to 0 or to ± 1, they can fill both σ- and π-orbitals.

Studies of molecular spectra have demonstrated that the orbitals of the molecules in question are arranged in the order of increasing energy as follows:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p < \pi 2p < \pi^* 2p < \sigma^* 2p$$

$$z\sigma < y\sigma^* < x\sigma < w\pi < v\pi^* < u\sigma^*$$

There is little difference in the energy of electrons in the $\sigma 2p$- and $\pi 2p$-orbitals, and in some molecules (B_2, C_2, N_2, O_2) the relationship between them is the reverse of that given because the $\sigma 2p$ level is higher than the $\pi 2p$ level. The above sequence determines the order in which the molecular orbitals are filled: when molecules are formed the electrons arrange themselves in orbitals with the lowest energy. In the line under the symbols of the orbitals are other denotations suggested by Mulliken (the symbols of the molecular orbitals are preceded by the letters of the Latin alphabet in the reverse order). This makes the notation more compact. Both systems are used in the literature.

In accordance with the foregoing, formation of the Li_2 molecule can be written

$$2 Li \, [K2s] \rightarrow Li_2 \, [KK \, (\sigma 2s)^2]$$
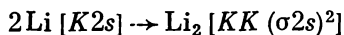
This molecule has two binding electrons.

The Be_2 molecule should have the following electronic configuration

$$Be_2 [KK (\sigma 2s)^2 (\sigma^* 2s)^2]$$

in which there are four electrons in molecular orbitals, two from each atom. In such a molecule the number of binding and antibinding electrons would be equal, and therefore it should be unstable. Like the He_2 molecule, the Be_2 molecule has not been discovered.

In the B_2 molecule there are six electrons in molecular orbitals, the electronic configuration being

$$B_2 [KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^2]$$

In this molecule there are two electrons on the $\pi 2p$ level which can accommodate four electrons. In accordance with Hund's rule they should have parallel spins. Actually, experimental investigations show that the molecule has two unpaired electrons.

In the carbon molecule, C_2, there are eight electrons in molecular orbitals. The molecule has the configuration

$$C_2 [KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^4]$$

There are two antibinding electrons in the C_2 molecule, and six binding electrons—an excess of four. Consequently it can be considered that the bond is double.

When the nitrogen molecule is formed ten electrons must be accommodated in molecular orbitals. In accordance with the sequence of filling the orbitals given above, the configuration of the N_2 molecule should be

$$N_2 [KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^4 (\sigma 2p)^2]$$

or in the alternative notation

$$N_2 [KK (z\sigma)^2 (y\sigma^*)^2 (w\pi)^4 (x\sigma)^2]$$

It follows that there are eight binding electrons in the nitrogen molecule, and two antibinding electrons, i.e., an excess of six binding electrons, that is the N_2 molecule has a triple bond. The formation of the molecular orbitals in the nitrogen molecule is illustrated in Fig. 14.25. For simplicity, only the formation of molecular orbitals from $2p$ atomic orbitals is shown.

In the O_2 molecule 12 electrons must be distributed among molecular orbitals. The molecule has the following configuration:

$$O_2 [KK (z\sigma)^2 (y\sigma^*)^2 (w\pi)^4 (x\sigma)^2 (v\pi^*)^2]$$

In this molecule there are only two electrons in the $v\pi^*$ antibinding orbital, although four are possible. In accordance with Hund's rule they should have parallel spins. This is not at variance with Pauli's exclusion principle, since one electron will have $\lambda = 1$, and the other, $\lambda = -1$. Thus the molecular orbital method explains the presence of two unpaired electrons in the molecule, which ac-

counts for oxygen's paramagnetism (see'Appendix VIII). The excess of binding electrons in the O_2 molecule comes to four.

The fluorine molecule has the electronic configuration

$$F_2 [KK (z\sigma)^2 (y\sigma^*)^2 (x\sigma)^2 (w\pi)^4 (v\pi^*)^4]$$
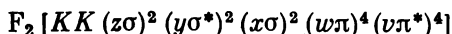
Here there is an excess of two binding electrons, and the bond is single.

It is evident that in the molecule

$$Ne_2 [KK (z\sigma)^2 (y\sigma^*)^2 (x\sigma)^2 (w\pi)^4 (v\pi^*)^4 (u\sigma^*)^2]$$
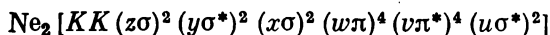
there would be an equal number of binding and antibinding electrons. Therefore, like the He_2 molecule, it is not formed.
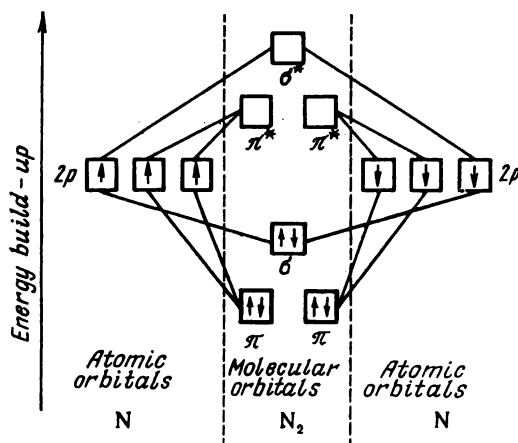
Fig. 14.25. Diagram of formation of molecular orbitals in N_2 molecule (only the 2p-electrons of the N atoms are shown)

It is interesting to examine the change in bond energy and bond length in the molecules discussed above. The data are given in Table 14.3. We see that an increase in the excess of binding electrons increases the strength of the bond. As we pass from Li_2 to N_2 the interatomic distance diminishes. This is due to the reduction in the size of the atoms because of the charge on the nucleus and to the increase in the strength of the bond. From N_2 to F_2 the bond length increases due to weakening of the bond. This explains the regularities in the change in the covalent radii of atoms (see p. 92).

We shall now consider some diatomic molecules formed from different atoms.

In the CO molecule there are 10 valence electrons in the orbitals, and the electronic configuration is the same as in the N_2 molecule

$$CO [KK (z\sigma)^2 (y\sigma^*)^2 (w\pi)^4 (x\sigma)^2]$$
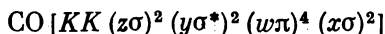
Table 14.3

Characteristics of Diatomic Molecules

Molecule	Li$_2$	B$_2$	C$_2$	N$_2$	O$_2$	F$_2$
Excess of binding electrons	2	2	4	6	4	2
E_{bnd}, kcal/mole	25	69	150	225	118	36
Interatomic distance, Å	2.67	1.59	1.31	1.10	1.21	1.42

The fact that the N_2 and CO molecules have the same electronic configuration, thus demonstrated by the molecular orbital method, logically explains the similarity in properties of the two substances (see p. 197).

The excess of binding electrons in the CO molecule is 6, and accordingly the bond can be considered triple, thus we have arrived in a different way at the conclusion drawn on p. 197.

In the NO molecule there are 11 electrons in the orbitals, which gives the configuration

$$NO \, [KK \, (z\sigma)^2 \, (y\sigma^*)^2 \, (w\pi)^4 \, (x\sigma)^2 \, (v\pi^*)]$$
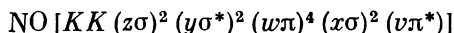
It can be seen that there is an excess of 5 binding electrons. In the ionized NO^+ molecule there is an excess of 6 binding electrons

$$NO^+ \, [KK \, (z\sigma)^2 \, (y\sigma^*)^2 \, (w\pi)^4 \, (x\sigma)^2]$$
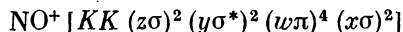
Therefore, the NO^+ molecule should be more stable than the NO molecule. Actually, whereas the bond energy in NO is 149 kcal/mole, it is 251 kcal/mole in NO^+. Nevertheless, $E_{CO^+} = 192$ kcal/mole is less than $E_{CO} = 256$ kcal/mole.

Thus even this small number of examples shows how effective the molecular orbital method is in interpreting and foretelling the properties of molecules.

14.11. Hückel Method

During recent years the molecular orbital method has been employed for calculating the characteristics of a very large number of molecules. It has been extensively applied even in fields of science where a few score years ago the very idea of the possibility of using quantum mechanics seemed sheer fantasy, such as the theory of organic reactions, biochemistry, molecular biology. The variant of the MO

LCAO suggested by E. Hückel has found particularly wide application in the above fields.

The Hückel method is employed to find the energy and wave functions of electrons forming delocalized π bonds. An enormous number of molecules containing such bonds are known, and they play a very important part in many organic·reactions and biological processes.

It was pointed out above (p. 194) that the movement of the electron in a system of delocalized π bonds can be examined by means of a one-dimensional potential well model. However, this does not always give correct results, since the model is very crude. Moreover, it only determines the energy level of electrons, and provides no information about the distribution of electronic density in molecules or the strength of the bond between atoms. For that reason such examinations find only limited application. The Hückel method is incomparably more effective.

Three conceptions have taken shape through the use of this method, which are of great importance in modern organic chemistry; they are ideas about the *bond order*, *π-electron density* and *the free valence index*. We shall now characterize these conceptions in the most general terms and show their applicability; a strict formulation will be given below after summarizing the essence of the method discussed.

It was previously stated that chemical bonds in molecules with delocalized electrons could be regarded as intermediate between single and double. The conception of the bond order characterizes this idea quantitatively. If the bond order is equal to one, the bond should be considered single, and if equal to two, double, but there can be intermediate values. The higher the bond order, the stronger it is, provided other conditions are the same. In the structural formula of butadiene

$$H_2C \xrightarrow{\ 1.894\ } CH \xrightarrow{\ 1.447\ } CH \xrightarrow{\ 1.894\ } CH_2$$
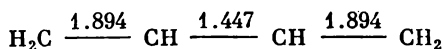
the figures over the bonds indicate their order[1]. These values were found by using the Hückel method. It is evident that the bond order is higher at the ends of the chain.

The π electron density characterizes the probability of a delocalized π-electron being found about the atom under consideration. The higher this value, the more negatively charged is the atom. This determines the direction of transformation of a molecule under the action of charged particles. Thus, for example, in the nitrobenzene molecule

---

[1] In such formulae where figures characterizing the bond are given, all bends are usually denoted with a single line.

NO$_2$

0.79 0.79

0.95 0.95

0.61
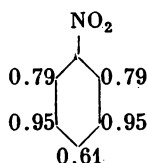
the π electron density is indicated with figures beside the atoms. It can be seen that these values are highest for atoms *meta* to the nitro group. Consequently, when nitrated (acted upon by NO$_2^+$ ions), the second nitro group will for the most part occupy the *meta* position. Thus the quantum-mechanical calculation explains why it is mostly meta-dinitrobenzene that is obtained through the nitration of nitrobenzene. The free valence index characterizes the ability of an atom in a molecule to react with neutral atoms and free radicals. This characteristic is denoted by an arrow pointing to the value. Thus in butadiene the free valence indices will be

H   H   H   H

C ——— C ——— C ——— C

H   H

0.838   0.391   0.391   0.838
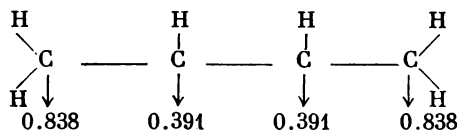
From this we can conclude that when butadiene is reacted with neutral atoms (e.g. on bromination) the latter will be added to the end carbon atoms, and this is found to be the case. The values of the free valence indices for naphthalene

0.452

0.104   0.404
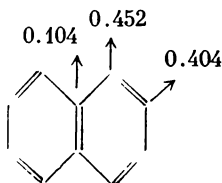
show bromination of naphthalene produces α-bromonaphthalene

Br
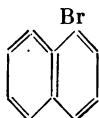
which fully accords with experimental findings.

We shall first consider the application of the Hückel method for the simplest case, the ethylene molecule CH$_2$=CH$_2$.

The structure of this molecule (carbon skeleton) can be represented by a diagram showing the carbon atoms and the bond between them

1   2

○———○

There are two electrons here which form a π bond, and it is to them that the calculation by the Hückel method relates. The wave function for each of these electrons, in accordance with the requirements of the molecular orbital method, is formed from the wave functions of the p-electrons of the carbon atoms φ_1 and φ_2

$$\psi = c_1\varphi_1 + c_2\varphi_2$$

For our discussion there is no need to know the formulae expressing φ_1 and φ_2, so we shall only note that in cases where they are required, the approximate expressions for the wave functions of electrons as obtained by Slater are usually taken.

As was pointed out previously (p. 165), in order to find coefficients c_1 and c_2 a system of secular equations must be set up and the secular determinant equated to zero.

The secular equations in our problem have the form

$$\left. \begin{array}{l} (H_{11} - ES_{11})\, c_1 + (H_{12} - ES_{12})\, c_2 = 0 \\ (H_{21} - ES_{21})\, c_1 + (H_{22} - ES_{22})\, c_2 = 0 \end{array} \right\} \qquad (14.37)$$

The integrals in these relationships have the following expressions and names:

$$S_{11} = \int \varphi_1\varphi_1\, dv = \int \varphi_1^2\, dv = 1 \text{ and } S_{22} =$$

$$= \int \varphi_2\varphi_2\, dv = \int \varphi^2\, dv = 1 \quad \text{—normalization integrals}$$

$$H_{21} = H_{12} = \int \varphi_1 H \varphi_2\, dv \qquad \begin{array}{l}\text{—exchange (or reso-}\\ \text{nance) integrals}\end{array}$$

$$S_{12} = S_{21} = \int \varphi_1\varphi_2\, dv \qquad \text{— overlap integrals}$$

$$H_{11} = \int \varphi_1 H \varphi_1\, dv \text{ and } H_{22} = \int \varphi_2 H \varphi_2\, dv \quad \text{—Coulomb integrals}$$

The expressions for the Coulomb and exchange integrals contain the Hamiltonian, but it does not enter the normalization or overlap integrals. The Coulomb integral contains two like functions, and the exchange integral, different functions. A similar difference is found in the normalization and overlap integrals.

The following assumptions are made in the Hückel method: (1) exchange integrals for wave functions not relating to neighbouring carbon atoms are considered equal to zero; (2) exchange integrals for any neighbouring carbon atoms are alike; all Coulomb integrals are also alike; (3) all overlap integrals are considered equal to zero. It is clear that these assumptions are very crude but they greatly simplify calculations. The last assumption seems the least substantiated since calculations show that the overlap integral containing

the wave functions of the p-electrons of neighbouring carbon atoms is approximately equal to 0.25. Nevertheless, more rigid treatment of the problem, including overlap integrals, has demonstrated that the error introduced by assumption (3) is not very great. Nor should it be thought that the overlap integral must not be equated to zero since the chemical bond originates as the result of the overlapping of atomic orbitals. It must be borne in mind that this overlapping also brings about the appearance of the exchange integral whose contribution to the bond energy is substantially greater than that of the overlap integral. Therefore the latter can be neglected when calculating to a first approximation.

In the simple problem under consideration assumptions (1) and (2) are not made, since the two carbon atoms in the ethylene molecule are neighbours. As a result of assumption (3) and the fact that the normalization integrals are equal to unity, the system of secular equations acquires a simpler form

$$(H_{11} - E) c_1 + H_{12}c_2 = 0 \atop H_{21}c_1 + (H_{22} - E) c_2 = 0 \Bigg\} \qquad (14.38)$$

The Coulomb integrals are customarily denoted by the letter α, and the exchange integrals, by the letter β[1]. In that case (14.38) has the form:

$$(\alpha - E) c_1 + \beta c_2 = 0$$
$$\beta c_1 + (\alpha - E) c_2 = 0$$

We divide both equations by β and substitute x from the equation

$$\frac{\alpha - E}{\beta} = x \qquad (14.39)$$

The system of secular equations is written in the final form

$$xc_1 + c_2 = 0 \atop c_1 + xc_2 = 0 \Bigg\} \qquad (14.40)$$

Equating the secular determinant to zero, we have

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = x^2 - 1 = 0$$

from which $x = \pm 1$. Substituting $x = -1$ and $x = 1$ in (14.39), we obtain two expressions for the energy of the electrons

$$E_1 = \alpha + \beta \qquad (14.41)$$

---

[1] In the Hückel method the values of α and β are found from experimental data, β being calculated from a comparison of the bond energy in different compounds. The numerical values of α and β are rarely used; ordinarily when explaining or foretelling the properties of compounds, relationships are employed in the general form containing the parameters α and β.

and

$$E_2 = \alpha - \beta \qquad (14.42)$$

We have obtained two relationships expressing the energy of the electrons forming the π bond in the C_2H_4 molecule. Exchange integral β is always negative, and consequently energy E_1 is less than E_2. Equation (14.41) determines the energy of the binding orbital; equation (14.42), the energy of the antibinding orbital. In the unexcited C_2H_4 molecule, the two electrons under consideration will be in the state having the lowest energy, i.e., they will be in the binding orbital. This is shown diagrammatically in Fig. 14.26.
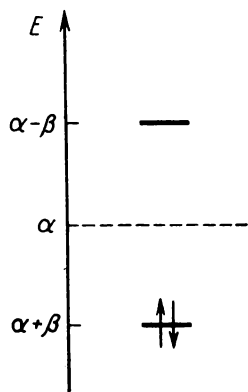
We shall now find the values of the coefficients in the wave function expression. For the binding orbital $x = -1$. Substituting this value of x in (14.40), we have

$$c_1 = c_2 \text{ or } c_1/c_2 = 1 \qquad (14.43)$$

Fig. 14.26. Energy levels of π-electrons in ethylene

We have obtained an expression determining the relationship of the coefficients. To determine their absolute values we must make use of the normalization equation

$$\int \psi^2 \, dv = \int (c_1\varphi_1 + c_2\varphi_2)^2 \, dv = 1 \qquad (14.44)$$

Opening the parentheses, we obtain

$$c_1^2 \int \varphi_1^2 \, dv + 2c_1c_2 \int \varphi_1\varphi_2 \, dv + c_2^2 \int \varphi_2^2 \, dv = 1$$

Since the atomic wave functions φ_1 and φ_2 have been normalized, the first and last integrals are equal to unity. The second integral—the overlap integral—is considered equal to zero in the Hückel method, from which we obtain

$$c_1^2 + c_2^2 = 1 \qquad (14.45)$$

Taking account of (14.43) and (14.45), we have

$$c_1 = c_2 = \frac{1}{\sqrt{2}}$$

Thus the expression for the wave function of the binding orbital is

$$\psi = \frac{1}{\sqrt{2}} (\varphi_1 + \varphi_2) \qquad (14.46)$$

Carrying out similar operations with $x = 1$, we find

$$c_1 = \frac{1}{\sqrt{2}} \quad \text{and} \quad c_2 = -\frac{1}{\sqrt{2}}$$

from which we have for the antibinding orbital

$$\psi_1 = \frac{1}{\sqrt{2}} (\varphi_1 - \varphi_2) \tag{14.47}$$

We have found expressions for the energy and wave functions of the π-electrons in the C_2H_4 molecule, i.e., we have solved the given quantum-mechanical problem.

We shall now consider a more complicated example, the state of the π-electrons in the free allyl radical

$$\begin{array}{ccc} CH_2 = CH - CH_2 - \\ 1 \quad\ 2\ \ \quad 3 \end{array}$$
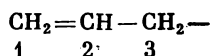
There are equal grounds for representing the structure of this particle by the formula

$$\begin{array}{ccc} - CH_2 - CH = CH_2 \\ 1 \qquad 2 \qquad 3 \end{array}$$
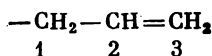
This shows that the π bonds in this structure are not localized. Three electrons not involved in the formation of σ bonds are to be assigned to π molecular orbitals. (In the Hückel method the σ bonds are not taken into account, it being considered that they do not interact in any way with the π bonds.)

The structure of the carbon skeleton is represented by the diagram

$$\begin{array}{ccc} \textit{1} & \textit{2} & \textit{3} \\ \circ\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!\!&\!\!\!\!-\!\!\!-\!\!\circ\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!\!&\!\!\!\!-\!\!\!-\!\!\circ \end{array}$$
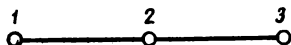
and the wave function of the electron, by the relationship

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3$$

where φ_1, φ_2 and φ_3 are the wave functions of the p-electrons in the corresponding carbon atoms.

The system of secular equations has the form

$$(H_{11}-ES_{11})\, c_1+(H_{12}-ES_{12})\, c_2+(H_{13}-ES_{13})\, c_3=0$$
$$(H_{21}-ES_{21})\, c_1+(H_{22}-ES_{22})\, c_2+(H_{23}-ES_{23})\, c_3=0$$
$$(H_{31}-ES_{31})\, c_1+(H_{32}-ES_{32})\, c_2+(H_{33}-ES_{33})\, c_3=0$$

With the assumptions given above and using the brief notation, it has the form

$$\left.\begin{array}{l} xc_1 + c_2 = 0 \\ c_1 + xc_2 + c_3 = 0 \\ c_2 + xc_3 = 0 \end{array}\right\} \tag{14.48}$$

The secular determinant has the solution

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} = x\,(x^2 - 1) - x = x^3 - 2x = $$
$$= x\,(x^2 - 2) = 0$$

From this we find three values of x

$$x_1 = 0; \quad x_2 = -\sqrt{2}; \quad x_3 = \sqrt{2}$$

Substituting each of these values in relationship (14.39), we obtain three expressions for the energy

$$E_1 = \alpha; \quad E_2 = \alpha + \sqrt{2}\beta; \quad E_3 = \alpha - \sqrt{2}\beta$$

We now examine the expressions obtained.

The first relationship does not contain the exchange integral β. The energy of the electron in the corresponding orbital is practically the same as in isolated atom—the Coulomb integral α expresses the energy of electrons in the absence of a chemical bond. This orbital is termed *nonbinding*. According to the Hückel method, an electron in such an orbital has no influence on the strength of the bond. This is, of course, over-simplification; actually, this electron does make a certain contribution to the energy of the bond, but it is not great, and can be neglected in a rough evaluation.
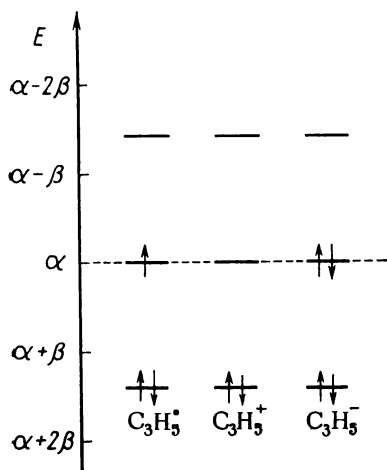
Fig. 14.27. Energy levels of π-electrons in C_3H_5 radical and in ions formed from it

The second expression gives the lowest value of E (the exchange integral is negative). This energy corresponds to a binding orbital. The third relationship gives the greatest energy, such an electron occupies an antibinding orbital.

Figure 14.27 gives a diagram of the energy levels in particles having the formula C_3H_5. In the neutral radical C_3H_5 there are three electrons in the Hückel molecular orbitals—two occupy a binding orbital, and one, a nonbinding orbital. In the $C_3H_5^+$ ion there are no electrons in the nonbinding orbital, but in the $C_3H_5^-$ ion there are two electrons in this orbital.

We now find the coefficients in the wave function expressions. For their calculation we must use the normalization equation; it is similar to (14.44) and gives the expression

$$c_1^2 + c_2^2 + c_3^2 = 1 \tag{14.49}$$

analogous to (14.45).

For the nonbinding orbital $x = 0$. Substituting this value in the system of secular equations and taking account of (14.49), we find

$$c_1 = \frac{1}{\sqrt{2}}; \quad c_2 = 0; \quad c_3 = -\frac{1}{\sqrt{2}}$$

The wave function is written

$$\psi_1 = \frac{1}{\sqrt{2}} \varphi_1 - \frac{1}{\sqrt{2}} \varphi_3$$

It can be seen that the electron cloud of the nonbinding orbital is concentrated about end atoms 1 and 3, wave function φ_2 is absent from the expression for the molecular orbital. Therefore, this electron has no appreciable influence on the strength of the bond.

For the binding orbital $x = -\sqrt{2}$. Using this value in the same way, we obtain

$$c_1 = c_3 = \frac{1}{2}; \quad c_2 = \frac{1}{\sqrt{2}}$$

The wave function is determined by the expression

$$\psi_2 = \frac{1}{2} \varphi_1 + \frac{1}{\sqrt{2}} \varphi_2 + \frac{1}{2} \varphi_3$$

The examples discussed give an idea of the Hückel method. The calculation procedure is standard. Solution of the secular determinant gives the values of parameter x from which are found the expressions for energy and the values of the coefficients in the wave function equations. The delocalized π-electrons are then assigned to the orbitals with the lowest energy.

The highest power of x in the equation obtained by opening the secular determinant is equal to the number of atoms in the molecule under consideration (for ethylene, a quadratic equation is obtained; for allyl, a cubic equation). Therefore, when performing calculations for polyatomic molecules, algebraic equations of a high power must be solved. Various mathematical techniques are known which make it possible to find the roots of such equations with a high degree of accuracy.

Computational difficulties are substantially less in the molecular orbital method than in the valence bond method. Whereas, when examining delocalized π bonds by the MO method, the power of the algebraic equation obtained is equal to the number of atoms in the molecule, it is equal to the number of valence diagrams used, when

employing the valence bond method. We have seen (p. 195) that even for fairly simple molecules the number of valence diagrams is high.

We shall now consider calculation of π electron densities, bond orders and free valence indices.

Electron density q, created by an electron on atom r under consideration, is determined by the square of the coefficients c_r with which the orbital of atom r enters the expression for the molecular wave function. The total electron density is taken as the sum of the electron densities created by each electron. It can be expressed by the equation

$$q_r = \sum_j n_j c_{jr}^2 \qquad (14.50)$$

where q_r is the electron density on atom r; c_{jr}, the coefficient for the wave function of atom r in the expression for the j molecular orbital occupied by n electrons. Thus for atom 1 in ethylene

$$q_1 = 2 \left(\frac{1}{\sqrt{2}} \right)^2 = 1$$

The same value of q is obtained for atom 2.

In allyl

$$q_1 = q_3 = 2 \left(\frac{1}{2} \right)^2 + \left(\frac{1}{\sqrt{2}} \right)^2 = 1$$

$$q_2 = 2 \left(\frac{1}{\sqrt{2}} \right)^2 = 1$$

Here, too, the electronic density on all atoms is equal to unity.

Bond order p is characterized by the contribution of neighbouring atoms (they can be denoted r and s) to the overlapping of the orbitals. It is determined by the product of the coefficients for the corresponding atomic wave functions, the sum of these values for all the electrons being taken

$$p_{rs} = \sum n_j c_{jr} c_{js} \qquad (14.51)$$

Thus for ethylene we obtain

$$p_{12} = 2 \left(\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} \right) = 1$$

For allyl

$$p_{12} = p_{23} = 2 \left(\frac{1}{2} \cdot \frac{1}{\sqrt{2}} \right) = \frac{1}{\sqrt{2}} = 0.707$$

The electron in the nonbinding orbital makes no contribution to the bond order, since for it $c_2 = 0$.

The above calculation gives the order of the π bond; to find the complete bond order, unity must be added, that is the order of

the σ bond. Thus the bond orders in ethylene and allyl will be

$$CH_2 \overset{2.00}{=\!=\!=\!=} CH_2; \quad CH_2 \overset{1.707}{=\!=\!=\!=} CH \overset{1.707}{=\!=\!=\!=} CH_2 \text{—}\!—$$
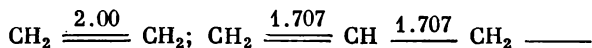
Free valence index F is determined by the relationships

$$F = N_{max} - N_r \qquad (14.52)$$

$$N_r = \sum p_{rs}$$

where N_r is the sum of the bond orders of all the π bonds in which atom r is involved, and N_{max}, the maximum value of the bond possible for the carbon atom; it is realized in the radical trimethylenemethane

$$\begin{array}{c} 3 \\ CH_2 \\ \| \\ C1 \\ 2\diagup \quad \diagdown 4 \\ \text{—}H_2C \quad\quad CH_2\text{—} \end{array}$$
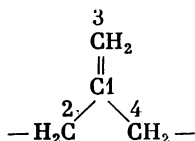
In this particle, the order of the π bond of the C atom is equal to $\sqrt{3} = 1.732$ which is the maximum value of N possible. Using relationship (14.52) and the values of the bond orders of the π bonds already obtained, we find the free valence indices in ethylene and allyl

$$\begin{array}{ccccc} 0.732 & 0.732 & 1.025 & 0.348 & 1.025 \\ \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ H_2C \!=\!=\! CH_2 & & CH_2 \!=\!=\! CH\text{——}CH_2\text{——} \end{array}$$
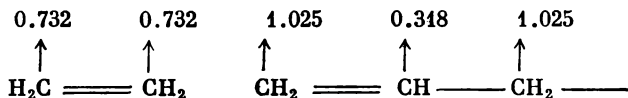
CHAPTER FIFTEEN

THE IONIC BOND

15.1. Energy of the Ionic Bond

Ionic molecules are something chemists encounter incomparably less often than particles in which the atoms are joined by a covalent bond. As we shall see later (p. 278) there are no individual molecules in ionic crystals. In most solutions of ionic compounds their molecules are also not found, since when dissolved in polar solvents, such as water, alcohols, etc., ionic compounds are completely dissociated, while in nonpolar solvents, CCl_4, C_6H_6, etc., they are insoluble.

Ionic molecules can be detected in the vapours of ionic compounds. As we know, such substances must be heated to a high temperature if they are to be vaporized. It should be noted that the vapours of ionic compounds contain not only molecules but other particles as well—associates of several molecules, and also simple and complex ions. In the vapour of sodium chloride, for example, are found, in addition to NaCl molecules, such associates as $(NaCl)_2$ and $(NaCl)_3$, and the ions Na_2Cl^+ and $NaCl_2^-$.

Since the attraction of ions obeys Coulomb's law, it is comparatively easy to calculate the energy of the bond for ionic molecules. If ions are regarded as undeformed charged spheres, the attraction between them is determined by Coulomb's law

$$f_{attr} = \frac{e_1 e_2}{r^2} \qquad (15.1)$$

where f_{attr} is the force with which ions at a distance r and bearing charges e_1 and e_2 are attracted to one another. The energy of the interionic bond which is liberated when oppositely charged ions approach
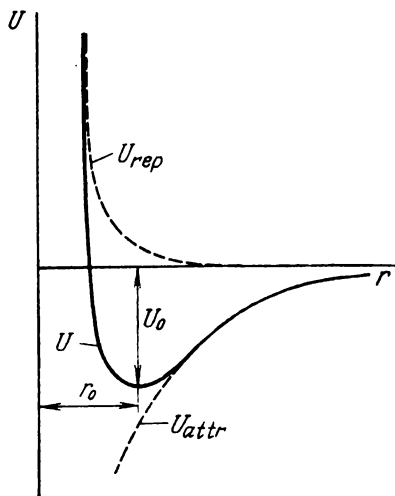
Fig. 15.1. Potential energy curves for the ionic molecule

one another from infinity to a distance r, will be equal to

$$U_{attr} = \int_{\infty}^{r} f_{attr}\, dr = \int_{\infty}^{r} \frac{e_1 e_2}{r^2}\, dr = -\frac{e_1 e_2}{r} \qquad (15.2)$$

The relationship $U_{attr} = f(r)$ is shown by the lower dotted curve in Fig. 15.1.

At very short distances the repulsive force due to the interaction of the electron shells also makes itself felt. In 1918 Born and Landé demonstrated that to a first approximation the repulsive force can be considered inversely proportional to the distance between the ions to the power n:

$$U_{rep} = \frac{B}{r^n} \qquad (15.3)$$

The relationship $U_{rep} = f(r)$ is shown by the upper dotted curve in Fig. 15.1.

Quantity n is called the *Born repulsion factor*. It is considerably greater than unity since the repulsive force diminishes rapidly as the distance increases. Factor n depends on the nature of the ion; for ions with the configuration of He, Ne, A, Kr and Xe it is equal to 5, 7, 9, 10 and 12, respectively. It can be determined by the compressibility of crystals (see p. 289) and on the basis of the optical properties of a substance. Since the force is the first derivative of

the energy with respect to distance, we obtain from (15.3)

$$f_{rep} = \frac{dU_{rep}}{dr} = -\frac{nB}{r^{n+1}} \tag{15.4}$$

As r changes, there are corresponding changes in f_{attr} and f_{rep}. At the equilibrium distance between the ions, r_0, these forces are equal. Therefore, in accordance with (15.1) and (15.4), and on condition that $e_1 = e_2$, we obtain

$$\frac{e^2}{r_0^2} = \frac{nB}{r_0^{n+1}}$$

from which

$$B = \frac{e^2 r_0^{n-1}}{n} \tag{15.5}$$

Combining (15.5) with (15.3) when $r = r_0$ gives

$$U_{rep} = \frac{e^2}{r_0 n} \tag{15.6}$$

In this way quantity B can be removed from equation (15.3).
Since the interaction energy

$$U = U_{attr} + U_{rep}$$

it is evident that in accordance with (15.2) and (15.6) for $r = r_0$ we obtain the equation

$$U_0 = -\frac{e^2}{r_0}\left(1 - \frac{1}{n}\right) \tag{15.7}$$

which gives the interaction energy of two ions at the distance r_0 from one another. It is known as the *Born equation*. The curve of the relationship $U = f(r)$ is also shown in Fig. 15.1, the minimum on it corresponding to the equilibrium distance r_0 and interaction energy U_0 in the equilibrium state. From the character of the curve it is evident that equation (15.7) could have been obtained from the conditions of the potential energy minimum

$$\left(\frac{dU}{dr}\right)_{r=r_0} = 0$$

The potential curves for ions fall comparatively slowly to the zero value which is due to the action of electrostatic attraction extending to a much greater distance than the action of the covalent bond.

For molecules consisting of two polyvalent ions equation (15.7) has the form

$$U_0 = -\frac{z_1 z_2 e^2}{r_0}\left(1 - \frac{1}{n}\right) \tag{15.8}$$

where z_1 and z_2 are the ionic charges. Equation (15.8) is used much less frequently than (15.7) since the bond in such molecules is almost always far from ionic; consequently equation (15.8) must be regarded as only a very rough approximation.

Two circumstances following from the character of equation (15.7) must be borne in mind: (1) the value of U_0 is only slightly sensitive to fluctuations in n; thus if we use $n = 11$ instead of $n = 9$ we change the value of U_0 by only $\sim 2\%$ ($10/11 - 8/9 = 2/99$); (2) approximation (15.3) has practically no effect on results, since the repulsive energy is only $\sim 10\%$ of U_0.

For the formation of an ionic molecule from atoms of monovalent elements, which can be represented by the general equation

$$A + B = A^+B^-$$
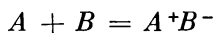
the relationship for the bond energy becomes

$$-E_{AB} = \frac{e^2}{r_0}\left(1 - \frac{1}{n}\right) + E_B - I_A \tag{15.9}$$

in which E_{AB} is the energy of formation of the gaseous molecule AB from free gaseous atoms which is equal in value to the bond energy; I_A, the ionization energy of atom A; and E_B, the electron affinity of atom B.

As an example we shall now use equation (15.9) for estimating the value of E_{AB} for the gaseous molecule KCl ($r_0 = 2.67$ Å; $E_{Cl} = 3.81$eV; $I_K = 4.34$eV). Assuming $n = 9$, we obtain in accordance with (15.9)[1].

$$-E_{KCl} = \frac{(4.8 \times 10^{-10})^2}{2.67 \times 10^{-8} \times 1.6 \times 10^{-12}}\left(1 - \frac{1}{9}\right) + 3.81 - 4.34 =$$
$$= 4.78 + 3.81 - 4.34 = 4.25 \text{ eV} = 97.8 \text{ kcal/mole}$$

The result obtained is close to the value of the bond energy of the KCl molecule obtained in experiments (101.2 kcal/mole).

It must be emphasized that even for atoms of the alkali metals and halogens, whose conversion into the cation (A^+) and anion (B^-) involves the loss and gain of only one ion, respectively, it is impossible to speak of an ideal, '100 per cent', ionic bond. Actually, because of the wave character of the electrons the probability of an electron being found around atom A in molecule AB, although very small, is not equal to zero, i.e., in this case complete separation of the charges, characteristic of free ions A^+ and B^-, is impossible. This is borne out by the following example: if the properties of the free ions Na^+ and Cl^- persisted in the gaseous molecule NaCl, the value of μ_{NaCl} for an interatomic distance of ~ 2.5 Å would be 12 D; actually, $\mu_{NaCl} < 12$ D.

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[1] The factor 1.6×10^{-12} has been introduced into the denominator to convert ergs into electron-volts.

15.2. Ionic Polarization

Deviation from the pure ionic bond in any compound can be regarded from another standpoint—it can be considered that the ions in the molecule act upon one another. This fact was not taken into account in equation (15.9), which is one of the reasons of the divergence from experiment.

The influence.on one another of closely situated oppositely charged ions . causes their mutual *polarization*. As the ions approach one

Fig. 15.2. Mutual polarization of ions
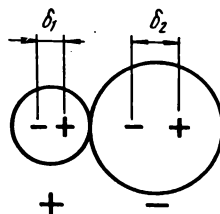
another, the electrons are displaced with respect to the nucleus, resulting in an induced dipole moment, μ_{ind} (Fig. 15.2). The more the ions are polarized, the greater the deviation from equation (15.9). Since this process strengthens the bond between the ions, the calculation according to (15.9) gives low results.

When estimating polarizability coefficient α (see p. 154), it must be taken into account that α is measured in units of length cubed. Actually the induced dipole moment is determined by the product of the charge by the length of the dipole; at the same time it is expressed by the product αE, where the strength of the field E, in accordance with Coulomb's law, is equal to $(F/e) = e/r^2$. From this it follows that polarizability has the above dimension, i.e., that it is a measure of the space occupied by the particles. When calculating to a first approximation it can be assumed that

$$\alpha \approx r^3 \tag{15.10}$$

i.e., $\alpha \approx 10^{-24}$ cm^3. This is borne out by the figures given in Table 15.1.

Polarization is a bilateral process; in it the *polarizability* of the ions and their *polarizing action* are combined.

The polarizability of ions depends on the type of electronic configuration, their charge and size. Since it is the outer electron subshell that is least strongly bound to the nucleus, for the sake of simplicity it can be assumed to a first approximation that the polarization of an ion involves only the deformation of that subshell, i.e., the displacement of the outer electron shells of the two ions relative to their nuclei. If the charges are alike and the radii approximately equal, minimum polarization is found in ions having the configura-

Table 15.1

Polarizability α (Å³) and Cubes of Radii r^3 (Å³) of Ions

Ion	α	r^3	Ion	α	r^3	Ion	α	r^3	Ion	α	r^3
Li⁺	0.029	0.32	Be²⁺	0.008	0.043	F⁻	0.96	2.35	O²⁻	2.74	2.30
Na⁺	0.187	0.92	Mg²⁺	0.103	0.29	Cl⁻	3.57	5.92	S²⁻	8.94	5.3
K⁺	0.888	2.35	Ca²⁺	0.552	0.97	Br⁻	4.99	7.5	Se²⁻	11.4	7.0
Rb⁺	1.49	3.18	Sr²⁺	1.02	1.40	I⁻	7.57	10.6	Te²⁻	16.1	9.4
Cs⁺	2.57	4.67	Ba²⁺	1.86	2.40						

tion of a noble gas, and maximum polarization in ions with 18 outer electrons; α has an intermediate value in the ions of the transition elements with an unfilled d-subshell. The high polarizability of ions of the non-noble gas type is explained by the large number of electrons in their outer shells.

In the subgroups (like electronic configurations and ionic charges), polarizability rises as the atomic number increases (Table 15.1). This is explained by the fact that the increase in the number of electron shells in the ion-analogues causes the outer electron shell to be further removed from the nucleus and at the same time increases the screening of the nucleus by the inner electron shells, which brings about greater deformation of the ions.

If an element forms ions having different charges, the polarizability will be smaller, the greater the charge, since increase in the latter diminishes the radius of the ion and strengthens the bond of the electrons with the nucleus.

In a group of isoelectronic ions with a noble-gas configuration the polarizability increases as the positive charge diminishes, as for example, in the group Mg^{2+}—Na^+—Ne^0—F^-—O^{2-} (see Table 15.1). In such series the number of electron shells is the same, and the increase in polarizability is due to the diminution of the nuclear charge.

The polarizing action of ions also depends on their type, charge and radius. It is greater, the greater the charge, the less the radius and the more stable the electron shell. The greatest polarizing action is exerted by ions that are themselves little polarized. For that reason, if an element forms ions having different charges, their polariz-

ing strength sharply rises as the charge increases because their radius decreases at the same time. Conversely, polyatomic (complex) ions of large size, which as a rule are greatly deformed, usually have an insignificant polarizing action.

The intensity of the polarizing action of ions is noteworthy. Employing Coulomb's law we shall estimate the strength of the electric field at a distance $r = 10^{-7}$ cm (10 Å) from an ion

$$\frac{e}{r^2} = \frac{4.80 \times 10^{-10}}{10^{-7} \times 10^{-7}} =$$

$$= 4.80 \times 10^4 \text{ esu/cm}^2$$

or $\quad 4.80 \times 10^4 \times 300 =$
$= 14.4 \times 10^6$ V/cm, which is an enormous value.

The above regularities in changes in polarizability can be made quantitative by using methods of comparative calculation. This is evident from the examples shown in Fig. 15.3. In Fig. 15.3a are compared values of α in groups of noble gas atoms and isoelectro-
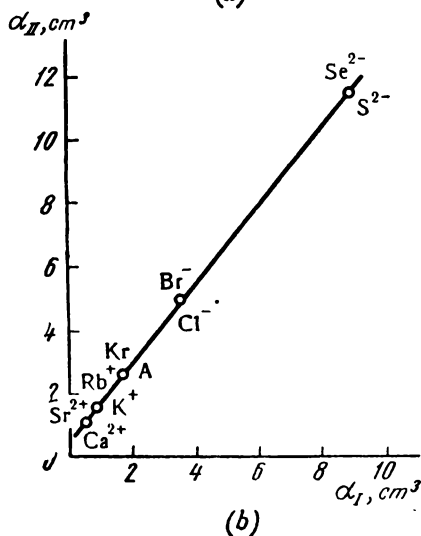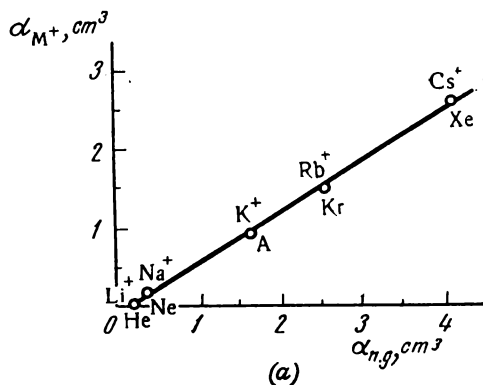
Fig. 15.3. Comparison of polarizabilities

(a) atoms of noble gases and ions of alkali metals; (b) two series of isoelectronic anions

nic single-charge cations of the lithium subgroup; in Fig. 15.3b the polarizability of pairs of particles selected by a different principle is compared. These examples of methods of comparative calculation like others, including those previously discussed (see Fig. 5.6, 5.7, 7.2, 8.1, 11.7, 11.8 and 13.3), provide further evidence of the regular change in the most diverse properties in Mendeleev's periodic system of the elements.

Since anions are characterized by large size and a small charge, while their electronic configuration corresponds, as a rule, to that

of a noble gas, their polarizing action on cations is usually small, and can often be neglected, that is, it can be considered that polarization is unilateral in character. If, however, a cation is easily deformed, the resulting dipole heightens its polarizing action on the anion, and the latter, in turn, exerts an additional action on the cation, and so on. This gives rise to a *supplementary polarization effect* which is the greater, the more the cation and anion are polarized.

The supplementary polarization effect, and with it, the total polarizing action are especially great for 18-electron cations, such as Zn^{2+}, Cd^{2+} and Hg^{2+}.[1]

The increased constriction of ions resulting from their deformation causes the length of the dipole to be less than the internuclear distance; for instance, the length of the dipole in the KCl molecule is 1.67 Å, whereas the internuclear distance is 2.67 Å. This difference is particularly great in hydrogen-containing compounds. If the size of the hydrogen ion is neglected the distance between the nuclei of hydrogen and halogen, in the case of a purely ionic bond, should be equal to r_{X^-}. But $d_{H-X} < r_{X^-}$ for all halogens. Thus $r_{Cl^-} = 1.81$ Å, but $d_{H-Cl} = 1.27$ Å. This means that unlike other cations, the proton penetrates the electron subshell of the anion, there exerting a strong polarizing action which causes a sharp reduction in the polarity of hydrogen compounds as compared to analogous compounds of other cations. Due to the polarization effect the HCl dipole has a length of only 0.22 A instead of 1.27 Å. Finally, the proton penetration into the anion causes a diminution of the latter's deformability.

The polarization of ions constitutes a certain degree of electron displacement, which is of great importance, since by causing a reduction in interatomic distances and, as a consequence, a reduction of the dipole moment, it converts an ionic bond into a polar covalent bond. As the deformability of the anion increases, there may be complete transfer of the electrons from the anion to the cation, i.e., a covalent bond is formed. The latter differs from the ionic bond in a number of properties, among them, direction. On the contrary, the less the polarization of the ion (an anion, for example), the closer a compound of the given atom will be to the ionic type. Since polarization sharply rises as the charge of the ions increases, it is evident that among compounds of the type $A^{2+}B^{2-}$ or $A_2^+B^{2-}$, and still more so $A^{3+}B^{3-}$ or $A_3^+B^{3-}$, there can be none with a purely ionic type of bond, and this applies even to noble-gas configurations.

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[1] In addition to the Coulomb and polarization interaction the so-called dispersion forces must also be taken into account (see p. 265). At this point we shall only state that these forces (a) act between like-charged ions, in this way weakening their Coulomb repulsion, and (b) increase in proportion to the product of the polarizability coefficients α of the interacting particles, and are therefore particularly great for 18-electron cations.

Polarization conceptions are important because they provide corrections to the Kossel diagram, thus making it possible more precisely to describe the properties and peculiarities of the most diverse compounds.

15.3. Effect of Polarization on Properties of Substances

Polarizability and the polarizing action explain many individual features of substances.

The polarization of the ions in a molecule, or in other words, the presence of a certain proportion of covalent bond, enhances its stability. In that case the member E_p which takes account of the polarization must be added to equation (15.9) for calculating th energy of the bond. The equation then has the form

$$-E_{AB} = \frac{e^2}{r_0}\left(1 - \frac{1}{n}\right) + E_p + E_B - I_A \qquad (15.11)$$

It should not be thought, however, that molecules with a substantial proportion of covalent bond are always more stable than ionic compounds. A distinction must be made between stability as regards dissociation into ions and dissociation into atoms.

Equation (15.11) represents the energy of the formation of a molecule from atoms; this quantity greatly depends on the atomic ionization energy I_A, which can vary over a wide range. It is evident from equation (15.11) that an increase in I_A lowers the bond-dissociation energy. The energy of the dissociation of the molecule into ions is determined by the first two members of equation (15.11).

What has been said can be illustrated by comparing two compounds $HgCl_2$ and $CaCl_2$. The $HgCl_2$ molecule which contains the strongly polarizing ion Hg^{2+} dissociates into ions to a much lesser degree than $CaCl_2$; in $\frac{N}{10}$ aqueous solution mercuric chloride is practically undissociated, whereas calcium chloride dissociates completely. However, the ionization energy of the mercury atom ($I_1 = 10.4$ eV; $I_2 = 18.7$ eV) is considerably greater than the ionization energy of the calcium atom ($I_1 = 6.1$ eV; $I_2 = 11.9$ eV). Consequently, the $HgCl_2$ molecule is much less stable as regards dissociation into atoms than the $CaCl_2$ molecule.

Polarization lessens the distance between ions and increases the energy of the bond between them. Therefore, although r_{Ag^+} is commensurable with r_{Na^+} and r_{K^+}, the polarizing action of Ag^+ is much greater than that of Na^+ and K^+. This is one of the reasons why the solubility of $AgCl$ is much lower than that of $NaCl$ and KCl. In a series of compounds of a given cation with anion-analogues, for example, with Cl^-, Br^- and I^-, the degree of dissociation in solutions diminishes, as a rule, here the increase in the polarizability of the anion makes itself felt.

The mutual polarization of ions facilitates the disintegration of crystals, i.e., lowers the melting point, this effect being the greater, the more the crystal lattice is deformed as a result of polarization. Thus, although the radii of the cations in RbF and TlF coincide, the Tl^+ ion polarizes more and exerts a considerably greater polarizing action on the F^- ion than the Rb^+ ion; among other things, this affects the melting points of the above salts: (m.p.) $_{RbF} = = 780$, but (m.p.) $_{TlF} = 327°C$.

The presence of maxima on the melting point-molecular weight curves of the halides of the alkali metals is understandable if the decrease in the polarizing action in the group $Li^+ — Na^+ —K^+ — Rb^+ — Cs^+$ and the increase in polarizability of the group $F^- — Cl^- — Br^- — I^-$ are taken into account.

Raising the temperature usually promotes polarization, since heating increases the swing of ionic oscillations, thus bringing them closer together, it can draw some ions to others, i.e., change the structure of the substance, which means that a polymorphic transformation takes place (see p. 271). The possibility that heating will draw the electron (electrons) completely from the anion to the cation is not to be ruled out. This will cause thermal dissociation of the substance. The greater the polarization (polarizing action), the lower the dissociation point will be. For that reason the d.p. for a given cation falls from MCl to MI, and for a given anion from NaX to LiX. Or another example: whereas a high temperature is required for the dissociation of CaI_2, the reaction $AuI_3 = AuI + I_2$ proceeds at a low temperature. The dissociation of CuI_2 should take place at a still lower temperature and therefore this compound does not exist in ordinary conditions.

Lowering of the dissociation point as the polarizing force increases can be illustrated with more complicated examples in which the mechanism of thermal dissociation is different. Thus, $CdCO_3$ $(r_{Cd^{2+}} = 0.97$ Å) decomposes at 360°C, while $CaCO_3$ $(r_{Ca^{2+}} = 0.99$ Å) decomposes at 850°C. In this case the process proceeds according to the equation

$$MCO_3 = MO + CO_2$$
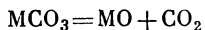
since one of the oxygen atoms is polarized not only by the carbon but by the metal as well (*contrapolarization*). The difference in the polarization of the bonds $M — O$ and $O — C$ diminishes as the temperature rises, which finally leads to dissociation. This contrapolarization diminishes in a series of ions of the same type (e.g., $Ca^{2+} — Sr^{2+} — Ba^{2+}$), which explains the rise in the dissociation points of the corresponding carbonates. Contrapolarization can be so great that a compound is only stable at very low temperatures.

Chemists know very well that free oxygen-containing acids are, as a rule, less stable than most of their salts. H_2CO_3 and H_2SO_3 are

èxamples. This is explained, firstly, by the strong polarizing action of H^+ and, secondly, by the different character of contrapolarization. A proton penetrates the oxygen anion, lowering its charge and diminishing deformability; for that. reason HCO_3^- and HSO_3^- are less stable than CO_3^{2-} and SO_3^{2-}, respectively. A second proton makes the particle still less stable; therefore H_2CO_3 and H_2SO_3 easily lose water. This is one of the reasons why oxygen-containing acids are stronger oxidizing agents than their salts.

The deformability of the electron subshell also affects optical properties. Absorption of certain rays is associated with excitation of the outer electrons. The more polarizable a particle is, the less the energy of electron transitions. If a particle is stable, excitation requires much energy, corresponding to ultra-violet radiation. If an atom (or ion) is easily polarized, the excitation energy is low, corresponding to the visible region of the spectrum, and the substance is coloured. For that reason, along with substances whose colouring is due to the colour of an ion (or ions) they contain, there are coloured compounds formed from colourless ions. In such cases the colour is the result of ionic interaction. The greater the polarization' and polarizing action of the ions, the greater the probability that a substance will be coloured. It is likewise evident that as these effects are heightened, the colour should deepen. These principles are confirmed by a multitude of examples. We shall limit ourselves to a few of them, leaving it to the reader to explain each case. PbI_2 is coloured but CaI_2 is colourless; much more coloured compounds are found among the sulphides of metals than among their oxides; in the group $NiCl_2$ — $NiBr_2$ — NiI_2 the colour deepens; if the bromide of an element is not coloured, it is very doubtful that its chloride will be; a number of compounds can be named that take on a colour when heated.

15.4. The Polar Bond and Electronegativity

The bonds in the molecules A_2 and B_2 consisting of like atoms are covalent. If the bond in the molecule AB is also covalent, Pauling suggests that the following equation should hold true:

$$E_{A-B} = \sqrt{E_{A-A}E_{B-B}} \tag{15.12}$$

in which E is the energy of the respective bonds, or to put it differently, in the expression

$$\Delta E = E_{A-B} - \sqrt{E_{A-A}E_{B-B}} \tag{15.13}$$

ΔE should be equal to 0 (replacing the arithmetical mean by the geometrical mean makes ΔE positive in all cases). The energy of the unsymmetric bond calculated from equation (15.12) is always

less than experiment. This is explained by the fact that a covalent bond between different atoms is always more or less polar. The degree of polarity of a covalent bond can be judged by the deviation of ΔE from zero, and this also indicates the ability of the atoms to attract electrons to themselves (the character of the change in ΔE and in the dipole moment is the same, and the latter increases as the degree of polarity of the bond rises).
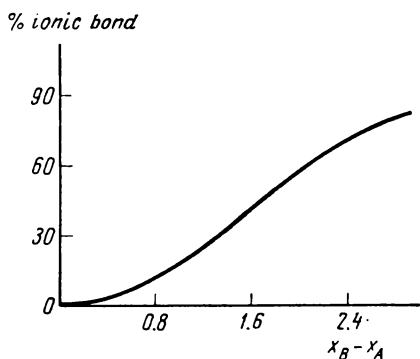
Fig. 15.4. Relationship between degree of ionic character of the bond and difference in electronegativity (according to Pauling)

The value of ΔE depends on the difference in the electronegativity x of the elements. Pauling found that this connection can be expressed by the approximate relationship

$$\Delta E = \text{const } (x_B - x_A)^2 \qquad (15.14)$$

In the Pauling system such electronegativities are chosen that their difference gives ΔE in electron-volts (const = 1); the electronegativity of fluorine is assumed to be 4.0. If ΔE is to be obtained in kilocalories, the value of the constant is put at 23.03. The value of E_{A-B} can be calculated by combining equations (15.13) and (15.14).

When $x_A = x_B$ the bond is covalent and $\Delta E = 0$; when $x_A \neq x_B$ the bond is polar. The greater the difference between x_A and x_B, the more polar the bond, if $x_A \ll x_B$ the bond can be considered ionic. Thus as the difference in electronegativity increases, there is a corresponding increase in the ionic character of the bond. The curve in Fig. 15.4 shows the approximate relationship between the difference in electronegativity of the elements and the ionic character of the bond. From this curve it follows that it is only in the fluorides of the alkali and alkaline earth metals [$(x_B - x_A)$ is 2.8 to 3.3] that the bond can be considered close to ionic.

We must again emphasize the approximate character of the conception of electronegativity (see p. 150) and particularly the fundamental inaccuracy of equation (15.14) (see also p. 226). Actually,

when the AB molecule is formed there may be a change in the number of binding and antibinding electrons. Consequently, to connect the interaction energy only with the partially ionic character of the bond will not always be justified. Calculation of electronegativity by the Pauling system may lead to substantial discrepancies between the computed bond energy and experiment, especially when the difference between the values of x_A and x_B is great. Nevertheless it is convenient for approximate estimations and for systematization.

CHAPTER SIXTEEN

THE CHEMICAL BOND IN COMPLEX COMPOUNDS

16.1. Complex Compounds

Structurally, complex compounds are made up of an *inner, coordination sphere* consisting of a central particle—a *complexing ion or atom*—surrounded by *ligands* (*addends*) which are molecules or ions of the opposite sign. In the formulae of complex compounds, the coordination sphere is denoted by brackets. Examples of such compounds are $K_4[Fe(CN)_6]$, $K_2[HgI_4]$, $[Ag(NH_3)_2]Cl$, $K_2[Zn(OH)_4]$ and $[Cr(H_2O)_6]Cl_3$. The number of ligands around the complexing particle is called the *coordination number*. Ions situated beyond the coordination sphere form the *outer sphere* of the complex.

The coordination sphere remains intact in solutions of complex compounds. For example, the compounds cited above dissociate in solution with the formation of the *complex ions* $[Fe(CN)_6]^{4-}$, $[HgI_4]^{2-}$, $[Ag(NH_3)_2]^+$, $[Zn(OH)_4]^{2-}$ and $[Cr(H_2O)_6]^{3+}$.

The ideas about the structure of complex compounds set forth here form the basis of the *coordination theory* originated and developed by Werner (Switzerland) in the latter half of last century. The coordination theory, like Butlerov's theory of the structure of organic compounds, made it possible to establish the structure of complexes long before the elaboration of physical methods of determining structure, methods which fully confirmed Werner's conclusions.

Many complexes can be formed through the combination of ordinary substances, for example:

$$CuCl_2 + 4NH_3 = [Cu(NH_3)_4]Cl_2$$
$$AgI + KI = K[AgI_2]$$
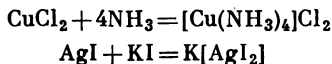
There are also many other methods of synthesizing complex compounds.

Considerably more complex compounds are known than all other inorganic substances, and they find practical application in the most diverse fields. Complexes play a very important part in orga-

nic processes. For instance, haemoglobin and chlorophyll, substances essential for the life of higher animals and plants, are both complexes. The complexing ion in haemoglobin is Fe^{2+}; in chlorophyll, it is Mg^{2+}.

Among complex compounds there are acids, bases and salts, and also substances which do not dissociate into ions, that is, *non-electrolytes*. Here are some examples:

Acids	Bases	Salts	Non-electrolytes
$H[AuCl_4]$	$[Ag(NH_3)_2]OH$	$[Ni(NH_3)_6](NO_3)_2$	$[Pt(NH_3)_2Cl_2]$
$H_2[SiF_6]$	$[Cu(NH_3)_4](OH)_2$	$Na_3[AlF_6]$	$[Ni(CO)_4]$

The formation of complexes is particularly characteristic of ions of the transition metals, very many complexes being known for the ions Cu^{2+}, Ag^+, Au^{3+} and Cr^{3+} and likewise for ions of elements of Group VIII of the periodic table.

The ligands in complex compounds are often ions of the halogens and the ions CN^-, NCS^-, NO_2^-, OH^-, SO_4^{2-}, $C_2O_4^{2-}$, CO_3^{2-}, as well as the neutral molecules H_2O, NH_3, N_2H_4 (hydrazine), C_5H_5N (pyridine) and $NH_2 - CH_2 - CH_2 - NH_2$ (ethylenediamine).

The coordination number of some complexing ions is constant; for example, in all Cr^{3+} and Pt^{4+} complexes it is six, but for most complexing ions it can vary, depending on the nature of the ligands and the conditions in which complexes are formed, for example, in Ni^{2+} complexes coordination numbers 4 and 6 are found. The most frequently encountered coordination numbers are six and four, and there are very few complexes with a coordination number greater than eight.

Some ligands have several groups in their molecules, which can unite with the complexing ion. For example, the $NH_2 - CH_2 - CH_2 - NH_2$ molecule contains two NH_2 groups which readily unite with the ions Cu^{2+}, Cr^{3+}, Co^{3+}, etc. Each of these ligands can occupy in complexes the place of two ordinary ligands, such as NH_3 or H_2O. Ligands occupying several coordination places are called *multidentate*; depending on the number of places they occupy, there can be bidentate, terdentate ligands and so on.

Complex compounds are classed as *aqua-compounds*, in which the ligands are H_2O molecules, e.g., $[Cr(H_2O)_6]Cl_3$ and $[Ca(H_2O)_6]Cl_2$; *ammines* (ligands: NH_3 molecules), such as $[Cu(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]Cl$; *hydroxo-compounds* (ligands: OH^- ions), such as $K_2[Zn(OH)_4]$ and $Na_2[Sn(OH)_6]$; and *acido-complexes* (ligands: acid residues), such as $K_4[Fe(CN)_6]$ and $K_2[HgI_4]$. There are also many compounds of a *mixed type*, such as $[Co(NH_3)_4Cl_2]Cl$ and $[Pt(NH_3)_4(H_2O)_2]Cl_4$.

The names of complex compounds are formed similarly to the names of ordinary salts (NaCl — sodium chloride, K_2SO_4—potassium sulphate, etc.), with the only difference that the ligands and

·degree of oxidation of the central ion are indicated. H_2O and NH_3 ·molecules are denoted 'aquo' and 'ammine', respectively. The follo-·wing examples illustrate the nomenclature of complexes:

$$K_2[PtCl_6]$$
Potassium hexachloroplatinate (IV)

$$[Cr(H_2O)_6]Cl_3$$
Hexaquochromium (III) chloride

$$[Pt(NH_3)_2Cl_2]$$
Dichlorodiammineplatinum (II)

$$[Co(NH_3)_4(NO_2)Cl]ClO_4$$
Chloronitrotetramminecobalt (III) perchlorate

$$K_2[Zn(OH)_4]$$
Potassium tetrahydroxozincate (II)
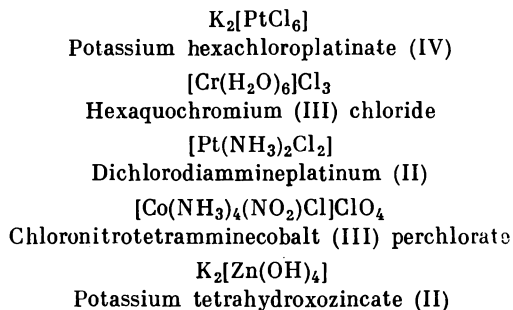
16.2. Isomerism of Complex Compounds

Isomerism is a wide-spread phenomenon among complexes, just as it is among organic compounds. It was the study of isomerism in complexes that first made it possible to establish their spatial structure.

We shall now briefly consider the main types of isomerism in complex compounds.

Ionization isomerism results from different distribution of ions between the inner and outer spheres of the complex, for example

$$[Co(NH_3)_5Br]SO_4 \quad \text{and} \quad [Co(NH_3)_5SO_4]Br$$
$$[Co(en)_2(NO_2)Cl]Cl \quad \text{and} \quad [Co(en)_2Cl_2]NO_2$$
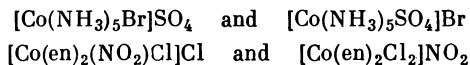
In the second example the letters 'en' are an abbreviation for ethylenediamine, $NH_2 - CH_2 - CH_2 - NH_2$.

Coordination isomerism is found in compounds in which both the cation and the anion are complexing particles, and results from different distribution of the ligands between them. Examples of such isomers are the following:

$$[Cu(NH_3)_4][PtCl_4] \quad \text{and} \quad [Pt(NH_3)_4][CuCl_4]$$
$$[Co(NH_3)_6][Cr(CN)_6] \quad \text{and} \quad [Cr(NH_3)_6][Co(CN)_6]$$
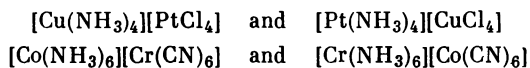
Ligand isomerism is possible in cases where the ligand molecules or ions can exist in isomeric forms. This type of isomerism is observed, for example, when the ligands are the compounds

$$\underset{NH_2-\overset{\overset{\displaystyle H_3C \quad CH_3}{\diagdown\diagup}}{C}-CH_2-NH_2}{} \quad \text{and} \quad \underset{NH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-NH_2}{}$$

or

$$NH_2-CH_2-CH_2-CH_2-CH_2-NH_2 \quad \text{and} \quad CH_3-NH-CH_2-CH_2-NH-CH_3$$
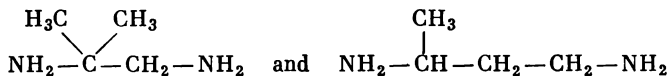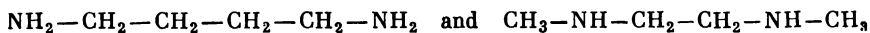
As in the case of organic compounds, there are also types of iso-merism involving different spatial arrangement of the particles—*cis—trans* isomerism and stereoisomerism.

For complexes with a coordination number of four, *cis—trans* isomerism is possible when the four ligands are in the same plane. $[Pt(NH_3)_2Cl_2]$ is an example:

Cis isomer   *Trans* isomer
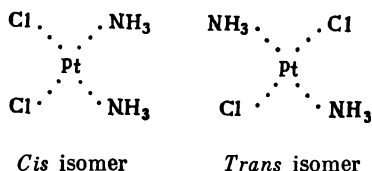
A tetrahedral arrangement of the ligands makes *cis—trans* isome-rism impossible.

Stereoisomerism is illustrated by complexes of trivalent chro-mium containing two molecules of ethylenediamine. The coordina-tion number of Cr^{+3} is six. The ligands are situated at the vertices
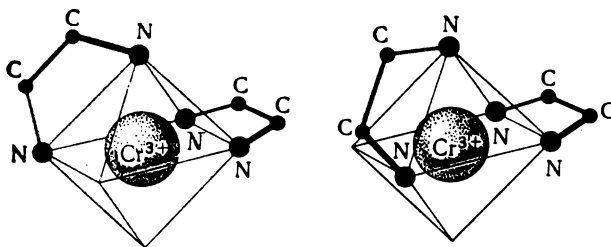
Fig. 16.1. Diagrammatic representation of the structure of mirror isomers of chromium-ethylenediamine complexes. Hydrogen atoms in ethylenediamine molecule are not shown

of an octahedron at the centre of which is the Cr^{3+} ion. The ethyle-nediamine molecule, curved in shape, is attached to the chromium ion by two NH_2 groups (as already noted, ethylenediamine occu-pies two coordination places). When there are two ethylenediamine molecules in the octahedral complex two different configurations are possible, as shown in Fig. 16.1. These forms are mirror images of one another.

As in the case of organic compounds, stereoisomers of complexes have identical chemical and physical properties. They differ only in the asymmetry of their crystals and in the direction in which they rotate the plane of polarized light.

Werner foretold the occurrence of stereoisomerism in complexes on the basis of the coordination theory, and he himself synthesized such compounds.

16.3. Explanation of the Chemical Bond in Complexes on the Basis of Electrostatic Conceptions

Formulation of a theory explaining the formation of complex compounds began in 1916-1922 in the investigations of Kossel and Magnus (Germany), and was based on electrostatic conceptions. It is evident that a complexing ion will attract ions of the opposite sign and also polar molecules. On the other hand, the particles surrounding the complexing ion will be repulsed from one another, and the repulsive force will be greater, as the number of particles grouped round the central ion increases.

If one considers, as did Kossel and Magnus, that the interaction of the particles in a complex is purely electrostatic and obeys Coulomb's law, the bond energy between ligands and the complexing ion can be calculated. In these calculations the complexing ion and the ligands are regarded as undeformable, charged spheres. The reader can easily carry out such calculations for such ions as $[HgI_4]^{2-}$ (tetrahedral configuration), $[AlF_6]^{3-}$ (octahedral arrangement of the ligands), $[AgI_2]^-$ (linear structure) if he uses the values of the ionic radii.

These calculations give values of the bond energy of the correct order for complexes of the specified type, but for complexes in which the ligands are polar molecules the results are worse. However, they can be improved somewhat if the polarization effect is taken into account (see p. 225).

Kossel and Magnus demonstrated by their calculations that when the number of ligands was substantially increased, the repulsive force between them became so great that the complexes were unstable. It was found that for complexes to be sufficiently stable, the coordination number must be two or three in the case of monovalent complexing ions; four for bivalent ions, and four, five or six for trivalent ions. These results are fairly close to what is observed in reality.

Thus electrostatic conceptions indicated in principle the cause of the formation of complex compounds, made it possible to estimate theoretically their stability and approximately explain the coordination numbers observed.

Nevertheless, the conception of complexes as aggregates consisting of undeformable, charged spheres is a very crude model and cannot explain many of their peculiarities. For one thing, electrostatic conceptions cannot explain why a number of complexes with a coordination number of four have a plane configuration (complexes of Cu^{2+}, Pt^{2+}, etc.). Since, if a model with charged spheres is used, a tetrahedral disposition of the four ligands about the complexing ion would energetically be the most advantageous arrangement.

Moreover, the charged-sphere model is completely useless for explaining the magnetic properties of complexes. As we know, study of the magnetic properties of a substance makes it possible to determine the number of unpaired electrons (Appendix VIII). Since according to Kossel and Magnus the interaction of complexing ions and ligands does not change the electronic configuration, the ions in the complex should have the same number of unpaired electrons as the free ion. It has been found, however, that in complexes this number may be different, the actual number depending on the nature of the ligands. Thus the ion Fe^{2+} has four unpaired electrons, and the same number is found in the complex $[FeF_6]^{4-}$, but in the ion $[Fe(CN)_6]^{4-}$ all the electrons are paired.

Therefore, the present-day theory takes account of the quantum-mechanical interaction of particles, along with electrostatic factors.

16.4. Quantum-Mechanical Interpretation of the Chemical Bond in Complex Compounds

Several quantum-mechanical methods are now used for explaining and calculating the chemical bond in complexes.

In the *valence bond method* it is assumed that there is a donor-acceptor bond between the ligands and the complexing ion, a pair of electrons being supplied by the ligands (see p. 196). Using this method it has been possible to explain the structure and many properties of a large number of complexes, including magnetic properties. However, in a number of cases difficulties are encountered when employing this method. It is likewise ill-suited for quantitative estimations.

The crystal field theory, on the contrary, is based on a purely electrostatic model, but unlike the original theory of Kossel and Magnus it takes account of changes in the electron subshells of the complexing ion which take place under the action of the ligands. This theory has proved extremely effective and it now finds considerably more application than the valence bond method.

Naturally, the crystal field theory which proceeds from an ionic model requires changes in cases where there is a noticeable proportion of covalent bond in the complex. When the proportion is comparatively small, use is made of the *ligand field theory* in which the presence of a covalent bond is taken into consideration by the introduction of certain corrections in calculations performed by the methods of the crystal field theory. If there is a substantial proportion of covalent bond, the *molecular orbital method* is employed, while taking account of the crystal field theory conceptions (sometimes this approach is also called the ligand field theory).

The valence bond method, the crystal field theory and the molecular orbital method will now be discussed in greater detail.

16.5. Valence Bond Method

We know that formation of the ammonium ion, NH_4^+, involves the unshared electron pair in the ammonia molecule (see p. 198), and can be regarded as addition of the NH_3 molecule to a hydrogen ion. Similarly, we can interpret the formation of ammines as the addition of ammonia molecules to metal ions, for example:

$$Cu^+ + 2NH_3 = [Cu(:NH_3)_2]^+$$
$$Zn^{2+} + 4NH_3 = [Zn(:NH_3)_4]^{2+}$$
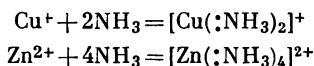
According to the valence bond theory complexes result from formation of donor-acceptor bonds by unshared electron pairs in the ligands. These electron pairs are held jointly by the ligand and the central ion, occupying the free hybrid orbitals of the latter.

In the examples cited, the Cu^+ and Zn^{2+} ions have a filled third shell, but there are free s- and p-orbitals in the next shell. In accordance with the principles set forth, two electron pairs from NH_3 molecules fill sp hybrid orbitals in the $[Cu(NH_3)_2]^+$ complex; as we know, this form of hybridization causes a linear configuration of the particle. In the $[Zn(NH_3)_4]^{2+}$ complex, four electron pairs occupy sp^3 hybrid orbitals, and the complex has a tetrahedral configuration.

Not only s- and p-orbitals can be used in the formation of donor-acceptor bonds in complexes, but d-orbitals as well. In such cases, according to the valence bond theory, there is hybridization invol-

Table 16.1

The Type of Hybridization and the Structure of the Complex

Hybridization	Configuration	Ions
sp	Linear	Ag^+, Hg^{2+}
sp^3	Tetrahedral	Al^{3+}, Zn^{2+}, Co^{2+}, Ti^{3+}, Fe^{2+}, Ni^{2+} (rarely)
sp^2d	Square, planar	Pt^{2+}, Pd^{2+}, Cu^{2+}, Ni^{2+}, Au^{3+}
sp^3d^2	Octahedral	Cr^{3+}. Co^{3+}, Ni^{2+}, Pd^{4+}, Pt^{4+}

ving d-orbitals. Table 16.1 lists some forms of hybridization and associated complex configurations. The last column in the Table shows the ions in whose complexes the valence bond method assumes the presence of the given type of hybridization.

The type of hybridization and the structure of the complex are chiefly determined by the configuration of the central ion, but they also depend on the nature of the ligands. We shall now consider this, taking the Ni^{2+} ion as an example. This ion has a d^8 configura-

tion. In accordance with Hund's rule, the eight d-electrons are distributed as follows in the quantum cells:
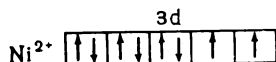
When complexes are formed with Cl^- ions which interact comparatively weakly with Ni^{2+} ions, since the Cl^- ion has a large radius, the electron pairs occupy orbitals of the next electron shell. This can be represented by the diagram
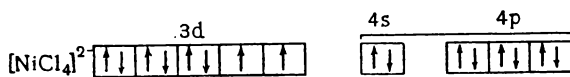
sp^3-hybridization,   tetrahedral   configuration

The Ni^{2+} ion reacts more strongly with NH_3 molecules than with Cl^- ions. Accordingly, it adds six NH_3 molecules, forming the $[Ni(NH_3)_6]^{2+}$ ion, which has the configuration
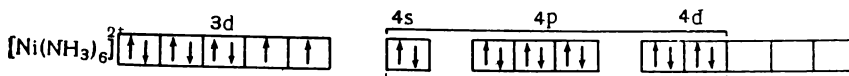
sp^3d^2-hybridization, octahedral configuration

The Ni^{2+} ion reacts still more strongly with CN^- ions. In this case two d-electrons of the Ni^{2+} ion are paired and the empty cell thus formed is filled with an electron pair from the CN^- ion:
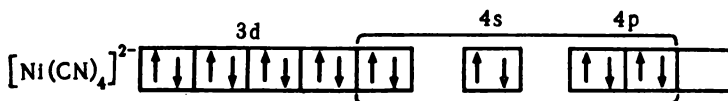
sp^2d-hybridization, square planar configuration

From the examples cited we see that the number of unpaired electrons in complexes formed by the ion of a certain metal is not always the same. In $[NiCl_4]^{2-}$ and $[Ni(NH_3)_6]^{2+}$ the number is two, but in $[Ni(CN)_4]^{2-}$ there are no unpaired electrons. The first two complexes are paramagnetic, while the third is diamagnetic.

From the above examples it is likewise evident that hybridization involving d-orbitals can be of two types—that in which the outer d-orbitals are occupied ($4d$ in the case of $[Ni(NH_3)_6]^{2+}$) and

that in which the inner d-orbitals are occupied ($3d$ in $[Ni(CN)_4]^{2-}$).
Here is another example of 'outer' and 'inner hybridization:

$[FeF_6]^{4-}$

3d   4s   4p   4d
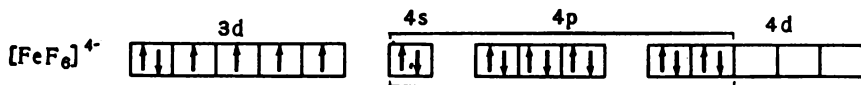
'Outer' sp^3d^2-hybridization; complex is paramagnetic

$[Fe(CN)_6]^{4-}$
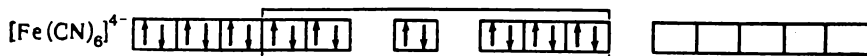
'Inner' sp^3d^2-hybridization; complex is diamagnetic

A great advantage of the valence bond method is that it can be used to foretell the *reactivity* of complex compounds. To a great degree this depends on the *rate* at which the ligands in a complex are replaced in solution by other ions or molecules. Conditions favourable for the replacement of ligands are: (1) 'outer' hybridization and (2) the presence of unoccupied 'inner' d-orbitals in the complexing ion.

If there is 'outer' hybridization, the bond between ligands and the complexing ion is weaker than in the case of 'inner' hybridization. Therefore, one of the ligands can separate from the complex comparatively easily, being replaced by another particle in the solution. Thus the complex $[Fe(NH_3)_6]^{2+}$, in which there is 'outer' hybridization, is much more reactive than $[Fe(CN)_6]^{4-}$, in which hybridization is 'inner'.

If there is an unoccupied 'inner' d-orbital, the replacement mechanism is different. In that case it is possible for an additional particle in solution to combine with the complex. After this combination, one of the ligands may be split off. In this way one of the ligands in the complex may be replaced.

The complexes $[Cr(NH_3)_6]^{3+}$ and $[V(NH_3)_6]^{3+}$ illustrate the above rule. According to the valence bond method these complexes can be assumed to have the following configuration:

$[Cr(NH_3)_6]^{3+}$

3d   4s   4p

$[V(NH_3)_6]^{3+}$

The second complex is much more reactive than the first, which is explained by the presence of an unoccupied 'inner' d-orbital.

16.6. Crystal Field Theory

This theory is concerned with the action of the ligands on the d-orbitals of the complexing ion. The shape and spatial arrangement of the d-orbitals are shown in Fig. 4.7. In the free atom or ion the energy of all the d-electrons belonging to the same electron subshell is equal — these electrons occupy a single energy level. The ligands
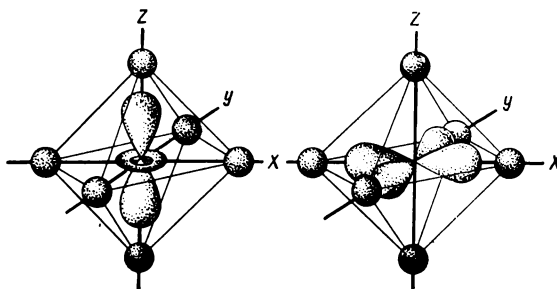
Fig. 16.2. d_{z^2}- and $d_{x^2-y^2}$-orbitals in an octahedral field

that combine with a positive ion are either negative ions or polar molecules with their negative end turned toward the complexing ion. A repulsive force acts between the electron clouds of the d-electrons and the negative ligands which increases the energy of the d-electrons. However, the action of the ligands on the different d-orbitals is not the same. The energy of the electrons in d-orbitals situated close to the ligands increases more than that of electrons in d-orbitals far removed from the ligands because under the action of the ligands the *energy levels of the d-orbitals are split.*

We shall now consider the situation which arises when the ligands are arranged in the form of an octahedron and in the form of a tetrahedron round the complexing ion.

It is evident from Fig. 16.2 that in an octahedral environment, the d_{z^2}- and $d_{x^2-y^2}$-orbitals, denoted d_γ, are arranged in such a way that they are subjected to strong action by the ligand field. Electrons occupying these orbitals have great energy. Electrons in the d_{xy}-, d_{xz}- and d_{yz}-orbitals (denoted d_ε), on the contrary, have less energy. The diagram in Fig. 16.3 shows the splitting of the energy levels in the octahedral field.

When the complexing ion is in a tetrahedral environment of ligands, it is evident from Fig. 16.4 that the d_{z^2}- and $d_{x^2-y^2}$-orbitals

have lower energy, while the d_{xy}-, d_{xz}- and d_{yz}-orbitals have higher energy. The resulting splitting of the energy levels is shown diagrammatically in Fig. 16.5.

The value of *energy split* Δ depends on the nature of the ligands and the configuration of the complex. If the ligands are the same, and they are at the same distance from the centre of the complexing ion, the value of Δ for a tetrahedral configuration is 4/9 of the value for an octahedral configuration.

The value of energy split Δ can be calculated theoretically by the methods
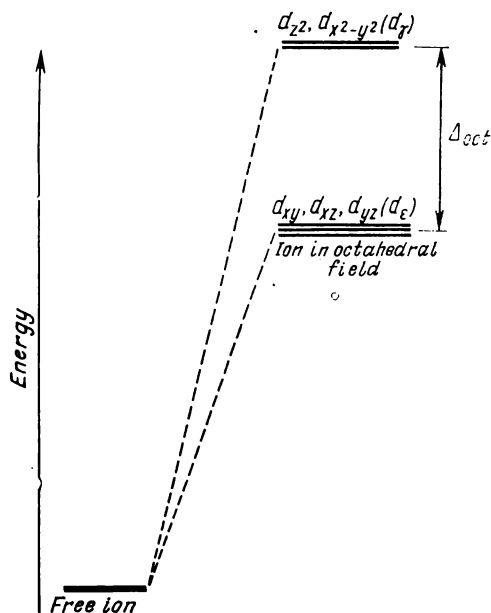
Fig. **16.3.** Splitting of *d*-electron energy levels in an octahedral field
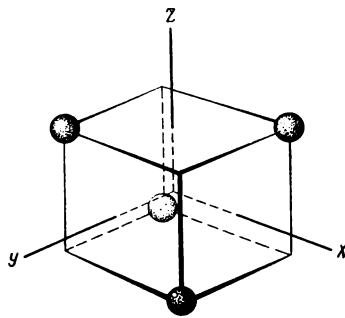
Fig. 16.4. Arrangement of coordinate axes in a tetrahedral complex

of quantum mechanics, and can be determined experimentally by the absorption spectra of complex compounds.

As we know, the absorption spectrum in the visible and ultraviolet regions is associated with the transition of electrons from certain energy levels to others (see p. 146). A substance absorbs light quanta whose energy is equal to the energy of the corresponding electron transitions. The absorption spectrum, and consequently the colour, of most complexes of *d*-elements is due to electron transitions from a lower *d*-orbital to a *d*-orbital having higher energy. For example, the complex $[Ti(H_2O)_6]^{3+}$ has maximum absorption at wave number $\bar{v} = 20{,}300$ cm^{-1}, which causes its violet colour. The Ti^{3+} ion has only one *d*-electron, which in the octahedral complex can be transferred from the d_ε-orbital to the d_γ-orbital. The energy of the

16*

quanta corresponding to $\bar{\nu} = 20{,}300$ cm^{-1} (which comes to 57 kcal per g-ion) is equal, as stated above, to the value of Δ.

Thus the crystal field theory explains the fact, well known to chemists, that the ions of elements of the groups of transition elements are coloured, while ions having the configuration of the noble gases are colourless. It likewise becomes understandable why Cu$^+$ ions are colourless, while Cu^{2+} ions are coloured. The Cu$^+$ ion has a d^{10} configuration in which all the d-orbitals are filled, making
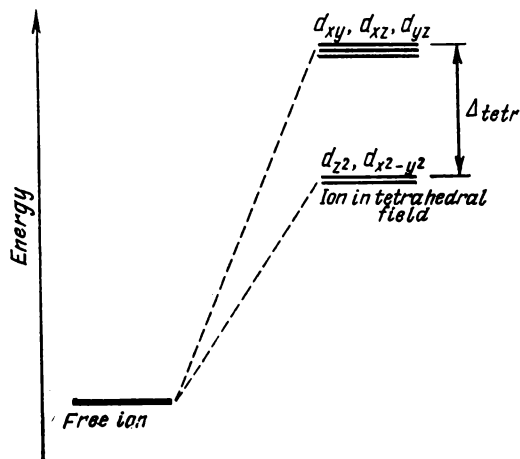
Fig. 16.5. Splitting of d-electron energy levels in a tetrahedral field

the transition of electrons from one d-orbital to another impossible. In the Cu^{2+} ion (d^9), one d-orbital is unoccupied. For the same reason the ions Ag$^+$, Zn^{2+}, Cd^{2+} and Hg^{2+} which have a d^{10} electronic configuration are colourless.

As already pointed out, the value of Δ, characterizing the strength of the field produced by the ligands, depends on the nature of the latter. Study of the spectra of complex compounds, making it possible to determine the values of Δ, has demonstrated that ligands can be arranged in the order of the descending strength of the crystal field as follows:

CN$^-$ > NO$_2^-$ > ethylenediamine > NH$_3$ > NCS$^-$ >
$$> H_2O > F^- > COO^- > OH^- > Cl^- > Br^- > I^-$$
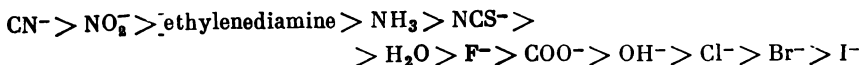
This series is for octahedral complexes but approximately the same order is maintained for other configurations.

If the number of d-electrons in the complexing ion does not exceed the number of low-energy d-orbitals, they naturally occupy these

orbitals. For example, the three d-electrons of the Cr^{3+} ion in the octahedral field occupy the three low-energy d-orbitals
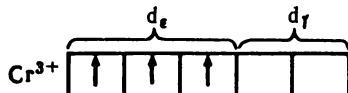
Because of this electronic configuration, trivalent chromium complexes are very stable since the electron clouds of the d_ε-orbitals are situated between the ligands and weakly screen the charge of the chromium nucleus. This explains why so many Cr^{3+} complexes are known.

As we know, electrons are distributed among the quantum cells (orbitals) in accordance with Hund's rule: if there is a sufficient number of cells, each will be occupied by a single electron (see p. 57). This is explained by the fact that electrons repel from one another and thus tend to occupy different orbitals. To transfer an electron from an orbital where it is alone, to an orbital already occupied by another electron requires the expenditure of a certain amount of energy, P. The value of P can be determined by quantum-mechanical calculation. Accordingly, if there are more electrons in a complexing ion than low-energy orbitals, two situations may arise. If $\Delta < P$, the electrons of the central ion in the complex will occupy the same orbitals as in the free ion; and the metal ion will be in a state with a *high spin*; if $\Delta > P$, the crystal field will cause transition of electrons to occupied cells having a lower energy. As a result of electron pairing the spin will diminish and the metal ion will be in a state with a *low spin*.

In Table 16.2 are shown values of Δ for various complexes as determined from their absorption spectra, calculated values of P

Table 16.2

Characteristics of Ions in an Octahedral Field

Configu-ration	Ion	P, kcal/g-ion	Li-gands	Δ, kcal/g-ion	Spin state
d^4	Cr^{2+}	67.2	H_2O	39.7	High
	Mn^{3+}	80.0	H_2O	60.0	Ditto
d^5	Mn^{2+}	72.8	H_2O	22.3	Ditto
	Fe^{3+}	85.7	H_2O	39.1	Ditto
d^6	Fe^{2+}	50.3	H_2O	29.7	Ditto
			CN^-	94.3	Low
	Co^{3+}	60.0	F^-	37.1	High
			NH_3	65.8	Low
d^7	Co^{2+}	64.3	H_2O	26.6	High

and information on the spin state of the ion obtained from magnetic measurements. It is evident that the data given in the Table accord with the principles set forth in the foregoing discussion. Thus the crystal field theory establishes the quantitative relationship between the magnetic and spectral characteristics of complexes—something that cannot be done by the valence-bond method.

When the d_ε- or d_γ-orbitals are not fully occupied, the symmetry of the complex is disturbed, and this disturbance can be very great. For example in the Cu^{2+} ion which has a d^9 configuration. there is only one electron in the $d_{x^2-y^2}$-orbital in an octahedral environment. This orbital screens the nuclear charge less than the others.
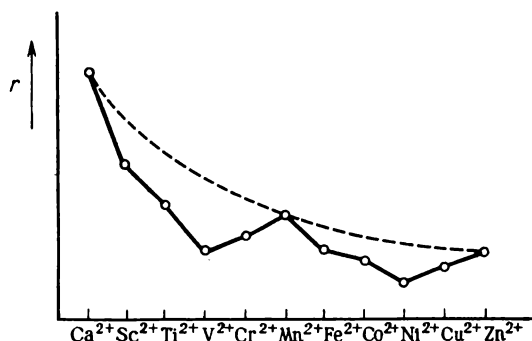
Fig. 16.6. Changes in ionic radii in Ca^{2+} —Zn^{2+} series

Therefore the four ligands located about it (see Fig. 16.2) will be bound considerably more strongly than the other two, and the latter can easily split off from the complex. Consequently the Cu^{2+} ion is characterized by a coordination number of four, and complexes have a flat structure.

The ligand field affects the most diverse properties of compounds of the d-elements. It must be taken into account that ions in aqueous solutions, as we shall see below, form *hydrated complexes*. In crystals, ions are surrounded by their neighbours, i.e., they are in a state similar to that found in complexes (it was from this that the term 'crystal field theory' originated). We shall confine ourselves to an examination of regularities in changes in ionic radii.

As we know, the radii of ions of elements of the groups of transition elements tend to diminish as the atomic number increases (see p. 94). Nevertheless, although there is a general tendency to diminution, the relationship between the ionic radius and the nuclear charge is quite complicate. This relationship for the radii of doubly charged ions of the Ca^{2+}—Zn^{2+} group is shown in Fig. 16.6. This regularity is explained well by the crystal field theory. Actually, during the transition from Ca^{2+} to V^{2+} the d-electrons occupy weakly scree-

ning d_ε-orbitals, which causes a marked decrease in the ionic radii as the atomic number increases. In the Cr^{2+} and Mn^{2+} ions the strongly screening d_γ-orbitals are filled and the ionic radii do not diminish as the atomic number grows, but increase. A similar pattern is seen in the following elements—electrons first fill unoccupied places in the d_ε-cells and then in the d_γ-cells.

Since the size of the ionic radius affects the strength of the bond in compounds, as well as acid-base properties and other characteristics, similar regularities are found in changes in these properties in the series of d-elements.

16.7. Molecular Orbitals in Complex Compounds

Since the central particle in a complex is regarded as an ion in the crystal field theory, results obtained in accordance with this theory cannot be considered satisfactory when the bond between the central atom and the ligands is far from being ionic. The inaccuracy of the ionic model is evidenced by the sequence of the diminishing strength of the crystal field (p. 244). In this series the CN^- ion precedes the F^- ion, although the F^- ion is the lesser of the two, and on the basis of electrostatics should be expected to have a greater effect on the central ion.

The strictest approach to the problem of the nature of the bond in complex compounds is to use the method of molecular orbitals (MO), although this involves much greater difficulties than the crystal field theory. Calculating the energy of the bond in complex compounds by the MO method requires high-capacity electronic computers. Calculations in accordance with the crystal field theory are incomparably easier and are often resorted to in cases where they are not strictly applicable, in order to obtain an approximate estimation.

In the MO LCAO variant, the wave function of the molecular orbital is developed from the wave functions of the atomic orbitals (AO) of the atoms forming the chemical bond. Every atom has many AO—strictly speaking, an infinite number—and the more AO are introduced into the MO, the more exact the calculation of the properties of the bond by the MO LCAO method will be. However, it is only AO whose energy does not differ too greatly that make an appreciable contribution to the MO. The AO contribution to the MO is characterized by the value of the coefficient c_i with which the AO wave function φ_i enters the MO expression. For orbitals differing greatly in energy, the values of c_i determined by the variational method are very small, and roughly they can be considered equal to zero. Therefore, when developing the wave function by the MO LCAO method, AO which differ greatly in energy are usually not included in the MO.

This is easily explained. Assume that in atoms 1 and 2 there are two AO which differ greatly in energy. Assume that the energy of AO (1) is substantially lower than that of AO (2). This means that an electron in AO (1) is attracted considerably more strongly by the nucleus of atom 1 than is an electron in AO (2) by the nucleus of atom 2. If electrons are added to the system of closely located nuclei 1 and 2, an electron that gets into AO (1) will be attracted by nucleus 1 and will not be shared, that is, it will not form a chemical bond. When AO (1) has been filled with two electrons, the next electron
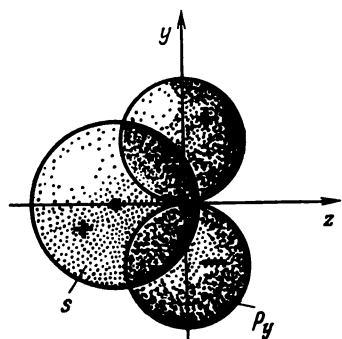
Fig. 16.7. Overlapping of s- and p_y-orbitals; '+' and '—' signs of wave function

will go into AO (2), rather than a molecular orbital made up of AO (1) and AO (2). Thus AO which differ greatly in energy do not form a chemical bond.

This circumstance limits the set of AO introduced into the MO wave function. Nevertheless, when examining complex compounds the set is still very large. Take the case of an octahedral complex of a d-element containing such simple ligands as F^- ions: if AO are limited to the orbitals of valence electrons, the MO expression must include the orbitals of the central atom, namely, one s-orbital, three p-orbitals and five d-orbitals, i.e., nine orbitals in all, and four orbitals from each ligand—one s-orbital and three p-orbitals. Thus the MO wave function for the given complex composed by the LCAO method will consist of 33 terms. This means that the values of 33 c_i coefficients must be found, that is, that a system of 33 equations with 33 unknowns must be solved. This is very difficult to do, even with an electronic computer.

To simplify calculations when applying the MO LCAO method to complex compounds, the symmetry of the atomic orbitals should be taken into consideration. The fact is that all atomic orbitals, even those close in energy, do not necessarily form a molecular orbital, or in other words, form a chemical bond. Besides having close energy levels, AO must have the same symmetry. In Fig. 16.7 is shown the superimposition of s and p_y atomic orbitals, the p_y-orbital being

positioned perpendicular to the z axis, the line connecting the centres of the atoms. Although there is mutual superimposition of the orbitals, the overlap and exchange integrals are in this case equal to zero since the contribution from the superimposition of the positive part of the p_y-orbital is cancelled by the contribution of the negative part of the s-orbital. The s- and p_y-orbitals have a different symmetry with respect to rotation round the z axis; when rotated through 180° the sign of the p_y-orbital is reversed but that of the s-orbital is not. Moreover, the s-orbital is superposed on itself when rotated through any angle round the z axis, whereas the p_y-orbital is only superposed on itself when rotated through 180°. It follows that AO which are unlike in symmetry need not be included in the MO, and this greatly simplifies the expression for the MO wave function in complex compounds.

There is a rigorous mathematical theory treating the properties of symmetry, which makes use of the conceptions and methods of the section of higher algebra called the *theory of groups*. By means of the theory of groups expressions are found for the wave functions of molecular orbitals in complex compounds. In this book it is impossible to carry out this mathematical treatment, and we shall only set forth its results for the case of the octahedral arrangement of the ligands round the central atom which is characteristic of many complex compounds.

The molecular-orbital wave function, ψ_{MO}, in a complex is a linear combination consisting of the orbital of the central atom, φ_M, and a linear combination of certain orbitals of the ligands, $\Sigma c\varphi_L$, which is called the *ligand group orbital*, the word 'group' indicating that the aggregate of these linear combinations meets the requirements of the theory of groups. Thus

$$\psi_{MO} = \alpha\varphi_M + \beta \sum c\varphi_L \qquad (16.1)$$

in which α and β are coefficients selected, like coefficients c, by the variational method. Here we shall examine the results of the maximum simplification of the MO LCAO variant in which the overlap integrals are considered equal to zero, as in the Hückel method (see p. 206 and 211). It then follows from the conditions of normalization that

$$\alpha^2 + \beta^2 = 1$$
$$\sum c^2 = 1$$

and if the bond between the central atom and the ligands is fully covalent

$$\alpha = \beta = \frac{1}{\sqrt{2}}$$

The plus sign in equation (16.1) corresponds to a binding orbital; the minus sign, to an antibinding orbital.

Table 16.3

Molecular σ-orbitals in Octahedral Complexes

MO desig-nation	AO of metal	Group orbital of ligands
a_{1g}	ns	$\dfrac{1}{\sqrt{6}}\,(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$
t_{1u}	np_x	$\dfrac{1}{\sqrt{2}}\,(\sigma_1-\sigma_3)$
	np_y	$\dfrac{1}{\sqrt{2}}\,(\sigma_2-\sigma_4)$
	np_z	$\dfrac{1}{\sqrt{2}}\,(\sigma_5-\sigma_6)$
e_g	$(n-1)d_{z^2}$	$\dfrac{1}{2\sqrt{3}}\,[2(\sigma_5+\sigma_6)-(\sigma_1+\sigma_2+\sigma_3+\sigma_4)]$
	$(n-1)d_{x^2-y^2}$	$\dfrac{1}{2}\,(\sigma_1+\sigma_3-\sigma_2-\sigma_4)$

In Table 16.3 are shown the orbitals of the central atom and the group orbitals of the ligands which form molecular σ-orbitals in octahedral complexes. The letter σ denotes orbitals of ligands, which overlap with orbitals of the central atom according to the σ type,
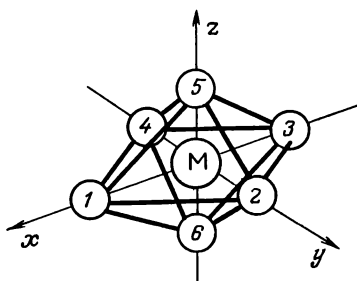
Fig. 16.8. Arrangement of coordinates and numeration of ligands in an octahedral complex

i.e., which are located along the lines connecting the ligands with the central atom. For example, if the ligands are ammonia molecules, σ denotes one of the sp^3-hybrid orbitals of the nitrogen atom (see p. 186) occupied by the unshared pair of electrons and directed toward the metal atom. The indices correspond to the numeration of the ligands given in Fig. 16.8.

The designations of the orbitals (a_{1g}, etc.) are taken from the theory of groups, in which the types of symmetry (the so-called *irreducible representations*) to which the aggregates of the group orbitals of the ligands belong are similarly designated.

When Table 16.3 and Figs 4.7 and 16.8 are compared it is easy to see that the only orbitals of the ligands which are included in the group orbital are those which overlap with the corresponding orbital of the metal according to the σ type. Thus the s-orbital of the metal overlaps equally with the orbitals of all six ligands, while the p_x-orbital overlaps only with the orbitals of ligands 1 and 3, and so on.

It is also evident from a comparison of Fig. 4.7 and 16.8 that metal orbitals d_{xy}, d_{xz} and d_{yz} cannot overlap with the ligand orbitals according to the σ type. These orbitals are denoted t_{2g}. They can overlap according to the π type with those ligand orbitals which have a suitable symmetry.

Many ligands, including NH_3, H_2O and halide ions, have no orbitals with an energy close to that of the t_{2g}-orbitals of the central ion. No π bonds are formed between these ligands and the metal atom.

Electrons occupying t_{2g}-orbitals in such complexes have an energy differing but little from their energy in the unbound metal atom. Approximately, it can be considered that they remain in their atomic orbitals. In a more rigorous treatment, it is considered that electrons occupying d_{xy}-, d_{yz}- and d_{xz}-orbitals in the free metal atom are transferred to t_{2g} nonbinding molecular orbitals when the complex is formed, the t_{2g}-orbitals differing little from the atomic orbitals in energy and the form of the electron cloud.

In Fig. 16.9 is given a diagram of the MO energy levels in the octahedral complex. The transfer of an electron from a nonbinding t_{2g}-orbital to an e_g^* antibinding orbital corresponds to energy change Δ. Thus, whereas it is assumed in the crystal field theory that the electron transfer, the energy Δ of which is determined from spectral data, takes place between an AO of low energy (d_{xy}, d_{xz}, d_{yz}) and an AO of higher energy (d_{z^2}, $d_{x^2-y^2}$), it is considered in the MO theory that the transfer is from a nonbinding MO similar to the AO d_{xy}, d_{xz}, d_{yz}, to an antibinding MO formed from a d_{z^2} or $d_{x^2-y^2}$ AO.

A number of ligands, such as CO, CN^-, etc., have orbitals which can overlap with d_{xy}, d_{xz} and d_{yz} metal orbitals according to the π type. These are the antibinding MO in such particles which are not occupied by electrons. Orbitals of the CO molecule are presented diagrammatically in Fig. 16.10. Orbitals occupied by electrons are hatched. Similar MO are found in the CN^- ion. The CO and CN^- particles are isoelectronic, they contain the same number of electrons and differ only in the charge on one of the atoms; for oxygen $Z = 8$, while for nitrogen $Z = 7$. The MO in these particles which

are occupied by unshared pairs of electrons are close to sp hybrid AO. They form σ bonds with metal atoms. On the other hand, the unoccupied antibinding MO in CN^- or CO form π bonds with the d_{xy}-, d_{xz}- and d_{yz}-orbitals of metals. A diagram representing the formation of these bonds is shown in Fig. 16.11. This results in a
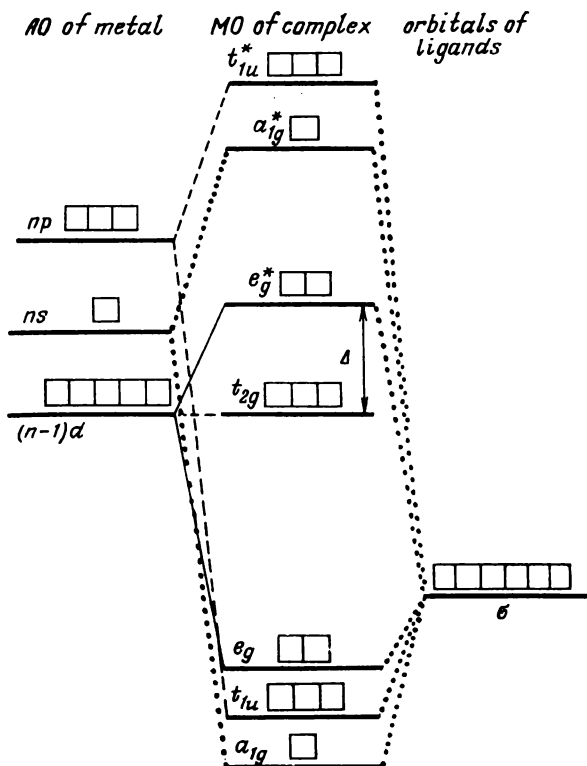
Fig. 16.9. Diagram of orbital energy levels in an octahedral complex. The cells show the number of orbitals each level contains

very strong linking of the ligand with the central atom. Metal-ligand bonds in complex cyanides and carbonyls (compounds of metals with CO) are very stable. Since the t_{2g}-orbital in such compounds becomes binding, its energy level falls and energy difference Δ increases. This explains the position of CN^- in the series shown on p. 244.

The transfer of the electrons of the metal to an antibinding orbital of the ligand makes the bond between the atoms composing the ligand less stable. This can be detected experimentally. Study of mole-

cular spectra and determination of the structure make it possible to find the interatomic distance r_0 and force constant k of the bond (p. 147). The less the r_0 and the greater k, the stronger the bond. It has been found that the $C \equiv O$ bond in carbonyls is longer and k
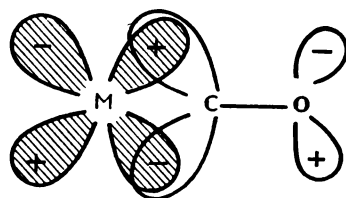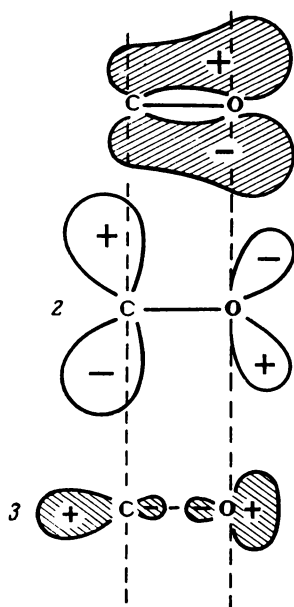
Fig. 16.11. Diagram showing formation of π bond between metal atom and CO molecule

Fig. 16.10. Diagrammatic representation of molecular orbitals in CO molecule

1—binding π-orbital; 2—antibinding π-orbital; 3—σ-orbital occupied by unshared electron pair

is less than in free CO. Thus for the CO molecule the values of r_0 and k are 1.13 Å and 18.6 dyne/cm, while for the $C \equiv O$ bond in $Ni(CO)_4$ they are equal to 1.15 Å and 16.2 dyne/cm, respectively.
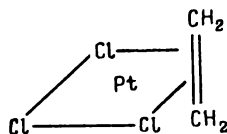
Fig. 16.12. Structure of $[Pt (C_2H_4)Cl_3]^-$ ion

A large number of complex compounds are known in which the ligands are uncharged and in many cases non-polar molecules containing π bonds. Such compounds are called π-*complexes*. Examples are $K[Pt(C_2H_4)Cl_3]$ (Zeise salt), $Fe(C_5H_5)_2$ (ferrocene) and $Cr(C_6H_6)_2$ (dibenzenechromium). Since the ligands in these complexes are completely non-polar, the formation of the latter cannot be explained either by simple electrostatic conceptions or on the basis of the

crystal field theory. Nevertheless, the bond in these compounds is easily explained by the MO theory.

The configuration of the $[Pt(C_2H_4)Cl_3]^-$ ion as established by X-ray analysis is represented in Fig. 16.12. The C_2H_4 molecule is arranged perpendicular to the plane in which the chlorine atoms lie. The configuration of the molecular orbitals binding Pt and C_2H_4 is diagrammatically presented in Fig. 16.13. The AO are shown with a solid line, and the MO formed from them, with a dotted line. The hatching indicates that electrons occupy the AO. It is evident that in this case both the binding and antibinding π-orbitals of C_2H_4 are involved in forming the bond. Development of the wave functions of these orbitals was described on p. 216. Comparison of Fig. 16.13 with equations (14.46) and (14.47) is advisable.
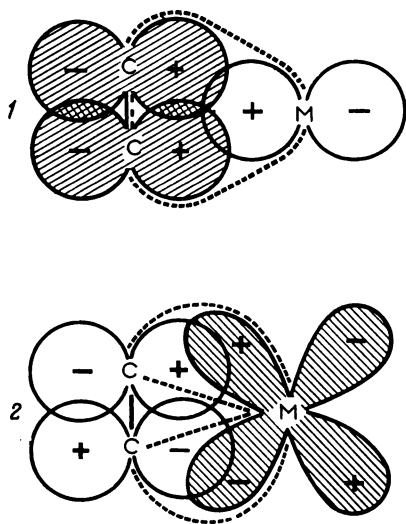
Fig. 16.13. Diagram showing formation of bond in π complexes

1—formation of bond through overlapping of binding π MO of ligand and *p*-orbital of metal; *2*—formation of bond through overlapping of antibinding π MO of ligand and *d*-orbital of metal

In $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ the metal atom is located between two flat, cyclic molecules, and these complexes are therefore said to be *sandwich compounds*. In this case the bond is likewise formed by overlapping of the *d*-orbitals of the metal and the lobes of the *p*-orbitals of the carbon, which have different signs and from which the MO in C_5H_5 and C_6H_6 are formed.

CHAPTER SEVENTEEN

THE HYDROGEN BOND

When hydrogen is joined to a strongly electronegative element it can form an additional bond, though this is considerably less stable than the usual valence bond. The ability of the hydrogen atom to bind two other atoms in a number of cases was demonstrated by M. Ilyinsky and N. Beketov in the 'eighties of last century. Several decades passed, however, before the conception of this bond, which is intermediate between chemical and molecular, was finally established, receiving the name *hydrogen bond.*

The hydrogen bond is caused by the displacement of the electron from the hydrogen atom, transforming it into a particle with unique properties. If it is considered a cation, it (a) has no electron and therefore, unlike other cations, is not repelled by the electron clouds of other particles, and is only subject to attraction, and (b) is infinitesimal in size, other ions being thousands of times larger than the proton.

The more electronegative the atom to which hydrogen is joined, and the smaller it is, the more strongly the hydrogen bond is manifested. Consequently, it is characteristic, above all, of fluorine compounds as well as compounds of oxygen, and to a lesser degree, nitrogen, followed by chlorine and sulphur. The energy of the hydrogen bond varies accordingly, depending in general on the species and state of the atom to which hydrogen is joined, and also on the former's neighbours. Thus the energy of the hydrogen bond H...F (here and below this bond is denoted with dots) is ~ 10 kcal, while the energies of the H...O and H...N bonds are, respectively, ~ 5 and ~ 2 kcal. Neighbouring electronegative atoms can likewise activate atoms of CH groups to form a hydrogen bond, although the electronegativities of carbon and hydrogen are almost the same. This explains the appearance of hydrogen bonds in such compounds as HCN, CHF_3 and the like.

As the hydrogen bond becomes stronger, relevant distances become smaller. Thus, whereas in H_2O the distance O — H is less than H...O, the distance H — F and F...H are the same in hydrogen fluoride, that is, the proton is situated midway between fluorine ions.

Through hydrogen bonds, molecules combine to form dimers and polymers. The latter may have a linear, branched or ring structure. Formic acid, for example, exists mainly in the form of a dimer, both in the liquid and gaseous phase. The dimer has the following structure, which has been established by electronography:
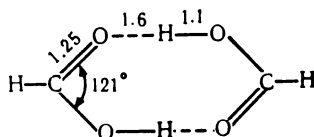
Association distinguishes water, ammonia, alcohols and many other liquids from unassociated liquids, such as hydrocarbons. Association causes a rise in melting points, boiling points and heats of vaporization, as well as changes in solvent properties, etc.

As noted above, the energy of the hydrogen bond is low, it is an order less than the energy of the chemical bond. Therefore, raising the temperature ruptures hydrogen bonds, although the process extends, as a rule, over a comparatively long temperature range.

In carboxylic acids, for instance, association persists even during vaporization.

In a series of similar substances it would be natural to expect a rise in the melting and boiling points and an increase in heats of vaporization as the molecular weight increases, but as can be seen

Table 17.1

Melting Points, Boiling Points and Heats. of Vaporization (at boiling point) of Some Substances

Substance	m. p., °C	b. p., °C	ΔH_{cap}, kcal/mole
H_2O	0.0	100.0	9.75
H_2S	−85.5	−60.7	4.50
H_2Se	−64.8	−41.5	5.1
H_2Te	−49.0	−2.0	5.8
HF	−83.1	−19.5	7.20
HCl	−112	−84.9	3.6
HBr	−87	−66.8	3.9
HI	−50.9	−39.4	4.2

from Table 17.1, these values are higher for H_2O than for H_2S, and higher for HF than for HCl. This is because there are strong hydrogen bonds between the H_2O molecules, and between the HF molecules. The scale of this effect is shown by the curve in Fig. 17.1.

The most convenient indicator for the hydrogen bond is the boiling point since it is easily measured. On determining the boiling point of an alcohol ROH and the corresponding mercaptan RSH we would see that it is higher for ROH than for RSH. Ethers, even those with a higher molecular weight than alcohols, are more volatile. If water were not associated it would have a melting point of about −100°C and a boiling point of about −80°C, which is evident from a curve similar to that in Fig. 17.1[1] which can be drawn using the figures given in Table 17.1

If one employs the method of comparative calculation and compares the boiling point in the groups HR (R = F, Cl, Br and I) and H_2R' (R' = O, S, Se and Te) (Fig. 17.2), one can conclude from the character of the deviation of the point for HF — H_2O and from the fact that water vapour molecules are practically not associated, that unlike water the association of hydrogen fluoride persists in the

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[1] These are approximate values, since such extrapolation does not take account of certain peculiarities in the properties of compounds of elements of the second period.

vapour phase, otherwise one would expect all four points to lie on a straight line. This shows the greater stability of the H...F bond as compared to the H...O bond. This conclusion is confirmed by the perceptibly lesser difference in the heats of vaporization of HF and
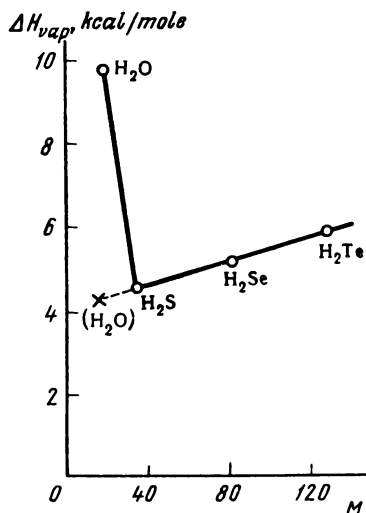
Fig. 17.1. Relationship between heat of vaporization and molecular weight for hydrogen compounds of Group VI elements
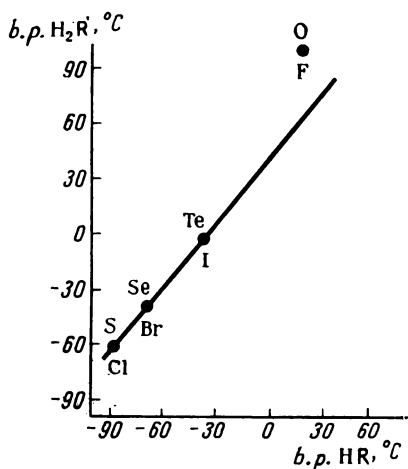
Fig. 17.2. Comparison of boiling points in HR and H_2R' series

HCl as compared to H_2O and H_2S (Table 17.1). Actually, $(HF)_n$ molecules exist in hydrogen fluoride vapour which have the structure
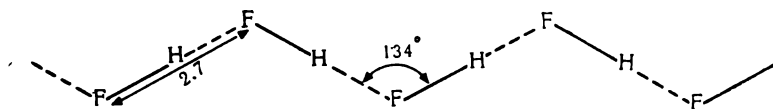
Although in most of the particles $n = 4$, there are some in which $n = 5$ or 6.

All the examples considered so far are cases of an *intermolecular* hydrogen bond. Often the hydrogen bond joints parts of a single molecule, that is, the bond is *intramolecular*. This is characteristic of many organic compounds. In most cases the hydrogen atom forms part of a flat, six-membered ring. If the formation of such a ring is hindered, an intramolecular hydrogen bond is not formed. Here are

some examples of an intramolecular hydrogen bond

Salicyl   aldehyde

Ortho-nitro-
phenol

2,6-Dihydroxy-
benzoic acid

Ortho-ethy-
nylphenol
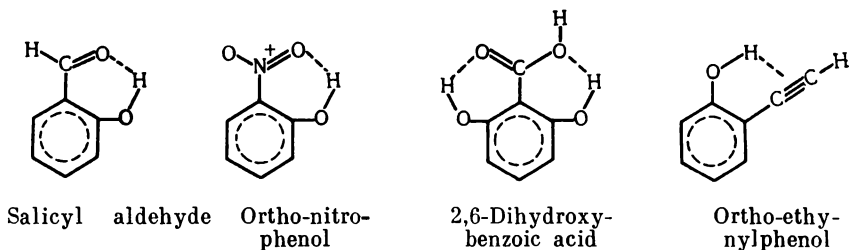
Whereas in *o*-nitrophenol the hydrogen bond is intramolecular, it is intermolecular in *n*-nitrophenol since the hydrogen is remote from the oxygen of the nitro group. The dissociation constant of 2,6-dihydroxybenzoic acid at 25°C is 5×10^{-2}, which is 550 times greater than the dissociation constant of 3,5-dihydroxybenzoic acid. This is explained by the fact that in the latter compound the
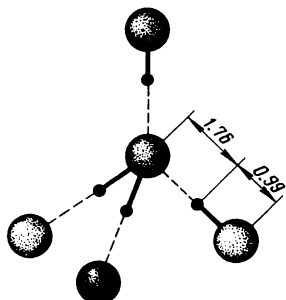
Fig. 17.3. Environment of wa-
ter molecule in ice

hydrogen bond is practically not manifested, which strengthens the O — H bond in the carboxyl group. The *ortho*-ethynylphenol molecule is noteworthy in that formation of the hydrogen bond involves the π-electrons of the triple bond.

Taking into account the effect of the hydrogen bond has provided a key to many facts which are otherwise difficult to understand. Thus formation of salts of the type KHF_2 and $NaHF_2$ is explained by the existence of the stable ion HF_2^-, formed through the process $H_2F_2 \rightleftarrows H^+ + HF_2^-$. Actually, the equilibrium $HF + F^- \rightleftarrows HF_2^-$ is displaced to the right ($K_{298} = 5.1$). The energy of the hydrogen bond in F — H...F$^-$ comes to 27 kcal/mole. The influence of the hydrogen bond also makes it understandable why hydrofluoric acid, unlike its analogues, HCl, HBr and HI, is not a strong acid, its dissociation constant being 7.2×10^{-4}.

Hydrogen bonds are of great importance in determining the structure of water and ice. A fragment of ice structure is shown in

Fig. 17.3. Each oxygen atom in this structure is tetrahedrally bonded with four other atoms, and between them are arranged the hydrogen atoms. Two of the latter are joined to the given oxygen atom with a polar, covalent bond ($d = 0.99$ Å); two others, with a hydrogen bond ($d = 1.76$ Å; $E_{O \ldots H} \approx 5$ kcal/mole), that is, they form part of two other molecules of water. This makes the structure loose, not tightly packed. This accounts for the small density and considerable porosity of ice. When ice is melted the hydrogen bonds are broken to the extent of about 10%; and the molecules are drawn somewhat together. Water is therefore slightly denser than ice. Heating water causes it to expand, that is, it increases the volume, but on the other hand, it causes further disruption of the hydrogen bonds, which should reduce the volume. As a result the density of water exhibits a maximum at 4°C.

The hydrogen bond likewise plays an important part in processes of solution, since solubility depends, for one thing, on the ability of a substance to form hydrogen bonds with the solvent. Interaction products called *solvates* are often formed, the solution of alcohols in water being an example. This process takes place with the liberation of heat and a reduction in volume, which are indications of the formation of compounds. In such cases it is impossible to speak of the formation of solvates through electrostatic attraction by ions, of the polar molecules of the solvent, since we have to do with the solution of non-ionizing compounds. The absence of the influence of a hydrogen bond can likewise explain cases where polar compounds are insoluble in water. Thus polar ethyl iodide is a good solvent for non-polar naphthalene, but itself is insoluble in such a polar solvent as water.

The problem of the nature of the hydrogen bond has not been definitely solved. It is clear that this involves interdipole interaction, and the effect of polarization, as well as a donor-acceptor mechanism. The difficulty of the quantum-machanical calculation of the hydrogen bond is due to the fact that the error in calculation is substantially greater than the value of the energy of the hydrogen bond. Evidently the most promising results can be expected from the molecular orbital method.

The hydrogen bond is encountered almost universally—in organic crystals, since they contain C, H and O; in proteins, since they contain C, H and N; in polymers and in living organisms. It is suggested that memory involves the storage of information in configurations containing hydrogen bonds. The 'universality' of the hydrogen bond springs from the fact that water molecules are found everywhere, and each of them, possessing, as it does, two hydrogen atoms and two unshared electron pairs, can form four hydrogen bonds.

THE STRUCTURE OF MATTER
IN THE CONDENSED STATE

CHAPTER EIGHTEEN

INTRODUCTION

18.1. Aggregate States

Matter can be in the solid, liquid or gaseous state, depending on the distance between particles and on the forces acting between them.

At a sufficiently low temperature a substance is in the solid state[1]. The distances between the particles of a crystalline substance are of the order of the size of the particles. The mean potential energy of the particles is greater than their mean kinetic energy. The movement of the particles making up crystals is extremely limited. The forces acting between particles keep them close to equilibrium positions, and consequently the probability of particles being found in these spots is maximum. It is to this that crystalline bodies owe their shape and volume and great resistance to deformation.

When crystals melt, a liquid is formed. A liquid differs from a crystalline substance in that not all the particles are situated at distances of the same order as in crystals; some of the molecules are at substantially greater distances. In this state the mean kinetic energy of the particles is roughly equal to their mean potential energy.

The solid and liquid states are often grouped together under the general term *condensed state*.

As a result of evaporation or boiling a liquid is transformed into the gaseous state. In this state particles are at distances greatly exceeding their size, and for that reason forces acting between them are very small. Particles can move about freely. Whereas in a solid all the particles form a single aggregate, and in a liquid, a great number of large, stable aggregates, only particles consisting of two to five molecules can be found in gases, and their number is usually comparatively small. The mean kinetic energy of the particles of a gas is substantially greater than their mean potential energy. Consequently forces of attraction between them are insufficient to hold them near one another.

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[1] Helium is an exception. For a discussion of the amorphous state see p. 303.

The state and properties of an individual substance are determined by the temperature and pressure. If the pressure is low and the temperature sufficiently high, the substance will be in the gaseous state; at low temperatures it will be a solid, and at moderate temperatures, a liquid. Accordingly the *phase diagram of a substance* consists of three fields (Fig. 18.1), corresponding to the crystalline (*C*), liquid (*L*) and gaseous (*G*) states. These regions are separated from one another by the melting (crystallization) curve *Ob*, boiling (condensation) curve *OK* and sublimation (desublimation) curve *Oa*. Point *O* at which they meet is called the *triple point*: at $P = P_0$ and $T = T_0$ the substance exists in three aggregate states simultaneously. Point *K* at the end of the boiling curve is called the *critical point*: at $P = P_K$ and $T = T_K$ the boiling liquid and dry saturated vapour are absolutely indistinguishable.
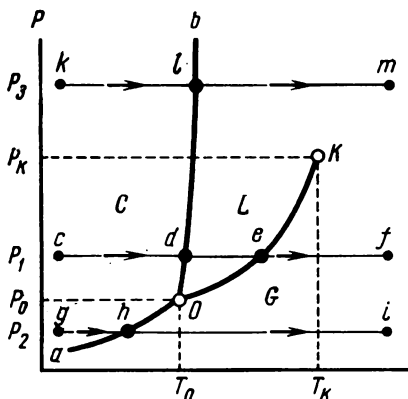
Fig. 18.1. Phase diagram of a single
        component system

From Fig. 18.1 it can be seen that at a pressure greater than P_0 but less than P_K, for example, at P_1 (point *c*) isobaric heating of a solid will cause it to melt (point *d*). After all the substance has melted, further heating will again cause the temperature to rise (process *de*). At point *e* the liquid will boil and the temperature will again cease to rise. When all the liquid has been vaporized, further heating will overheat the vapour (process *ef*). The length of time at which the temperature remains constant (points *d* and *e*) is determined by the amount of the substance and its nature, assuming that other conditions remain unchanged. The greater the amount of substance and the greater the heat of fusion and heat of vaporization, i.e., the greater the bond energy in the solid and liquid phases, the more protracted the isothermic 'crossings' of the *Ob* and *OK* curves will be.

When $P < P_0$, for example, at P_2 (point *g*), a solid will be transformed directly into the gaseous state (at point *h*), i.e., *sublimation* will take place. For most substances $P_0 < 1$ atm. In the case of the few substances for which $P_0 > 1$ atm, such as carbon dioxide, heating the crystals at $P = 1$ atm will cause sublimation.

Finally, at $P > P_K$, for example, at P_3 (point *k*), further heating after crystals have melted (point *l*) will put the substance into the

supercritical state. This term simply emphasizes the fact that in this region, for example, at point m, liquid and gas are indistinguishable.

The higher the pressure, the higher the temperature at which melting, vaporization and sublimation take place. A few substances present exceptions, among them H_2O and Bi; in their case increasing the pressure lowers the melting point.

We have considered the simplest phase diagram. If a substance has several modifications the phase diagram is complicated, since for each additional phase there is an additional region.

A direct or reverse sequence of the transformations 'solid-liquid-gaseous' is not universal. It was pointed out that there are cases where heating a solid converts it directly into the gaseous state. There are likewise cases where the sequence is broken as the result of a chemical change. Thus when crystalline $MgCO_3$ is heated it will, at a certain temperature, decompose into MgO and CO_2, not melt, the decomposition point being the higher, the greater the CO_2 pressure. It is also impossible to condense NO_2 from the gaseous state into a liquid or solid since cooling or compression causes the formation of a different substance—N_2O_4.

We return to the gaseous state. The higher the temperature and the lower the pressure, the greater the independent motion of the gas particles will be. At the limit where $P \to 0$, the interaction between the particles, as well as their volume compared to the space occupied by the gas become negligible. Such a gas is said to be *perfect*.

Naturally the relationship between pressure P, temperature T and volume V of a perfect gas is described by the simplest equation, that of *Mendeleev—Clapeyron*

$$PV = nRT \tag{18.1}$$

in which n is the number of moles of gas in volume V; T, the absolute temperature; and R, the universal gas constant. For one mole

$$Pv = RT \tag{18.2}$$

here v is the molar volume.

In conditions of moderate and high pressures and low temperatures, i.e., when compression involves a volume not occupied by the particles themselves, equation (18.2) should be replaced by the equation

$$P(v - b) = RT \tag{18.3}$$

in which the correction term b takes into account the volume of the molecules and their mutual repulsion at short distances. The equation $P(V - b) = const$ might be called Lomonosov's equation

since it was he who first pointed out that "...the density of air[1] under great compression is not proportional to its pressure", and explained this fact as being due to the ultimate size of the particles. Actually, it is only at the assumption that $b = 0$, that at a given temperature $PV =$ const or $d =$ const$' \times P$, where d is the density of the gas.

Moreover, in the nonperfect gas the forces of mutual attraction of the molecules must be taken into account, that is, we must employ an equation of the form

$$(P + P_{int})\,(v - b) = RT \qquad (18.4)$$

in which the correction term P_{int} is introduced to take into account the mutual attraction of the molecules, which is called *internal pressure*. Equation (18.4) in which this term is directly proportional to the square of the density is called *Van der Waals' equation*. It is one of the earliest and most thoroughly studied *equations of the state of real gases*. In all, about 200 of these equations have been proposed, which shows the difficulty of giving a precise description of the properties of real gases.

If such great energy is imparted to a gas that electrons begin to break away from its molecules, there will be positively and negatively charged particles in the space occupied by the gas. *Thermal ionization* takes place and as a result the gas will become a conductor of electricity and will go over to the *plasma state*. There is no sharp boundary between gas and plasma but plasma appears as soon as the substance finds itself in a magnetic field because in this case the motion of the charged particles becomes orderly.

18.2. Molecular Interaction

When studying the properties of substances much attention is given to intramolecular interactions due to the action of valence or chemical forces and characterized by saturation, great energy changes and specificality, but along with this the interaction between the molecules of a substance must be taken into account. In processes of gas expansion, condensation, adsorption, solution, etc., the action of these forces makes itself felt. They are often called *Van der Waals' forces*, which emphasizes that their existence explains the difference between real gases and a perfect gas, the difference of the value of P_{int} in equation (18.4) from zero.

Molecular interaction is of an electric nature; it differs from chemical interaction in that it is manifested at comparatively great distances and is characterized by the absence of saturability and specificity, and by small energies. To give an idea of the magnitude of these forces it can be noted that the heat of condensation of vapour into liquid, which characterizes the energy of interaction between the vapour molecules, is relatively small, for example, for

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[1] Air was the only gas known in the first half of the 18th century.

HI it is about 5 kcal/mole. The energy of intermolecular forces in the liquid is of the same order. The energy of chemical interaction is much greater; thus, the energy of the H — I bond exceeds 70 kcal/mole.

At comparatively large distances r between molecules where their electron subshells do not overlap, only the action of the *attractive forces* is manifested.

If the molecules are polar, electrostatic interaction is exhibited. This is called the *orientation effect*, and the greater the dipole moment μ of the molecules, the greater the effect. Raising the temperature should weaken this interaction since thermal motion tends to disturb the relative orientation of the molecules. The attraction of polar molecules decreases rapidly as the distance between them grows. In the simplest case, theory (Keesom W., 1912) gives the following relationship for the energy of the orientation effect:

$$U_{or} = -\frac{2\mu^4 N_0}{3RTr^6} \tag{18.5}$$

in which N_0 is Avogadro's number; R, the universal gas constant; and T, the absolute temperature. This equation is quite exact at high temperatures and low pressures, where the distance between the dipoles is substantially greater than their length.

If the molecules of a substance are non-polar, there is no orientation effect. But if molecules come into the field of neighbouring particles (molecules, atoms or ions) they are polarized, and an induced dipole moment appears. The easier the molecules are deformed, the greater the *induced effect* (see p. 154). The interaction energy of such molecules increases with the increase in μ and quickly diminishes with the increase in r, but it does not depend on temperature, since the induction of dipoles takes place whatever the spatial arrangement of the molecules. Theory (Debye, 1920) gives the following relationship for the energy of the induction (deformation) effect of two like polar molecules:

$$U_{ind} = -\frac{2\alpha\mu^2}{r^6} \tag{18.6}$$

where α is the polarizability.

Intermolecular attraction is not limited to these two components. The orientation and induction interactions are only part of the Van der Waals attraction, and for many compounds they are the smaller part. For such substances as Ne and A both components are equal to zero—the particles of these elements are non-polar and their electron shells are very rigid; nevertheless the noble gases can be liquefied. This shows that there must be another component of intermolecular forces. What is its nature?

Let there be two atoms of a noble gas. If the static distribution of their charges is considered, it would seem that these atoms should have no effect on one another. But experience and the quantum theory have it that under all conditions, even at absolute zero temperature, the particles in an atom are in constant motion. During the movement of the electrons, distribution of the charges within the atoms becomes unsymmetrical, resulting in the appearance of momentary dipoles. As molecules approach one another, the motion of these dipoles ceases to be independent, thus causing attraction. The interaction of momentary dipoles is the third source of intermolecular attraction. This effect, which is quantum-mechanical in character, is called the *dispersion effect*, since the oscillations of electrical charges cause the dispersion of light—different refraction of light rays of different wavelength. The theory of the dispersion effect was elaborated by London in 1930. From the above discussion it follows that dispersion forces act between the particles of all substances. Their energy is approximately expressed by the equation

$$U_{disp} = -\frac{3h\nu_0\alpha^2}{4r^6} \tag{18.7}$$

where h is Planck's constant; ν_0, the frequency of oscillations corresponding to zero energy E_0, i.e., the energy at $T = 0$ (the zero energy of a vibrating particle is expressed by the relationship $E_0 = \frac{h\nu_0}{2}$); and α, the polarizability. The value of $h\nu_0$ can be considered approximately equal to the ionization potential.

Table 18.1

Values of $Ur^6 \cdot 10^{60}$ (erg·cm^6) Characterizing the Orientation, Induction and Dispersion Interaction Between Like Molecules

Molecules	Interaction		
	orientation	induction	dispersion
CO	0.0034	0.057	67.5
HCl	18.6	5.4	105
HBr	6.2	4.05	176
HI	0.35	1.68	.382
NH_3	84	10	93
H_2O	190	10	47

In Table 18.1 are given the components of Van der Waals' forces for certain substances. These figures show: (a) that the dispersion effect is high in value and is foremost for non-polar and slightly

polar molecules; (b) that for strongly polar molecules the contribution of the orientation effect is large; and (c) that the induction effect is usually of minor significance. It only becomes important when polar molecules occur together with strongly polarizable molecules. Thus, as a result of polarization interaction, nitrobenzene forms with naphthalene the molecular compound $C_6H_5NO_2 \cdot C_{10}H_8$. A great many compounds of this type are known.

Adding together the orientation, induction and dispersion energies and combining all the constants in conformity with equations (18.5), (18.6) and (18.7) we obtain the energy of intermolecular attraction

$$U_{attr} = - \frac{n}{r^6} \qquad (18.8)$$

where

$$n = \frac{2\mu^4 N_0}{3RT} + 2\alpha\mu^2 + \frac{3\alpha^2 h\nu_0}{4}$$

Thus the attractive forces are inversely proportional to the intermolecular distance to the seventh power.

When distances between molecules are small and their electron
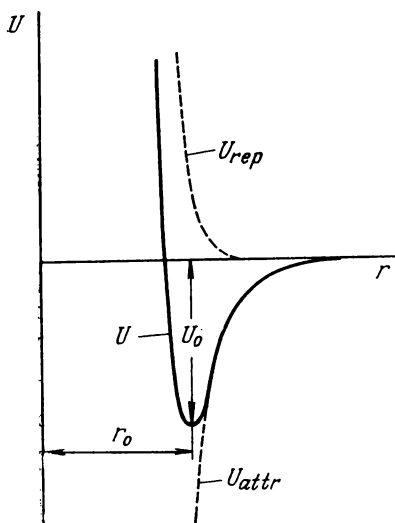
Fig. 18.2. Potential energy curves of intermolecular interaction

subshells overlap intensely, i. e., when the electrostatic repulsion of the nuclei and electrons becomes greater than their mutual attraction, the action of *repulsive forces* is manifested. Many facts point to the existence of these forces, one of them being the small compressibility of liquids and solids.

The repulsive energy can be expressed to a first approximation by the equation

$$U_{rep} = \frac{m}{r^{12}} \qquad (18.9)$$

which is similar to (18.8); here m is a positive constant—the *repulsion constant*. It is evident from equation (18.9) that the repulsive forces begin to be manifested at very small distances and increase rapidly as r diminishes.

The total interaction energy between molecules is equal to

$$U = U_{attr} + U_{rep} \qquad (18.10)$$

or in conformity with (18.8) and (18.9)

$$U = -\frac{n}{r^6} + \frac{m}{r^{12}} \tag{18.11}$$

This equation is called the *Lennard-Jones formula* (1924)[1]. It corresponds to the curves in Fig. 18.2. The minimum on the summary curve represents energy of molecular interaction U_0 and equilibrium distance between the molecules, r_0. These curves resemble the curves characterizing the relationship between the energy of ionic interaction and the interionic distance (see Fig. 15.1). Nevertheless, the curves in Figs 15.1 and 18.2 greatly differ in the quantitative aspect since both the scale of the values of U and r, and the relationships between energies U_{attr} and U_{rep} and distance r are different.

<div align="center">

CHAPTER NINETEEN

THE CRYSTALLINE STATE

</div>

19.1. Characteristics of the Crystalline State

The word 'crystal' is always associated with the image of a polyhedron of some kind. Crystalline substances, however, are characterized not only by their occurrence as bodies of definite form but by their *anisotropy* or the *vectorial character of their properties*—the fact that such properties as tensile strength, thermal conductivity, compressibility, etc. depend on the direction through the crystal.

This is best explained by examples. A figure of exactly the same form as a crystal of calcite ($CaCO_3$) can be made from glass, but the difference between the calcite crystal and its glass model is easily detected; calcite, unlike glass, exhibits double refraction (see Appendix IV). Here is another example. A ball can be fashioned from rock salt which has all the appearance of a glass ball, but a simple test will show that the ball has been made from a crystalline substance. If the ball is heated and placed on a slab of paraffin wax, the paraffin round the ball will melt unevenly because the thermal conductivity of an NaCl crystal is different in different directions.

We must now take up briefly some matters relating to the form of crystals.

The forms of crystals are the subject of *geometric crystallography*. This science began to develop in the 18th century. It is based on two laws: *the law of the constancy of interfacial angles and the law of rational indices.*

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[1] Two limitations should be noted: (1) equation (18.11) can be considered only as a first approximation since when r is of the order of 1 Å, equations (18.5)—(18.7) are not exact; (2) everything set forth above is only partially applicable to molten salts and metals.
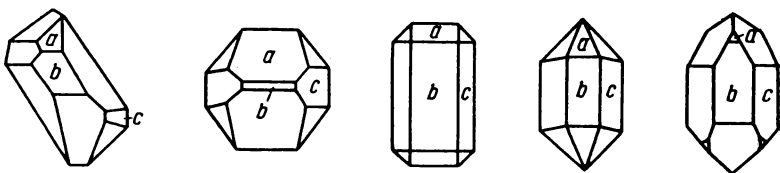
Fig. 19.1. Forms of quartz crystals
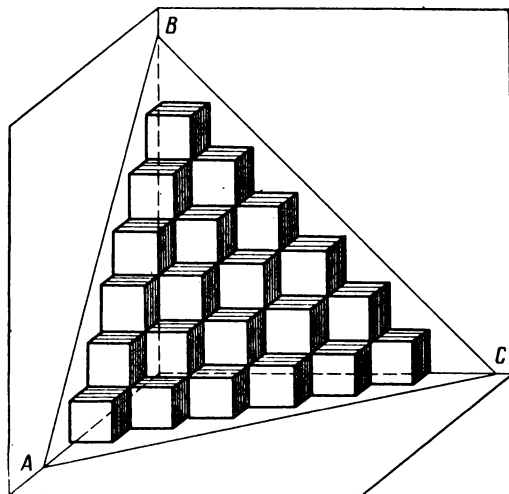
Fig. 19.2. Formation of face of an octahedral crystal consisting of unit cells of cubic form

(a)   (b)
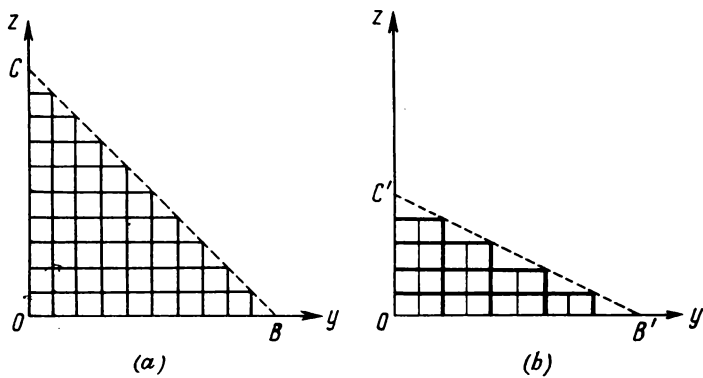
Fig. 19.3. Illustration of the law of rational indices. Sections OC and OC' cut off on z axis by faces CB and $C'B'$ are in the ratio of 2 : 1

The first law, which was formulated by Romé de L'Isle (France) in 1783, states that *in all crystals of the same substance, the angles between corresponding faces are equal.* For example, in sodium chloride crystals all the angles between faces are equal to 90°. This does not mean that crystals of the same substance always have the same form. This can be illustrated by quartz crystals (Fig. 19.1)[1]. In spite of the fact that the crystals presented in the Figure are different in form, the angles between corresponding faces, e.g., *a* and *b* or *b* and *c* are equal.

According to the law of rational indices, discovered in 1784 by R. Haüy (France), *the faces of a crystal are always oriented in space in such a way that the ratios of sections cut off on the three coordinate axes of a crystal by one of the faces to sections cut off on the same axes by another face are integers.* Haüy explained this as being due to the fact that crystals are constructed of particles having the form of polyhedrons. Fig. 19.2 shows the formation of the face of a crystal consisting of cubes, and the diagrams in Fig. 19.3 show how two faces of a crystal constructed of cubes cut off sections *OC* and *OC'* on the *z* axis, which are related to one another in the ratio of 2:1.

Haüy's law of rational indices which showed the discrete structure of matter preceded Dalton's investigations and influenced the formation of his views. The formulation of this law can be considered an important landmark in the development of atomic-molecular theory.

It goes without saying that the particles of which crystals consist—atoms, ions or molecules—are not cubes or parallelepipeds, but, as we shall see below, are arranged in the crystals in an orderly way, forming *crystal lattices,* which can be considered as consisting of *unit cells* having the form of parallelepipeds.

Despite the great diversity of crystal forms they can be rigidly and unambiguously classified. This systematization was introduced by A. Gadolin, Russian Academician, in 1867; it is based on the symmetry characteristics of crystals.

Symmetrical geometrical figures have one or several *elements of symmetry,* they have centres, axes or planes of symmetry. *Centre of symmetry C* is a point which bisects every straight line passing through it and drawn to its intersection with the boundaries of the figure (Fig. 19.4). The *plane of symmetry* divides a figure into two parts, which are mirror images of one another (Fig. 19.5). The *axis of symmetry* is a line such that the figure when rotated on it through an angle of 360° coincides with itself *n* times (Fig. 19.6). The number *n* is called the *order of the axis.* Axes are said to be of the second order, third order, and so on (axes of the first order are not conside-

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[1] Figure 19.1 was taken from G. Boky's 'Kristallokhimiya', Moscow, 1960; the author stated that the illustration was taken from Romé de L'Isle's monograph (1783).

red because a figure will coincide with itself when rotated through 360° on any line). Besides the usual axes of symmetry, there are *inversion axes* and *axes of mirror rotation symmetry*. For a figure to coincide with itself when such axes are present, revolution round the axis must be accompanied by rotation through 180° round another axis which is perpendicular to the first (inversion), or by a mirror reflection from the plane. Examples of figures having such axes of symmetry are shown in Fig. 19.7.

In 1867 A. Gadolin mathematically demonstrated that 32 types of crystal symmetry were possible, each of them characterized by a
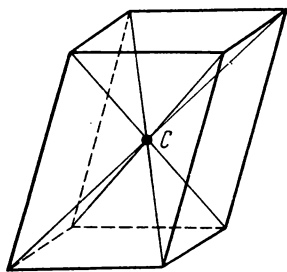
Fig. 19.4. Figure with centre of symmetry *C*
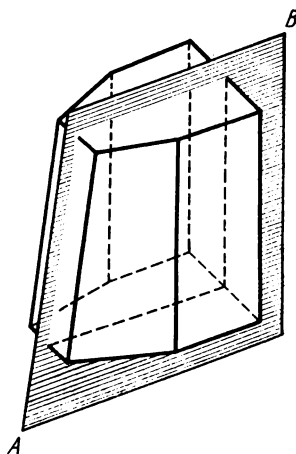
Fig. 19.5. Figure with plane of symmetry *AB*

certain combination of symmetry elements. In Gadolin's time some 20 of these types were known but today crystals of all 32 symmetry types have been described.

According to symmetry types, crystals are divided into three *categories: lower, intermediate* and *higher*. Crystals of the lower category have no axes higher than the second order; crystals of the intermediate category have one axis of a higher order, while those of the higher category have several axes of a higher order. Categories are divided into *crystal systems*.

The lower category includes three systems, namely, *triclinic, monoclinic* and *orthorhombic*. Crystals of the triclinic system have neither axes nor planes of symmetry; there may or may not be a centre of symmetry. Examples of substances crystallizing in the triclinic system are $K_2Cr_2O_7$ and $CuSO_4 \cdot 5H_2O$. In monoclinic crystals ($CaSO_4 \cdot 2H_2O$, $C_4H_6O_6$—tartaric acid, etc.) there may be both an

axis and a plane of symmetry but there cannot be several axes or planes of symmetry. Crystals of the orthorhombic system ($BaSO_4$, $MgSO_4 \cdot 7H_2O$, etc.) are characterized by the presence of several elements of symmetry, several axes or planes.

The intermediate category is divided into three systems which are named according to the type of the principal axis (axis of higher order): *trigonal* (has axis of the third order; examples: calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$); *tetragonal* (has axis of fourth order;
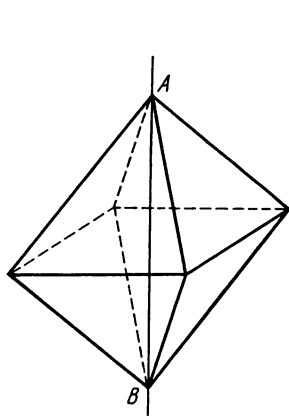
Fig. 19.6. Figure with axis of symmetry *AB* (*n* = 4)
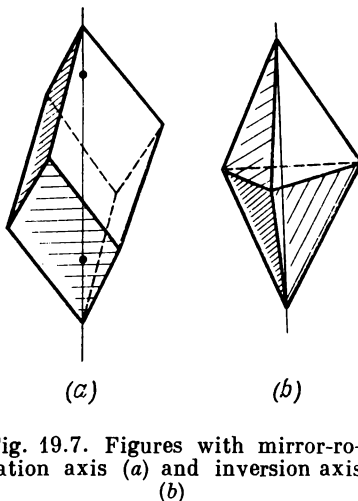
Fig. 19.7. Figures with mirror-rotation axis (*a*) and inversion axis (*b*)

examples: SnO_2, $CaWO_4$ and $PbMoO_4$); and *hexagonal* (has axis of sixth order; examples: quartz, SiO_2, as well as KNO_3 and AgI).

The higher category has only one system—the *cubic*. The crystals of this system, for example, CaF_2, $NaCl$ and $NaClO_3$, have several axes of a higher order. Examples of crystals of the systems mentioned are shown in Fig. 19.8.

A prerequisite for the formation of crystals of high symmetry is that the particles of which they are composed should be symmetrical. Since most molecules, including a multitude of organic molecules are unsymmetrical, crystals of high symmetry constitute only a small proportion of those known.

Many cases are known in which a substance exists in different crystalline forms, i.e., differs in internal configuration and therefore in physical and chemical properties. This is termed *polymorphism*. Silicon dioxide, for example, is known in three modifications: quartz, tridymite and cristobalite. At a certain temperature only one of the polymorphic varieties of a substance is stable. At ordinary temperatures the stable form of SiO_2 is quartz; from 870 to

1470°, tridymite; and above 1470°, cristobalite. Transition of an unstable form to a stable form often takes place very slowly at a low temperature. A substance can remain in an unstable, or as it is called, a *metastable state* for a very long time[1].
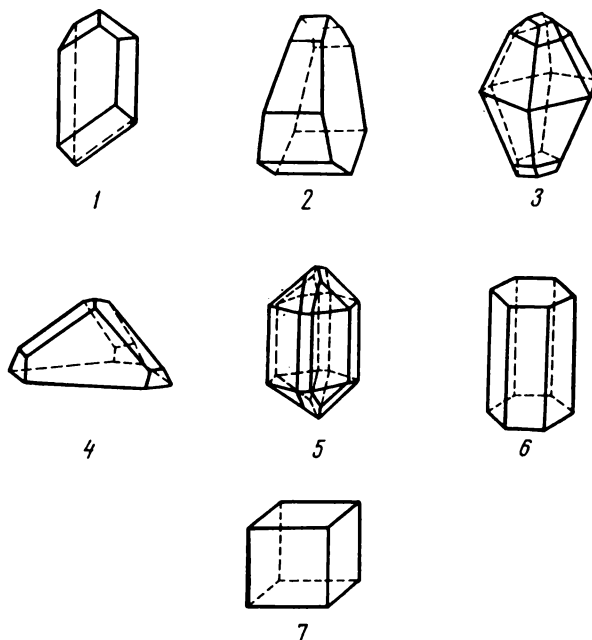
Fig. 19.8. Systems of crystals

Lower category

1—triclinic (strontium bitartrate Sr[COOH(CHOH)$_2$COO]$_2$); *2*—monoclinic (lactose C$_{12}$H$_{22}$O$_{11}$·H$_2$O); *3*—orthorhombic (sulphur)

Intermediate category

4—trigonal (sodium periodate trihydrate NaIO$_4$·3H$_2$O); *5*—tetragonal (cassiterite SnO$_2$); *6*—hexagonal (nepheline NaAlSiO$_4$)

Higher category

7—cubic (rock salt NaCl)

Many gaseous substances which crystallize on cooling, do so with the formation of several modifications. Extensive high pressure investigations carried out during the last few decades have revealed that the formation of crystalline modifications at high pressures is likewise typical. This shows that polymorphism is a widespread phenomenon. It has been found that there are seven modifications

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[1] The term 'metastable state' denotes the state of a system which is unstable but, nevertheless, can persist for a lengthy period. For example, a mixture of hydrogen and oxygen does not react at room temperature but the slightest spark causes it to explode. At ordinary temperatures such a mixture is in a metastable state.

of KNO_3, eight modifications of Na_2SO_4 and 16 modifications of naphthalene.

Another phenomenon frequently observed among crystalline bodies is *isomorphism*, which is the property of atoms, ions or molecules to replace one another in a crystal lattice, thus forming mixed crystals. For example, the colourless crystals of potassium aluminium sulphate, $KAl(SO_4)_2 \cdot 12H_2O$, and the violet crystals of chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$, have the same octahedral form. If a solution containing both substances is evaporated, crystals are formed which contain both aluminium and chromium. Mixed crystals are formed in the same way when a solution containing $KAl(SO_4)_2 \cdot$ $\cdot 12H_2O$ and $RbAl(SO_4)_2 \cdot 12H_2O$ is evaporated. Mixed crystals are completely homogeneous mixtures of solid substances, they are *solid solutions by replacement*.

Therefore, it can be said that *isomorphism is the ability to form solid solutions by replacement*.

We have cited examples of the most perfect isomorphism—that of substances which are similar in chemical composition, type of chemical bond, crystalline form, structure and valence of their elements and the dimensions of the particles which replace one another.

If some of the indications of similarity are not present, and especially if there is only one, say congruent structure, isomorphism is imperfect, which may be manifested in limited miscibility, or there may be no isomorphism of any degree. Thus the isomorphism of $SrSO_4$ and KBF_4 is imperfect; crystals of $NaCl$ and KCl are not isomorphous although they are similar in chemical composition, type of bond, form and structure; here the difference in the radii of Na^+ and K^+ makes itself felt. The difference in atomic radii and type of chemical bond explains why crystals of $CuCl$ and $CuZn$ are not isomorphous despite their similar structure and form. Although $r_{Na^+} \approx r_{Cu^+}$, $NaCl$ and $CuCl$ are likewise not isomorphous, their similarity is cancelled by the substantial difference in the polarization properties of the cations.

19.2. Study of Crystal Structure

The regular form of crystals is brought about by the orderly arrangement of their components—atoms, ions or molecules. This arrangement can be represented in the shape of a crystal lattice—a spatial framework formed by intersecting straight lines. At the points of intersection are the centres of the particles forming the crystal. Such ideas about the structure of crystalline bodies were expressed long ago by many investigators, including Lomonosov, who explained the properties of saltpetre on this basis. But it was only in the 20th century that it became possible to demonstrate this experimentally and begin studying the internal structure of crystals.

This followed the discovery in 1912 by Laue, Friedrich and Knipping (Germany) of the diffraction of X-rays by crystals. This is the basis of *X-ray diffraction analysis*.

The wavelength of X-rays is of the same order as the dimensions of atoms. For that reason a crystal, consisting as it does of orderly arranged particles, is a natural diffraction grating for X-rays.

Let us consider the passage of a beam of monochromatic[1] X-rays of wavelength λ through a crystal. Because of the great penetrating power of X-rays, the greater part of the radiation passes through the crystal. However, a certain proportion of the radiation is reflected
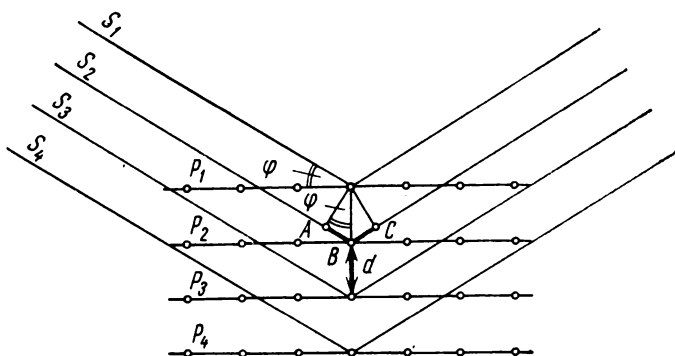
Fig. 19.9. Derivation of Bragg—Vulf equation

from the planes in which the atoms comprising the crystal lattice are located (Fig. 19.9). The reflected rays interfere with one another which brings about their mutual intensification or damping. It is evident that the result of interference depends on the path difference δ of rays reflected from parallel planes. There will be intensification when δ is a multiple of the wavelength; in that case the reflected waves will be in phase. As can be seen from Fig. 19.9 ray S_1 reflected from atomic plane P_1 traverses a shorter path than ray S_2 reflected from neighbouring plane P_2. The difference δ between these paths is equal to the sum of the lengths of sections AB and BC. Since $AB = BC = d \sin \varphi$, it follows that $\delta = 2d \sin \varphi$, where d is the distance between the reflecting planes and φ, the angle formed by the incident ray and the plane. Intensification of the reflected radiation takes place when

$$n\lambda = 2d \sin \varphi \qquad (19.1)$$

where n is a whole number. Equation (19.1) was derived in 1913, simultaneously and independently by W. Bragg (England) and

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[1] Monochromatic radiation consists of rays of one wavelength.

Yu. Vulf (Russia); it is the principal relationship employed for determining crystal structure.

If the crystal is oriented with respect to the incident X-ray in such a way that relationship (19.1) is fulfilled, the reflection of the ray can be observed. If condition (19.1) is not met, there is no reflection. Thus if δ is equal to half the wavelength, rays reflected from neighbouring planes P_1 and P_2 will be in antiphase and will be damped; if δ = 3/2 λ, a ray reflected from plane P_1 will be damped by a ray reflected from plane P_3, and so on.

Obviously very many planes can be drawn through the atoms in a crystal lattice, but as can be seen from Fig. 19.10 the density with which many planes are filled with atoms is small, and reflections from them will therefore be weak. Moreover, when the distance d between neighbouring planes is less than λ/2, equation (19.1) is not

Fig. 19.10. Planes drawn through atoms in crystal lattice
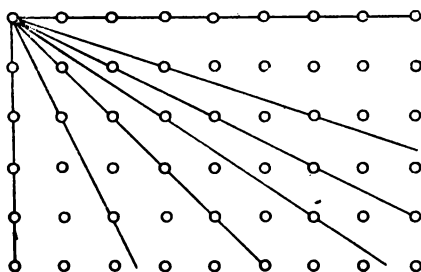
fulfilled whatever the value of φ. Consequently, only a few planes give bright reflections. The intensity of the reflections is not the same in all cases but depends on the number of atoms per unit area of the reflecting plane, and on the scattering power of the given species of atom.

At present it is the *rotation method* that is mostly employed for X-ray studies of crystals. In this method the crystal is secured to a rod in the centre of a cylindrical chamber, on the inside wall of which a photographic film is fastened (Fig. 19.11). The crystal is slowly rotated by a clockwork mechanism. A beam of monochromatic X-rays is passed into the chamber from the side, perpendicular to the axis of rotation.

The X-rays are reflected when the crystal is in positions which make possible fulfilment of relationship (19.1), and the reflections are recorded on the film. The X-ray pattern obtained consists of rows of dots which are traces of the reflected rays. To determine crystal structure, several X-ray patterns are made with the crystal in different positions relative to the axis of rotation.

As in the electron diffraction technique (see pp. 142-144), the method of trial and error can be used for interpreting X-ray patterns — this was the method used in the first investigations in this

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field. A certain structure is assigned to the test substance, and the X-ray pattern calculated by means of relationship (19.1), and compared with that obtained experimentally, taking into account the
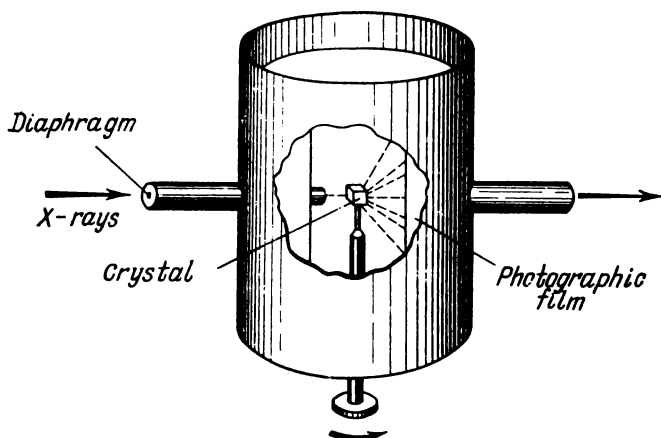
Fig. 19.11. Diagrammatic representation of a chamber for producing X-ray diffraction patterns by the crystal rotation method

intensity of the different reflections. Naturally this method is only applicable when the structure of the substance is fairly simple. Other techniques, which cannot be gone into here, must be used for
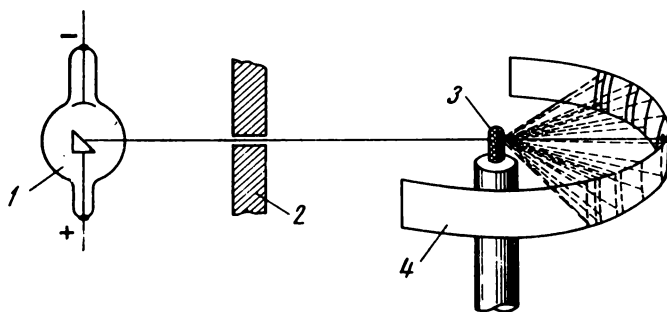
Fig. 19.12. Diagram of arrangement for producing Debye powder patterns
1—X-ray tube; 2—diaphragm; 3—substance under examination; 4—photographic film

establishing complex structures. In many cases deciphering X-ray patterns is very difficult, and the calculations involved are extremely laborious; they are performed today with electronic computers.
It is often difficult to obtain the comparatively large crystals required for the rotation method. In such cases the *powder method of Debye and Scherrer* is employed. In this case (Fig. 19.12) the beam

of X-rays is passed through a cylinder moulded from fine crystals of the test substance. Among the large number of tiny crystals in the powder there are always some whose orientation satisfies equation (19.1), and which, therefore, produce reflections. The X-ray patterns obtained are called *Debye powder patterns.* Experimentally the powder method is simpler than the rotation method, but deciphering the powder pattern is usually more difficult; for some types of crystals complete establishment of the structure by this method is impossible.

Reflection of X-rays from crystals results from the interaction of the radiation and the electrons. Therefore, the centres of the atoms determined roentgenographically are the 'centres of gravity' of the electron subshells. In many-electron atoms these centres practically coincide with the nuclei, but in light atoms the position of the nuclei can differ perceptibly. Since hydrogen ions—protons—have no electron subshells, their position cannot be established by X-ray diffraction analysis, and the method of *neutron diffraction* is used instead. Beams of neutrons are obtained from an atomic reactor. Unlike X-rays, neutrons do not interact with paired electrons but they are reflected by atomic nuclei.

Electron diffraction technique is also employed for studying crystal structure. Since electrons are retarded by matter to a much greater degree than are X-rays, in the electron diffraction study of solid bodies, either a small layer of the test substance is used or the diffraction of electrons is investigated when reflected from a surface. The latter method is particularly valuable in that it enables study of thin surface layers such as films of oxides, nitrides and other compounds on metals.

The structure of several tens of thousands of crystalline substances has now been studied by methods of diffraction analysis and fresh information is being published every month. By means of these methods investigators have succeeded in establishing the general features of a molecular structure which is apparently the most complex in nature, the structure of the substance governing the heredity of living organisms.

19.3. Types of Crystal Lattices

Crystal lattices are divided into several types according to the kind of particles at the points of the lattice and the character of the bond between them.

At the points of *atomic* crystal lattices are neutral atoms joined by covalent bonds. There are comparatively few substances with an atomic lattice, among them diamond, silicon and some carbides and silicides, that is, compounds of other elements with carbon and silicon. In these solid bodies all the atoms are bound, one to

another, in the same way. It is impossible to distinguish individual molecules in the structure of the atomic crystal and the entire crystal can be considered a giant molecule. Since covalent bonds are very strong, substances having atomic lattices are always hard, high-melting and non-volatile; they are practically insoluble.

At the points of *molecular* crystal lattices are molecules. Most substances with a covalent bond form crystals of this type. Solid hydrogen, chlorine and carbon dioxide and other substances which are gases at ordinary temperature form molecular lattices. The crystals of most organic compounds are also of this type. This means that very many substances with molecular crystal lattices are known. The molecules at the nodes of the lattice are bound together with intermolecular forces, the nature of which was discussed in Chapter Eighteen (see pp. 263-267). Since intermolecular forces are weaker than chemical bonds, molecular crystals are low-melting, quite volatile and fairly soft. Substances whose molecules are non-polar have particularly low melting and boiling points. Thus crystals of paraffin wax are very soft although the covalent C — C bonds in the hydrocarbon molecules of which the crystals consist are as strong as the bonds in diamond. Crystals formed by the noble gases should also be classed as molecular, consisting of monoatomic molecules, since valence forces play no part in their formation; the bonds between the particles are of the same character as in other molecular crystals, which results in the comparatively large interatomic distances in these crystals.

At the points of *ionic* crystal lattices are positive and negative ions arranged alternately; such lattices are characteristic of compounds of elements which differ greatly in electronegativity, such as the fluorides of the alkali metals. As in the case of atomic crystals, individual molecules cannot be distinguished in ionic crystals because there is no preferred ion with which a given ion of opposite sign interacts; the entire crystal can be considered a giant molecule. The bonds between the ions are strong, and consequently ionic compounds have high melting points and low volatility; they have great hardness but in this respect they usually stand below substances with an atomic lattice. Attention must be called to two points. Firstly, hardness and a high-melting point are not necessarily associated with ionic forces. Hardness and melting points are frequently lower than in substances with an atomic lattice. Secondly, many ionic crystals are made up of polyatomic ions, such as SO_4^{2-}, NO_3^-, $[HgI_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[AlF_6]^{3-}$, etc. While the bonds between the particles forming the lattice are ionic, the atoms within the complex ions are usually joined with covalent bonds. Since complex ions are of large size, it follows that when the charges are equal the forces acting between particles in the lattice will be considerably weaker than in a lattice consisting of monoatomic ions. Consequently the

melting points and hardness of substances containing polyatomic ions are lower. For example, NaCl has a melting point of 801°C, while the melting point of $NaNO_3$ is only 311°C.

The crystal lattices formed by metals are said to be *metallic*. At the points of these lattices are positive metal ions, and the valence electrons can move between them in different directions. The aggregate of electrons is sometimes called *electron gas*. Such a structure of the lattice brings about the high electric and thermal conductivity, and high plasticity of metals—mechanical deformation does not rupture the bonds and destroy the crystal, since the ions of which it is composed float, as it were, in a cloud of electron gas.

19.4. Some Crystal Structures

As was already pointed out, the particles in crystals are arranged in a definite order, thus forming a crystal lattice.

Like the outer form of crystals, crystal lattices can be classified according to their symmetry. In 1890, long before the development of experimental methods for studying structure, Y. Fedorov worked out such a classification mathematically. He demonstrated that 230 variants of the combination of symmetry elements were possible for crystal lattices. These combinations are called *Fedorov symmetry groups*. There are many more combinations of symmetry elements for crystal lattices (230) than for the outer forms of crystals (32), because of the presence of additional elements characterizing inner symmetry.

Any crystal lattice can be considered as consisting of unit cells. *The unit cell is the smallest part of a crystal having all the structural characteristics of the given lattice*. The diagram in Fig. 19.13 represents the crystal lattice of metallic sodium in which one of the unit cells is hatched. The unit cell is a parallelepiped, by moving which in the direction of each of the coordinate axes x, y and z, arranged parallel to the edges of the figure, the crystal lattice can be constructed. This operation resembles bricklaying. The lengths of the edges of the unit cell, denoted by the letters a, b and c (corresponding to the coordinates x, y and z) are called the *parameters of the cell*. The unit cell can be fully characterized by stating the lengths of the edges of the parallelepiped, the angles between them and the coordinates of the atoms in the cell; the latter are often expressed in fractions of the corresponding parameters of the cell. By way of example, the unit cells of copper and sodium are shown in Fig. 19.14. In the structures described below, some atoms are shown for greater clarity in addition to those that form the unit cells.

When considering the structure of crystalline substances a distinction must be made between *structure and structural type*. Structural type relates to the relative arrangement of the atoms in space with-

out specifying the distances between them. When characterizing the structure of a substance, the parameters of the unit cell must
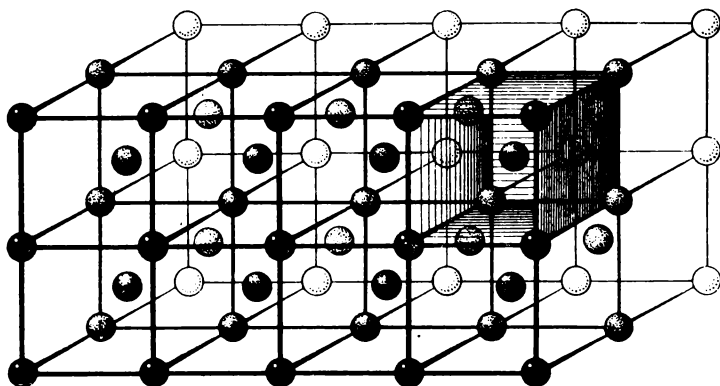
Fig. 19.13. Crystal lattice of sodium (one unit cell hatched)

be stated in addition to the structural type. A structural type takes its name from a substance having this type of structure. A great

(a)   (b)
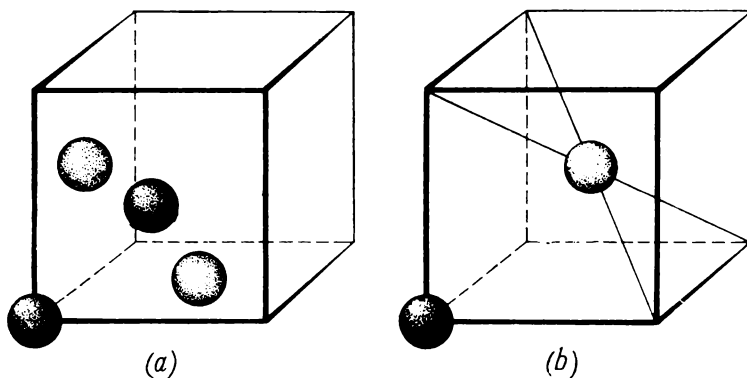
Fig. 19.14. Unit cells of crystal lattices
(a) copper (face-centred cubic); (b) sodium (cube-centred cubic)

number of structures may belong to the same structural type. Thus many metals form crystals of the magnesium structural type. Some structural types characteristic of inorganic substances are described below.

We begin with structures of metals. As was noted in Chapter One, packing of the particles in most metals is as close as possible

(see p. 16). There are two variants of the *closest packing* of spherical bodies—cubic and hexagonal.

Consider the case of a single layer of balls—the closest arrangement will be that shown in Fig. 19.15. Four of the fourteen balls are in contact with six others. We now place balls above and below this layer. It is evident that to obtain the packing, the balls of the upper and lower layers must be arranged in such a way that they fill the hollows between the balls of the middle layer. Two layers of balls are shown in Fig. 19.16; the balls in the bottom layer are indicated with dashed lines, the hollows they fill are black. It can be seen that
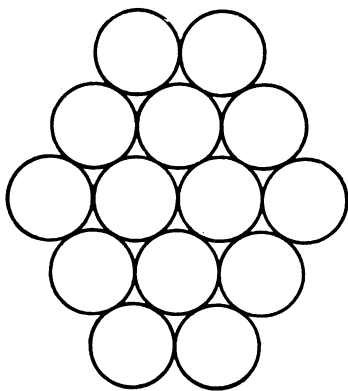
Fig. 19.15. Close arrangement of balls on a plane surface
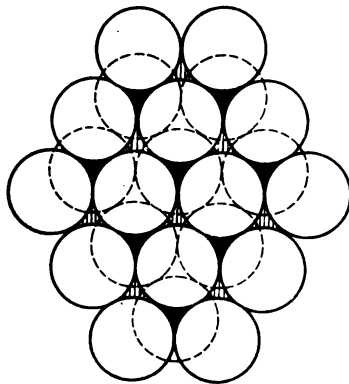
Fig. 19.16. Fragment of close packing of two layers of balls

half the hollows in the top layer are left unfilled, these hollows are hatched. When arranging the third layer, two patterns are possible: the balls can be placed in the black hollows or in those that are hatched. In the first case we have *hexagonal packing* (Fig. 19.17a), and in the second, *face-centred cubic* (Fig. 19.17b). In both cases the extent to which the space is filled with the balls is the same, and comes to 74.05%. The coordination number of the atoms in both structures is twelve. Copper is an example of a metal having a face-centred cubic structure, while magnesium is an example of a metal having a hexagonal structure.

Some metals have a different type of crystal lattice—the *cube-centred cubic* (the unit cell of such a lattice is shown in Fig. 19.14b). An example of a substance having this structure is the α-form of iron which is stable at room temperature. It can be seen from Fig. 19.14b that in this case the coordination number is eight. The structural types of the lattices of various metals are given in Table 19.1.
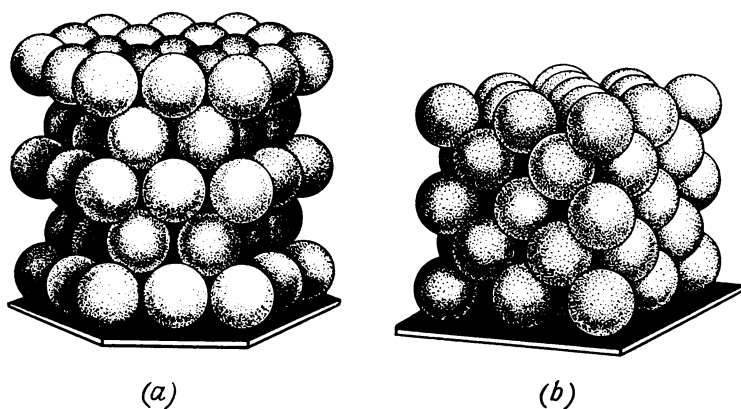
Fig. 19.17. Closest packing of balls
(a) hexagonal; (b) cubic
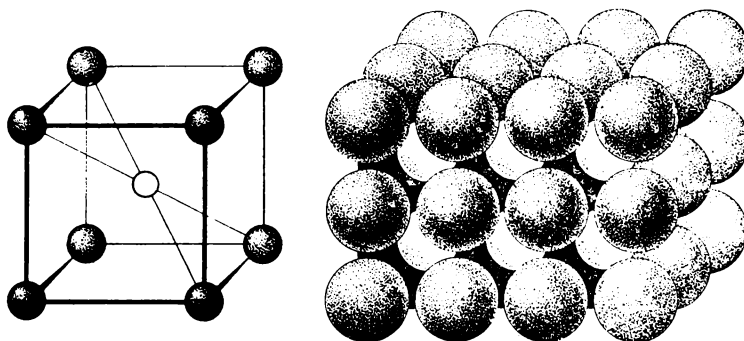
Fig. 19.18. Crystal structure of caesium chloride
Light balls are Cs+ ions; dark balls are Cl-. CsCl unit cell is shown to the left
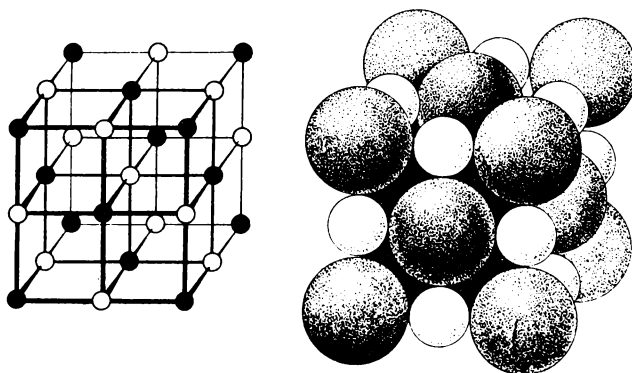
Fig. 19.19. Crystal lattice of NaCl
Light balls are Na+ ions; dark balls are Cl-

Crystal Structures of Metals

Li	Be										
3	2										
Na	Mg										
3	2										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3	1;2	1;2	2;3	3	3	---	1;3	1;2	1;2	1	2
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pb	Ag	Cd
3	1	2	2;3	3	2;3	2	1;2	1	1	1	2
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
3	3	1;2	2;3	3	3	2	1;2	1	1	1	—

Lattice types: 1 — face-centred cubic; 2 — hexagonal; 3 — cube-centred cubic.

Caesium chloride has a structure similar to the cube-centred cubic lattice of metals, it is represented in Fig. 19.18. Unlike metal lattices, this structure consists of two kinds of particles, Cs^+ and Cl^- ions. The coordination number for both ions in this structure is eight. It can be seen from Fig. 19.18 that around the Cs^+ ion are eight Cl^- ions. In the same way around each Cl^- ion are arranged eight Cs^+ ions, though only one is shown in Fig. 19.18, that in the centre of the unit cell. The others are outside this cell.

Sodium chloride has a different structure (Fig. 19.19). The arrangement of one kind of ions, e.g. the Cl^- ions, is the same as in the face-centred cubic lattice, these ions are at each corner of the cube and in the centre of each face. In the centre of the cube is a sodium ion, while the other sodium ions are arranged in the centre of each edge. Together they form the same kind of a lattice as the chloride ions. The coordination number for both the Cl^- and Na^+ ions is six; around each ion of one sign are arranged six ions of the opposite sign, thus forming a regular octahedron.

The NaCl and CsCl structural types are quite common among inorganic substances; all the alkali halides, for instance, have structures of these types. In ordinary conditions caesium bromide and iodide have the same type of lattice as the chloride; other alkali halides have structures of the NaCl type. At very high pressures it is natural to expect a polymorphous transition to the more compact CsCl structure. This was recently established experimentally for many alkali halides.

A number of elementary substances (silicon, germanium, grey tin) have *crystal lattices of the diamond type*. The unit cell of such a lattice is represented in Fig. 19.20. In diamond each carbon atom is joined with covalent bonds to four other atoms. The unit cell of this lattice is constructed by adding four atoms to the fourteen atoms

of the face-centred cubic lattice. The additional atoms are inside the cube at the centre of tetrahedrons formed by atoms at alternate corners of the cube and their three nearest neighbours in the centres of the faces. The coordination number of the atoms in the diamond lattice is four.

The *sphalerite structural type* (sphalerite is a variety of zinc sulphide, ZnS) is similar to the diamond lattice. The sphalerite lattice is represented in Fig. 19.21. This structure can be obtained from the
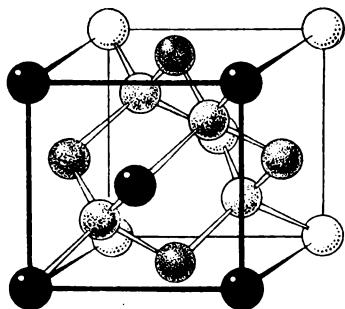
Fig. 19.20. Structure of diamond
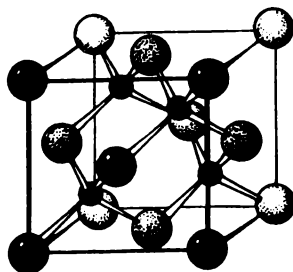
Fig. 19.21. Structure of spha-
lerite

Small balls are Zn^{2+} ions; large balls are S^{2-}

diamond structure by replacing half the carbon atoms by zinc ions and the other half by sulphur ions (compare Fig. 19.20 and 19.21). The sphalerite structural type is characteristic of binary compounds in which the total of valence electrons of the two elements is the same as in carbon. Examples of compounds having this structure are SiC, BN (cubic form), AlP, InAs, InSb, GaAs and CuCl. The total of outer electrons of the atoms forming these compounds is eight.

The structure of *wurtzite*, another variety of ZnS is shown in Fig. 19. 22. In the lattice fragment represented in the Figure, the atoms of one element are arranged at the corners of the hexagonal prism, in the centres of its upper and lower faces and inside three of the six triangular prisms composing the hexagonal prism. The atoms of the other element are on the lateral edges of all six triangular prisms, and also inside three of the six triangular prisms where there are atoms of the first element.

The particles in wurtzite are arranged in such a way that each atom of one element is tetrahedrally surrounded by four atoms of the other element. Thus, as regards the nearest neighbouring atoms there is no distinction between the structures of wurtzite and sphalerite. The difference between these lattices is that like atoms in sphalerite are arranged in the same way as in the face-centred cubic

lattice, and like atoms in wurtzite, in the same way as in the hexagonal lattice.

The structure of ice is similar to that of wurtzite. If atoms of zinc and sulphur in wurtzite are replaced by water molecules, we obtain their position in ice. A fragment of this structure is shown in Fig. 19.23. Each molecule is connected with four others by hydrogen bonds. The hydrogen bonds in the H_2O molecule have a tetrahedral orientation owing to the tetrahedral arrangement of the sp^3-
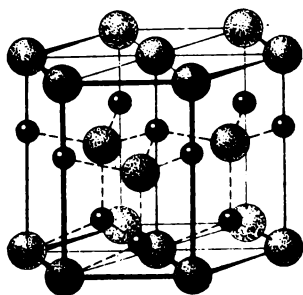
Fig. 19.22. Structure of wurtzite
Large balls are S^2- ions; small balls are Zn^{2+}
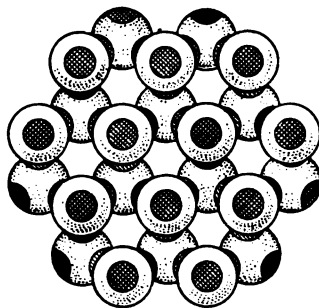
Fig. 19.23. Structure of ice

hybrid orbitals of the oxygen atom, two of which form a covalent bond with the hydrogen atoms, while the other two are occupied by unshared electron pairs which attract the hydrogen ions of neighbouring H_2O molecules. In Fig. 19.23 the black circles show the position of the hydrogen, and the hatching, the region where the negative charge is concentrated.

It can be seen from Fig. 19.23 that there are voids in the crystalline of ice, which accounts for its low density which is less than that of water. The voids in the crystal lattice of ice can be filled with other molecules, for example, CH_4, H_2S, the single-atom molecules of the noble gases, etc. This results in the formation of a sort of chemical compound. Compounds formed by the filling of the voids in a crystal lattice by molecules of other substances are called *clathrates.*

As we shall see later, fragments of the crystalline structure of ice persist in water, which explains many of the latter's properties.

We have described some structural types of compounds of the general formula AB—an atom of one element is combined with an atom of another element. We shall now consider two examples of the structure of compounds having the formula AB_2.

In the *structure of fluorite*, CaF_2 (Fig. 19.24), eight fluorine atoms at the corners of a cube are in the environment of fourteen calcium ions, eight of which occupy the corners, and six, the centres of the faces of a larger cube. In the representation of the unit cell there are more calcium ions than fluoride ions. However, all the fluoride ions belong solely to the given cell because they are within it. All the calcium ions, on the other hand, belong not only to the given cell but also to neighbouring cells. The ions at the corners of the cube simultaneously 'serve' eight cells; those situated at the centres of
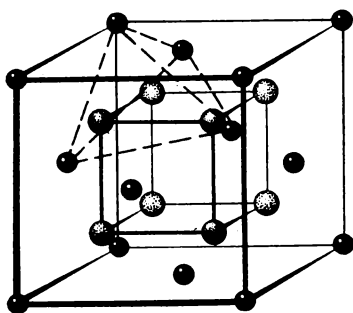
Fig. 19.24. Structure of fluorite

Light balls are F^- ions; dark balls are Ca^{2+}; each fluoride ion is tetrahedrally surrounded by four calcium ions. In the diagram only one tetrahedron is indicated with dotted lines
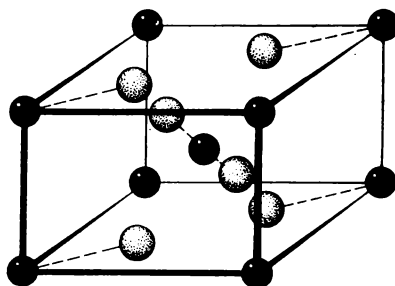
Fig. 19.25. Structure of rutile

Light balls are oxygen atoms; dark balls are Ti

the faces, two neighbouring cells. It follows that for eight fluoride ions, there are, on an average, $8 \times 1/8 + 6 \times 1/2 = 4$ calcium ions, which corresponds to the formula CaF_2.

Another widely encountered structure of compounds of the general formula AB_2 is that of *rutile*, TiO_2 (Fig. 19.25). The titanium atoms in the rutile unit cell form a body-centred rectangular parallelepiped with a square base—a distorted cube. The oxygen atoms are arranged on the diagonals. In this structure, each titanium atom is surrounded by six oxygen atoms which form a regular octahedron round it, while each oxygen atom is in the centre of an isosceles triangle defined by three titanium atoms. Thus the coordination numbers of titanium and oxygen in this structure are six and three, respectively.

Such are some examples of crystal structure. Other types of crystal structure are taken up in inorganic chemistry courses.

19.5. Energetics of Ionic Crystals

Since the chemical bond between the particles in many inorganic compounds is close to ionic, this type of crystal lattice is of great interest for inorganic chemistry. Particularly important is the *value of the lattice energy U_0 which is measured by the work that must be done to remove the ions composing the crystal to an infinitely great distance from one another.* This value is usually expressed on the basis of a gram-molecule of the substance in question.

The value of the lattice energy determines the strength and solubility of crystals and other properties. As we shall see later (p. 298), if the energy of the crystal lattice is known, it is possible to find the *solvation energy*, that is, the energy of interaction of the ions of a dissolved substance and the molecules of the solvent. The solvation energy determines, to a great extent, the behaviour of substances in solutions.

The lattice energy can be found from experimental data or calculated theoretically. We shall first consider the theoretical calculation.

An equation for calculating the lattice energy was first derived by M. Born. It has the form

$$U_0 = a \frac{z_1 z_2 N_0 e^2}{r_0} \left(1 - \frac{1}{n} \right) \tag{19.2}$$

It will be noticed that this equation differs from Born's formula for calculating the energy of ionic molecules [equation (15.8), p. 223] in the presence of the factors N_0 and a. The first quantity is Avogadro's number, and is introduced into the equation to obtain the energy per mole of substance[1]. Quantity a is known as the *Madelung constant*, Madelung being the investigator who in 1918 first calculated this quantity for NaCl. This constant is introduced into equation (19.2) because in the crystal lattice, unlike the ionic molecule, each ion instead of interacting with a single ion of the opposite sign, interacts with a large number of positive and negative ions at different distances from the ion under consideration. The principle of calculating the Madelung constant can be explained, using sodium chloride as an example.

Let us consider one of the sodium ions in the NaCl lattice (see Fig. 19.19). The nearest neighbours of each sodium ion are 6 chloride ions at a distance r. The Coulomb energy of interaction with these ions will be

$$u_1 = -6 \frac{e^2}{r}$$

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[1] The lattice energy is a positive quantity, since by definition it is the *energy of the disruption of the lattice. The energy of formation of the lattice* from free ions has the same value, but with the sign reversed.

Next, 12 sodium ions are arranged around the chosen sodium ion at a distance of $r\sqrt{2}$. Since these ions have the same sign as the ion under consideration, the interaction energy is written

$$u_2 = 12\,\frac{e^2}{r\sqrt{2}}$$

The following neighbours of this particular ion are 8 chloride ions at a distance of $r\sqrt{3}$, which gives the contribution to their interaction energy

$$u_3 = -8\,\frac{e^2}{r\sqrt{3}}$$

In the general form the expression for the Coulomb interaction energy can be written in the form

$$U_C = u_1 + u_2 + u_3 + \ldots$$

This is a convergent series[1]; by calculating a sufficient number of members in the same way as was done for u_1, u_2 and u_3 it will be found that

$$U_C = -a\,\frac{e^2}{r} = -1.7475\,\frac{e^2}{r}$$

It follows that the Coulomb interaction energy of one ion with all the other ions in the sodium chloride lattice is a times greater than the interaction energy of two single-charged ions at a distance r. Thus Madelung constant a for NaCl is 1.7475. This quantity can be calculated in the same way for other crystal lattices. Values of the Madelung constant for some crystal structural types are given in Table 19.2.

Table 19.2

Madelung Constants a for Some Types of Crystal Lattices

Structural type	Formula	Coordination number	a
Sodium chloride	NaCl	Na 6; Cl 6	1.7475
Caesium chloride	CsCl	Cs 8; Cl 8	1.763
Sphalerite	ZnS	Zn 4; S 4	1.638
Wurtzite	ZnS	Zn 4; S 4	1.641
Calcium fluoride	CaF$_2$	·Ca 8; F 4	2.520
Rutile	TiO$_2$	Ti 6; 0 3	2.408

A comparison of equation (15.8) for calculating the bond energy in the ionic molecule and equation (19.2) for calculating the crystal

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[1] A series is said to be convergent if the algebraic sum of its members approaches a limit as the number of members is increased.

lattice energy shows if the comparatively small change in r_0 during the transition of gaseous molecules into the crystalline state is neglected, it can be considered that the energy of forming a crystal from ions is a times greater than the energy of forming a corresponding number of ionic molecules. It can be seen from Table 19.2 that the Madelung constant is greater than unity. Therefore, a substantial amount of energy is liberated when a crystal is formed from ionic molecules and, conversely, converting a crystal into gas consisting of molecules requires a substantial expenditure of energy. Consequently ionic crystals have high melting points and high heats of sublimation.

Repulsive energy of the electron shells U_B (Born repulsion) rapidly diminishes as the distance between the particles increases, and therefore, when calculating its value, one need only consider the interaction of the ion with its nearest neighbours, at distance r. Therefore, one can write

$$U = U_C + U_B = -a\frac{N_0 z_1 z_2 e^2}{r} + \frac{N_0 B}{r^n} \qquad (19.3)$$

Quantity B is determined from the conditions of the equilibrium of forces at distance r_0 as was described on p. 222; as a result equation (19.2) is obtained.

Born repulsion factor n in equation (19.2) is found from crystal *compressibility* data. We shall now consider the principle of this calculation.

Crystal compressibility $\varkappa$ is understood to mean the relative reduction in volume per unit of applied pressure P, that is,

$$\varkappa = -\frac{1}{V} \cdot \frac{dV}{dP} \qquad (19.4)$$

When a crystal is compressed, the ions are brought closer together, distance r in equation (19.3) decreases. It is evident that the molecular volume of the crystal is proportional to the cube of the interionic distance, that is,

$$V = \beta r^3 \qquad (19.5)$$

Proportionality factor β can easily be found from the geometric relationships if the structural type of the crystal is known; for crystals of the NaCl type $\beta = 2N_0$.

A decrease in r causes a change in the potential energy, dU. Equating this change to the work performed by the pressure, PdV we have

$$-dU = PdV$$

Therefore,

$$P = -\frac{dU}{dV}$$

and

$$\frac{dP}{dV} = -\frac{d^2U}{dV^2} \tag{19.6}$$

It thus follows that crystal compressibility determined by relationship (19.4) can be expressed through the second derivative of the potential energy of the ions with respect to volume.

Since we have relationships (19.4) and (19.6), and an expression for the potential energy of the ions in the crystal is also known (19.3), compressibility can be represented as a function of r_0 and n. Performing the appropriate operations, which are not difficult but cumbersome and are therefore omitted here, gives for crystals of the A^+B^- type the expression

$$n = 1 + \frac{18r_0^4}{\varkappa ae^2} \tag{19.7}$$

from which n can be calculated if $\varkappa$ and r_0 are known. Crystal compressibility $\varkappa$ can be determined experimentally. This determination made it possible to find the values of n given on p. 222. We shall now consider calculation of lattice energies from experimental data. This requires knowledge of energy changes in a number of processes, which in the aggregate can be represented by a diagram called the *Born—Haber cycle*. Let us examine this cycle, taking sodium chloride as an example:
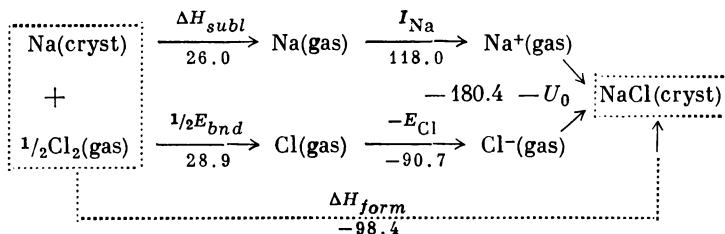
In this cycle we pass from solid metallic sodium and gaseous chlorine (lefthand part of diagram) to crystalline sodium chloride (righthand part of diagram) in two ways. The first consists in converting sodium and chlorine into the ions Na^+ and Cl^- and forming crystalline sodium chloride from them. In accordance with the definition of the energy of the crystal lattice, energy is liberated when NaCl is formed from gaseous ions, which is equal in absolute value to U_0. To obtain sodium ions metallic sodium must be vaporized, which involves expenditure of the heat of sublimation, ΔH_{subl}. This can be determined by thermochemical methods. The atoms must then be ionized, necessitating the expenditure of ionization energy I_{Na} which can also be measured (see p. 60). To obtain chlorine ions the bond in the Cl_2 molecule must first be broken. To obtain one

chlorine atom requires the expenditure of $1/2E_{bnd}$ (for the determination of this quantity see p. 148). The electron detached from the sodium atom must then be joined to the chlorine atom, which takes place with the liberation of the energy of electron affinity, E_{Cl}.

The second way proceeds directly from sodium and chlorine to crystalline sodium chloride. The heat effect in this process is comparatively easy to measure, it is the heat of formation of sodium chloride from the elements, ΔH_{form}.

According to Hess's law the heat effect of a given process is independent of the way in which the process takes place but is determined solely by the initial and final conditions of the system. Since in both variants of the process considered, the initial and final conditions are the same, the total heat effect in the first variant is equal to the heat effect in the second. Therefore, we can write

$$\Delta H_{form} = \Delta H_{subl} + I_{Na} + \,^1\!/_2 E_{bnd} - E_{Cl} - U_0$$

from which

$$U_0 = -\Delta H_{form} + \Delta H_{subl} + I_{Na} + \,^1\!/_2 E_{bnd} - E_{Cl} \qquad (19.8)$$

All the quantities in the righthand part of this relationship can be measured, and therefore the value of U_0 can be found. In the Born—Haber cycle for NaCl given above the energy effect is given for all the relevant processes (in kcal).

The quantity most difficult to measure, among those included in the Born—Haber cycle, is electron affinity E. For that reason the cycle was first used for determining electron affinity rather than finding crystal lattice energies. In that case the lattice energy was calculated theoretically by the Born method. Later, when experimental methods were developed for determining electron affinity, it was found that values of E calculated from theoretical values of lattice energies were quite close to experiment. Thus the theoretical calculation of U_0 for ionic crystal lattices gives correct values. The difference between theoretical values of U_0 and values calculated from the Born—Haber cycle comes to several per cent for alkali halides, but it is greater for salts of multivalent metals. This can be explained by the presence of a certain proportion of covalent bond in these compounds.

Values of the crystal lattice energy for some compounds determined on the basis of experimental data are given in Table 19.3. It can be seen that for salts consisting of singly charged ions these values are of the order of 200 kcal/mole; for compounds containing multiply charged ions, they are considerably greater. Parallelism in the variation of U_0 in series of similar compounds is illustrated by the comparison in Fig. 19.26.

Table 19.3

Crystal Lattice Energies of Some Substances, kcal/mole

Cation	Anion					
	F-	Cl-	Br-	I-	O²-	S²-
Li+	247	202	191	177	703	—
Na+	219	180	177	165	623	—
K+	194	169	162	153	563	—
Rb+	186	164	158	149	544	—
Cs+	179	156	151	144	527	—
Be²+	82ɔ	713	692	670	1080	—
Mg²+	689	595	577	553	940	778
Ca²+	617	525	508	487	842	722
Sr²+	580	504	489	467	791	687
Ba²+	547	468	463	440	747	656
Zn²+	718	642	633	620	970	852
Cd²+	662	598	593	563	911	802
Hg²+	—	624	624	630	940	842
Pb²+	590	534	528	497	850	732
Mn²+	—	589	555	542	920	841
Cu²+	—	660	652	—	990	890

Both the experimental and theoretical methods of finding lattice energy require information to obtain which involves certain difficulties. Thus in order to calculate the Madelung constant it is necessary to know the crystal structure of the substance, which must be determined by the difficult interpretation of crystal X-ray patterns; it is likewise necessary to know the value of compressibility $\varkappa$, whose measurement is a problem for high-pressure technology and can be performed by only a few laboratories. For that reason the equation suggested by A. Kapustinsky for calculating lattice energies is extensively employed; the only information required for calculating U_0 by this method is the ionic radii.

A. Kapustinsky noticed that the Madelung constant for different salts was aprroximately proportional to the number of atoms in their molecules. He also suggested that the Born repulsion factor n should be considered the same for all compounds and that interionic distance r_0 should be replaced by the sum of the radii of cation and anion. Equation (19.2) then had the form

$$U_0 = A \frac{z_c z_a \sum n}{r_c + r_a} \qquad (19.9)$$

where A is a constant; Σn, the number of ions in the formula of the salt (e.g., for $CaCl_2$, $\Sigma n = 3$); z_c and z_a, the charges of cation and anion, and r_c and r_a, their radii. From crystal-lattice energy data, A was found to equal 256.1 (assuming that U_0 was expressed in kcal/mole).

In spite of the fact that the Kapustinsky equation contains a number of simplifications not found in Born equation (19.2) the results
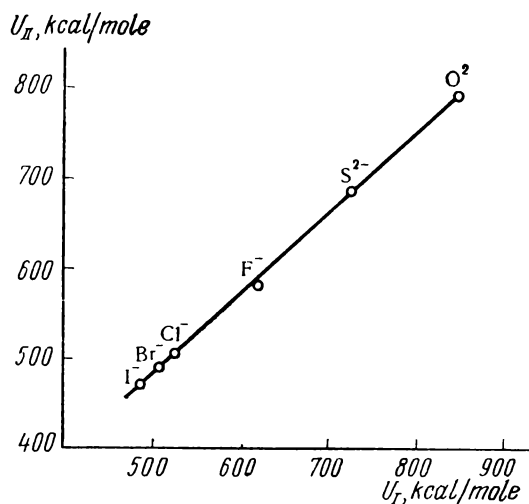
Fig. 19.26. Relationship of lattice energy of calcium compounds (U_I) and strontium compounds (U_{II})

are as exact. This is evidently because inaccuracies introduced by the simplifications are largely compensated by the deviation of the theoretical values of U_0 obtained with the Born equation from the true values. It was noted above that this deviation is due to the presence of a certain proportion of covalent bond in all crystalline compounds. Calculations with the Kapustinsky equation are extremely simple, and it is therefore widely employed in many fields of science.

CHAPTER TWENTY

LIQUID AND AMORPHOUS STATES

20.1. Structure of Liquids

The liquid state of aggregation is intermediate between crystalline and gaseous (see Fig. 18.1). Consequently at high temperatures the properties of a liquid approach those of a non-perfect gas in

which collisions of the molecules are very frequent, while at low temperatures they approach the properties of a crystalline substance. If a liquid is heated under increasing pressure (otherwise it would be vaporized) a state will be reached in which vaporization of the liquid does not involve the expenditure of energy. This is called the *critical state* and it corresponds to the critical temperature and pressure, which are different for different substances (see Fig. 18.1). At the *critical point* all the properties of a liquid and the corresponding vapour—energy, density, etc.—become identical. Consequently, if a liquid is heated while under its critical pressure, it will, on reaching the critical temperature, be in no way distinguishable from its vapour—neither in the character of the movement of its particles, nor in its structure, nor in any other property[1].

On the other hand, as the temperature is lowered, the similarity of a liquid to a gas (the terms gas and vapour are to be considered synonymous) gradually gives way to its similarity to the corresponding crystals. This is maximal near the crystallization point, although even there the two states remain distinguishable[2]. But the change in properties of a substance as it solidifies or melts is not, as a rule, very great. This is seen from the data for several metals in Table 20.1, giving changes in volume v, heat capacity c and compressibility factor $\varkappa$ on melting, as well as heats of fusion ΔH_{fus}.

Table 20.1

Characteristics of Some Metals at Their Melting Points

Metal	m.p., °C	$\dfrac{v_{lq} - v_{cr}}{v_{cr}} \cdot 100$	$\dfrac{c_{lq} - c_{cr}}{c_{cr}} \cdot 100$	$\dfrac{\varkappa_{lq} - \varkappa_{cr}}{\varkappa_{cr}} \cdot 100$	ΔH_{fus}, kcal/g-at
Cd	321	4.7	3.4	30.0	1.47
Hg	−39	3.6	−2.4	6.4	0.55
Pb	327	4.8	7.7	8.3	1.20
Sn	232	2.8	−6.3	21	1.66

It should be emphasized that the close similarity in the properties of liquids and crystals near the melting point is not limited to metals but is found in widely diverse substances, and this applies to many other properties besides density, heat capacity and compressibility factor. Thus for most substances the change in volume du-

[1] The similarity of gas and liquid is likewise seen in the fact that under high pressure some mixtures of gases separate into layers, as do some liquids which are only partially soluble in one another.

[2] Experiments have shown that even under very high pressures the distinction in properties of a substance in the liquid and crystalline states does not disappear.

ring crystallization comes to approximately 10%. This means that the inter-particle distance changes by only ~3%, that is, that the arrangement of particles in a liquid closely resembles their arrangement in the corresponding crystals. The closeness of the heat capacity of the melted and solidified substance indicates the similarity of the thermal motion of particles in liquid and solid bodies. Their energetic similarity at the melting point is borne out by the fact that unlike heats of vaporization ΔH_{vap}, heats of fusion ΔH_{fus} are small. Thus for HI, $\Delta H_{vap} = 5$ kcal/mole, but ΔH_{fus} is only 0.7 (cf also Table 20.1). In other words, the ordered arrangement of the particles which is characteristic of crystals is only partially lost in liquids, at least near the crystallization point. Conceptions based on the close resemblance of liquid to crystal were first propounded by Ya. Frenkel (1934).

The presence of a spatial ordering of the molecules in a liquid is confirmed by many other facts, including results of experiments in the scattering of light, X-rays, neutrons and electrons.

Debye liquid X-ray patterns at temperatures close to crystallization points are similar to the X-ray patterns of the corresponding crystals, differing only in the blurring of the rings, which increases as the temperature rises.

The results of the X-ray analysis of liquids can be explained by assuming that their structure is either an accumulation of ultramicroscopic, considerably deformed aggregates, or a continuous network in which the elements of the structural order are restricted by their nearest neighbours.

The first assumption signifies that an enormous number of 'crystal islets', termed *cybotaxes*, are divided by areas of randomly arranged particles. These groups have no distinct boundaries but merge with the areas of randomly arranged particles; they shift about, losing some particles and adding others, and can disintegrate and form again. As in a gas, they move about spatially; as in crystals, they oscillate about a position of equilibrium. Heating reduces the time the cybotaxes spend in a 'settled way of life', while cooling has the reverse effect. It follows that this conception of a liquid is a synthesis of the conceptions of gas and crystal—a combination of an orderly arrangement of molecules in a small volume and an unordered arrangement in the entire volume.

The second assumption amounts to a conception of a *quasicrystalline* structure in which each molecule in a liquid is surrounded by neighbours arranged about it in almost the same way as in a crystal of the same substance. But in the second layer there is a departure from orderlines, and this increases with the distance from the molecule first considered. In other words the deviation from an orderly arrangement increases regularly in proportion to the distance from the given molecule; the order in liquids is *short-range*, whereas in

crystals it is *long-range*: a strict repetition of the structural element — ion, atom, groups of atoms or molecules — in all directions. Thus at temperatures close to the crystallization point a liquid is a distorted crystal in which long-range order has been lost. Figuratively speaking, a crystal can be likened to a roadway of paving blocks, and a liquid, a roadway of cobblestones.

It is hard to say which viewpoint is preferable. What is important is that there is a certain order in liquids, which is manifested the more distinctly, the closer the temperature to the melting point; it is likewise important that both hypotheses explain the properties of liquids.

Study of the scattering of X-rays in liquids consisting of polyatomic molecules has demonstrated not only the orderly arrangement of the molecules but also a certain tendency in the mutual orientation of the particles, which is pronounced in the case of polar molecules, and enhanced by a hydrogen bond.

Although in general the arrangement of particles in a liquid changes insignificantly during crystallization, there are some substances in which the arrangement of the particles remains practically unchanged, while in others it becomes substantially different. In the latter case, where crystallization requires considerable 'repacking' of the particles, the process is more difficult. Delay in crystallization makes possible supercooling of the liquid, i.e., cooling of the liquid to below the melting point. Since the possible degree of supercooling, other conditions remaining the same, will be greater, the less 'isostructural' matter there is in the liquid and solid states, the tendency to supercooling provides indirect evidence concerning the structure of a liquid.

The unordered motion of the molecules in a liquid continually changes the distances between them. It can be said that the structure of a liquid is statistical in character. This is the essential distinction between a liquid and crystals. The statistical character of the ordered arrangement of the molecules in a liquid leads to continual *fluctuations* — deviations not only from the mean density but also from the mean orientation, since the molecules can form groups in which a certain orientation predominates. The less the value of these deviations, the more frequently they occur.

Water and aqueous solutions of electrolytes are the liquids of greatest importance for inorganic chemistry, and we shall therefore take up their structure in greater detail.

20.2. The Structure of Water

It was pointed out previously (see p. 258) that in the crystal lattice of ice, H_2O molecules are joined together with hydrogen bonds. The crystal structure of ice is far from being the closest packing. If a

calculation inverse to that on p. 16 is performed, and the density of ice determined for the closest packing, proceeding from the radius of the H_2O molecule in the structure of ice as determined by X-ray analysis (1.38 Å), we obtain the value 2.0, more than twice the actual density (0.9).

Bernal and Fowler (Great Britain) who were the first to conduct a thorough X-ray diffraction study of water, demonstrated in 1933 that there remain in water fragments of ice structure—'crystalline islets' (see p. 295). This phenomenon is more pronounced in water than in most other liquids. The greater part of the molecules in water still have the tetrahedral environment found in the ice structure. The *mean coordination number* of water molecules is close to four, at temperatures of 2, 30 and 83°C it is equal, respectively, to 4.4, 4.6 and 4.9. The greater part of the hydrogen bonds joining the H_2O molecules in the ice lattice persist in water—the proportion of disrupted hydrogen bonds at temperatures of 0, 25, 60 and 100°C is respectively 9, 11, 16 and 20%.

As a result of the presence of elements of a crystalline structure in water, along with the high value of the dipole moment of the H_2O molecule, water has a very large dielectric constant $\varepsilon = 79.5$ at 25°C. This means that the interaction between charged particles in water is approximately $1/80$ as strong as in a vacuum. Consequently, all ionic compounds dissociate in aqueous solution. Unlike solvents with a smaller value of ε, water causes practically complete dissociation. In aqueous solution many compounds with a polar bond in the molecules, such as hydrogen halides, H_2S, cadmium salts, etc., are also ionized; in such compounds the degree of dissociation may be less than 100%.

20.3. Solutions of Electrolytes

Most inorganic compounds are ionized to a considerable extent in solution. The presence of ions in solutions of electrolytes makes them capable of conducting an electric current, accelerates exchange reactions and explains many other properties.

What causes the dissociation of a dissolved substance into ions is *solvation*—the vigorous interaction of the ions with the molecules of the solvent. *Hydration*, that is, the interaction of the ions with water, is a special case of solvation.

Mendeleev was the first to call attention to the importance of the interaction between the dissolved substance and the solvent. In the 'sixties of the last century he advanced a *chemical theory of solutions*, according to which aqueous solutions contain a number of *hydrates*—unstable compounds of the dissolved substance with water which change into one another. Employing physicochemical methods of investigation, Mendeleev demonstrated the existence of such com-

pounds in the liquid phase in the systems $H_2SO_4 - H_2O$, $C_2H_5OH -$
H_2O and $CH_3OH - H_2O$. Actually, we now know that in solutions
there are comparatively stable molecular groups formed by molecu-
les of the solvent and solute. As the polarity of the solvent dimini-
shes, the tendency to form molecular compounds declines. Frequently
the bond between solvent and solute is maintained in the solid
state; *crystalline solvates* are often formed during crystallization
from solution, examples being $CuSO_4 \cdot 5H_2O$, $CaCl_2 \cdot 6H_2O$, 'LiClO_4
$\cdot 4CH_3OH$ and $AlBr_3 \cdot C_6H_6$. Whereas water of crystallization is
found in many salts, 'alcohol of crystallization' is not frequently
encountered and 'octane of crystallization', for example, very rare-
ly indeed.

The conception of the *hydration of ions* introduced in 1890 by
I. Kablukov and V. Kistyakovsky, which combined Arrhenius's
theory of electrolytic dissociation with Mendeleev's chemical theory
of solutions was very effective in explaining the properties of solu-
tions of electrolytes.

The intensity of the interaction of ions with water molecules can be
characterized by the *heat of hydration* ΔH_h —*the amount of heat
liberated during the transition of a gram-ion* $(6.023 \times 10^{23}$ *ions) from
a vacuum into aqueous solution.* The value of ΔH_h can be found from
experimental data, and there are also methods of theoretical calcu-
lation.

In order to calculate ΔH_h from experimental data the energies of
the crystal lattices U_0 and the heats of solution of the salts ΔH_s must
be known. The process of the solution of a salt can mentally be divi-
ded into two stages: disintegration of the crystal lattice into ions
which is accompanied by the absorption of heat equal to U_0, and
hydration, resulting in the liberation of heat ΔH_h^1. It is evident that
the heat effect when a salt is dissolved is equal to the algebraic sum
of these quantities:

$$\Delta H_s = \Delta H_h + U_0$$

from which

$$-\Delta H_h = U_0 - \Delta H_s \qquad (20.1)$$

As we know the energy of the crystal lattice in many salts has
been found (see p. 292), and heats of solution are comparatively easy
to determine experimentally. Having this information, the heat of
hydration can be determined by means of equation (20.1). The
change in entropy during hydration ΔS_h can also be determined,
and from the equation

$$\Delta G_h = \Delta H_h - T\Delta S_h$$

it is possible to compute the change in the isobar-isothermal poten-
tial during the transition of ions from a vacuum into solution. The

---

[1] It is now accepted that heat liberated is indicated with the minus sign.

quantity ΔG_h is frequently called the *energy of hydration*. The energy and heat of hydration differ by several per cent and ΔG_h is replaced in rough calculations and comparisons by the value of ΔH_h, which is known for a large number of ions.

When calculating with equation (20.1) we obtain the sum of the heats of hydration of both the cations and anions forming the salt. To find the heats of hydration of the individual ions, this value must be divided into the cation and anion components. Finding the correct method of dividing is quite difficult. In 1953 A. Kapustinsky, S. Drakin and B. Yakushevsky demonstrated that isoelectronic ions having charges of different signs, e.g. Na^+ and F^-, K^+ and Cl^-, etc., differ little in properties in aqueous solutions, and that the difference diminishes as the size of the ions increases. Therefore the characteristics of the ions Cs^+ and I^- can be determined with sufficient precision by dividing summary values for CsI in half. Having

Table 20.2

Characteristics of the Hydration of Ions with Noble-Gas Configuration (ΔG_h, kcal/g-ion)

Ion	n	d_{M-H_2O}, Å	ΔG_h^I	ΔG_h^{II}	ΔG_h
Li^+	4	2.02	-91	-48	-121
Na^+	6	2.42	-81	-43	-97
K^+	6	2.79	-67	-39	-79
Rb^+	8	2.92	-72	-38	-74
Cs^+	8	3.10	-66	-36	-66
Be^{2+}	4	1.62	-379	-216	-577
Mg^{2+}	6	2.04	-287	-190	-450
Ca^{2+}	6; 8	2.42	-234	-171	-373
Sr^{2+}	8	2.60	-214	-163	-341
Ba^{2+}	8	2.74	-188	-158	-310
Al^{3+}	6	1.88	-670	-448	-1091
Y^{3+}	9	2.44	-507	-384	-850
La^{3+}	9	2.74	-457	-355	-771

these values, it is possible to obtain values for other ions. Energies of hydration of some ions, calculated in this way, are given in the last column of Table 20.2.

It can be seen from Table 20.2 that energies of hydration of singly-charged ions are of the order of 100 kcal; those of doubly-charged ions, ca. 300-600 kcal; triply-charged ions, ca. 800-1100 kcal. Thus the energetic effect of hydration is no less significant than the effect of the ordinary chemical reaction. It is likewise evident from the

Table that the energy of hydration of ions in a group of the periodic system diminishes, which is due to the increase in the ionic radii.

In Fig. 20.1 is shown the parallelism in changes in the heats of hydration of singly- and doubly-charged ions with noble-gas configuration.

Most of the ions in a solution are firmly bound with the water molecules surrounding them, forming *hydrated complexes*. These not infrequently persist in the *crystalline hydrates* formed when the
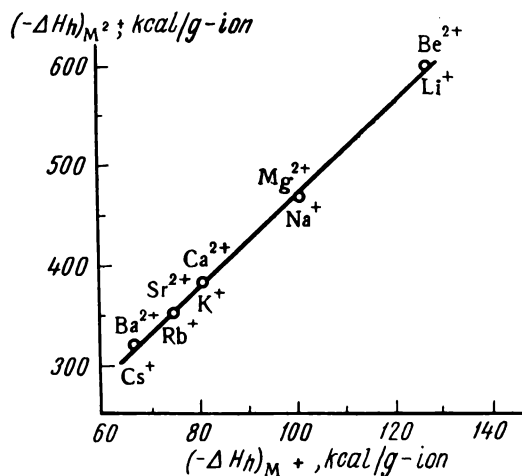
Fig. 20.1. Relationship of heats of hydration of M^+ and M^{2+} cations

salt is crystallized from the solution. For example, X-ray structural analysis of such compounds as $MgCl_2 \cdot 6H_2O$, $Na_2SO_4 \cdot 10H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, $NiSO_4 \cdot 7H_2O$ and $Nd(BrO_3)_3 \cdot 9H_2O$ shows that they contain the complex ions $[Mg(H_2O)_6]^{2+}$, $[Na(H_2O)_6]^+$, $[Al(H_2O)_6]^{3+}$, $[Ni(H_2O)_6]^{2+}$ and $[Nd(H_2O)_9]^{3+}$.

In Table 20.2 are given the coordination numbers of the ions n, according to the data of X-ray structural analysis of the crystalline hydrates, as well as the distances between the ions and the surrounding water molecules, d_{M-H_2O}. Precise X-ray studies of the structure of solutions recently conducted by A. Skryshevsky and A. Dorosh have shown that the same distances between ions and the surrounding H_2O molecules are maintained in the liquid phase.

Thus hydration can be divided into *primary*, the interaction of the ion with the nearest water molecules, and *secondary*, interaction with more distant water molecules.

The first equation for the theoretical calculation of the energy of hydration was proposed in 1920 by M. Born. This equation proceeds

from the assumption that the energy of the transition of an ion from a vacuum into aqueous solution can be represented as the difference in the *work of charging* particles in these media. For simplicity's sake the ion is considered a conducting sphere of radius r.

The work of charging the sphere can be calculated if one pictures the charge being transferred from infinity to the surface of the sphere in small portions dq_1, dq_2, ... The work dA performed in creating an additional charge dq on the surface of a sphere whose charge is already equal to q, is expressed by the relationship

$$dA = \frac{q\,dq}{r}$$

The total work performed in increasing the charge from 0 to q will be equal to

$$A = \int_0^q \frac{q}{r}\,dq = \frac{q^2}{2r} \tag{20.2}$$

For a charge placed in a medium with dielectric constant ε, it follows that

$$A = \frac{q^2}{2\varepsilon r} \tag{20.3}$$

Subtracting equation (20.2) from equation (20.3) gives the equation for the energy of hydration:

$$-\Delta G_h = \frac{q^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \tag{20.4}$$

Since for ions, $q = ez$, equation (20.4) can be written in the form

$$-\Delta G_h = \frac{e^2 z^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \tag{20.5}$$

The Born equation (20.5) gives values for the energy of hydration which, as a rule, differ from experiment by several tens of per cent. Such a discrepancy is natural as a consequence of the grossly approximate character of the model employed in its derivation—the ion is considered to be a charged conducting sphere. and the solvent, a continuous medium with dielectric constant ε. Nevertheless, the equation is very simple and makes it possible to judge correctly of the order of the value ΔG_h, and is therefore extensively employed.

During the last few years an increasing number of investigations have been published which show that the interaction of ions with molecules of a solvent is to a great extent due to quantum-mechanical factors, and is similar in nature to the formation of a coordination bond in complex compounds.

This treatment of solvation was initiated by the work of Bernal and Fowler already mentioned (see p. 297), in which attention was called to the fact that the hydration energy of cations is close in value to the sum of ionization energies $\sum I$ corresponding to the conversion of a neutral atom into an ion. Bernal

and Fowler therefore assumed that the interaction of ions with a solvent consisted, for the most part, in the return of the missing electrons to the ion so that a neutral particle was formed.

This approach was developed by V. Mikhailov and S. Drakin, who worked out a method of calculating the energy and entropy of hydration, and the values obtained agree well with experiment.

Since an ion in solution mainly forms a solvated complex by interacting with the unshared electron pairs of the solvent's donor atoms (usually oxygen or nitrogen), the rest of the solvent molecule has comparatively little effect on the solvation energy. For that reason the solvation energies of ions in different solvents having the same electron-donor atom are very close. For example, the solvation energies of the Li^+ ion in H_2O, CH_3OH, C_2H_5OH and $HCOOH$ are —121.0, —120.0, —119.0 and —120.0 kcal/g-ion, respectively.

The donor-acceptor interaction of the hydrogen ion with a solvent is particularly vigorous. It firmly combines with one molecule of the solvent, forming, in aqueous solutions, the hydroxonium ion, H_3O^+.

When considering the solvation of ions, one must take into account the effect of the penetration of the ion into the structure of the solvent, resulting in the formation of a void in the solvent and the rupture of intermolecular bonds. For aqueous solutions the energy of formation of such a void, A_{vd}, can be calculated approximately from the energy of the hydrogen bond, $E_{O...H}$, which is equal to 5 kcal/g-ion, according to the equation

$$A_{vd} = 0.9nE_{O...H} \qquad (20.6)$$

where n is the coordination number of the ion, and the factor 0.9 takes account of the fact that about 10% of the hydrogen bonds in water are already ruptured at 25°C (see p. 297). As we know, each H_2O molecule can form four hydrogen bonds with its neighbours. Since one side of the molecule is turned toward the ion, only two hydrogen bonds can be formed with the molecules of another hydrated shell. Inasmuch as a bond is formed between two molecules, 1/2 the energy of the bond is assigned to each, whence the product $nE_{O...H}$ appears in the expression.

From what has been said it follows that the expression for the hydration energy of an ion ΔG_h can be represented by the sum

$$\Delta G_h = \Delta G_h^{I} + \Delta G_h^{II} - A_{vd} \qquad (20.7)$$

where ΔG_h^{I} and ΔG_h^{II} are the energies of primary and secondary hydration, respectively.

The Born equation (20.5), which does not take account of the donor-acceptor interaction of the ion with the solvent, does not give a precise result when calculating the complete hydration energy, but it is quite suitable for calculating the secondary hydration energy. To calculate ΔG_h^{II}, the radius of the hydrated complex (radius of the ion plus diameter of the water molecule) must be substituted in equation (20.5). Having found A_{vd} and ΔG_h^{II}, and knowing the experimental values of ΔG_h, ΔG_h^{I} can be calculated by means of equation (20.7). Results of such calculations are given in Table 20.2, from which it is evident that ΔG_h^{I} is usually substantially greater than ΔG_h^{II}. The curve in Fig. 20.2 shows that ΔG_h^{I} for ions of the noble-gas type is proportional to $\sum I$.

Everything said above about the solvation of ions relates to very dilute solutions. When we go over to solutions of medium and high concentration the picture is considerably more complicated. Here the interaction of the ions with one another is superimposed on the interaction of the ions with the solvent. In the case of low concentrations of the electrolyte, this is manifested in the formation around ions, of *ionic atmospheres* of ions of the opposite sign. In more con-

centrated solutions associations of solvated ions are formed — *ion-pairs*, trip-lets, etc. Finally, in very concentrated solutions, there is not enough solvent for the formation of solvated shells and the ions are desolvated. In this con-nection K. Mishchenko and A. Sukhotin introduced the concept of the *boundary of complete solvation*, the concentration of a solution in which there is still sufficient solvent for the formation of the first solvated spheres. If the boundary of complete solvation is crossed there is a sharp change in many of the pro-perties of solutions.

Many investigators are working today to elaborate a quantitative theory of the liquid state, but great difficulties are involved—theore-tical analysis is complicated by the circumstance that in a liquid
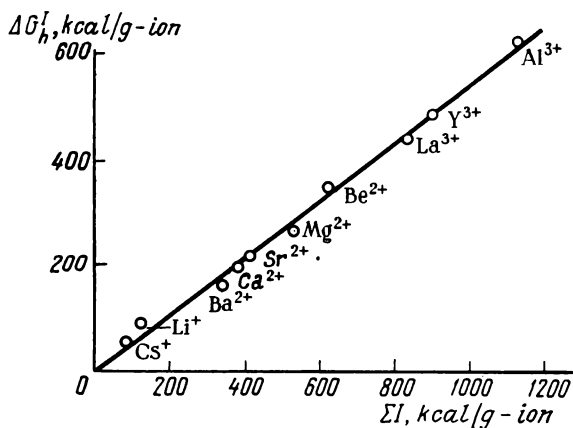
Fig. 20.2. Relationship between primary hydration energy and total ionization energy

vigorous interaction of the particles is combined with great disor-derliness. This prevents, for one thing, the use of simple models like those which rendered such good service in the formulation of the theory of gaseous and solid states — the concept of a perfect gas as a substance in a state of utmost rarefaction with complete disorderliness of its particles, and the conception of the perfect cry-stal in which great density is combined with the complete orderli-ness of the particles.

20.4. The Amorphous State

Amorphous substances are distinguished from crystals by their *isotropism*, that is, like liquids, the value of a given property is the same no matter in what direction it is measured within the substan-ce. An amorphous structure, like the structure of a liquid, is chara-cterized by short-range order. For that reason the *transition of an amorphous substance from the solid to the liquid state is not marked by*

a sudden change in properties, which is a second important distin-ction between an amorphous solid and a crystalline solid. Thus unlike a crystalline substance which has a *melting point* (m.p.) at which there is a sudden change in its properties (Fig. 20.3*a*), an amorphous substance is characterized by a *softening range*, $T_a - T_b$, and a continuous change in properties (Fig. 20.3*b*). This range may be of the order of tens or even hundreds of degrees, depending on the na-ture of the substance. The presence of a softening range over which an amorphous substance is in a plastic state, is direct evidence of the
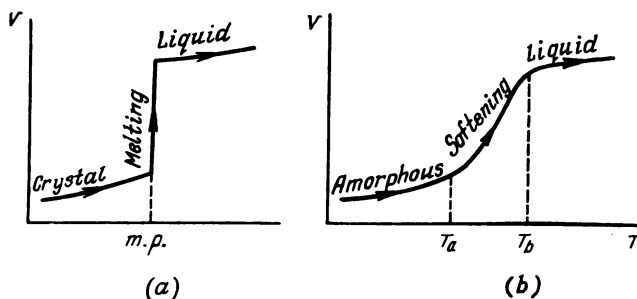
Fig. 20.3. Change in volume of crystalline substances (*a*) and amorphous sub-stances (*b*) when heated

structural nonequivalence of its particles. As a consequence there is only gradual rupture of the bonds when heated. This nonequiva-lence is not very great, however, this being indicated indirectly by the fact that the heat of converting an amorphous body into a crys-talline body is inconsiderable.

There was good reason for mentioning this particular transforma-tion, since an amorphous body is less stable than a crystalline one. Therefore, in principle, any amorphous body should crystallize and this process should be exothermic. For that reason the heat of formation of an amorphous body is always less than the heat of formation of a crystalline body from the same initial substances. Thus the heats of formation of the amorphous and crystalline modifi-cations of B_2O_3 from the elements are -301 and -306 kcal/mole, respectively. This example confirms the insignificant difference in the structure of amorphous and crystalline substances, and the com-mensurability of the heat of transformation (in the given case it is equal to 5 kcal/mole) with the heats of fusion confirms the simila-rity of the amorphous to the liquid state.

There are often amorphous and crystalline forms of the same sub-stance. Thus there are amorphous forms of a number of elements, such as sulphur, selenium, etc., and oxides—B_2O_3, SiO_2, GeO_2,

etc. Nevertheless, it has been impossible to crystallize many amorphous substances, including most organic polymers.

In practice the crystallization of amorphous substances is very rarely encountered since structural changes are hampered by the high viscosity. Therefore, unless recourse is had to special treatment, for example, to the lengthy action of high temperature, the transition to the crystalline state proceeds at an infinitely slow rate. In such cases it can be considered that the amorphous state is, practically speaking, quite stable.

When likening an amorphous body to a liquid and regarding it as a supercooled liquid which has solidified because of its great viscosity, it should be remembered that unlike liquids, neighbouring particles in an amorphous substance practically do not change places with one another. The high viscosity of melts impedes the movement and reorientation of molecules, which blocks the formation of crystal nuclei. For that reason when liquids (melts) are quickly cooled they solidify in the amorphous rather than the crystalline state.

Since silicate glasses are typical amorphous bodies, the amorphous state is often termed *vitreous*, a glass being understood to be an amorphous (that is, uncrystallized), solidified melt. Because of their extremely high viscosity glasses can remain without visible signs of crystallization for thousands of years.

Polymers are also amorphous substances, but they differ from ordinary amorphous bodies in that they are formed from monomers by the chemical combination of molecules, not by lowering of the temperature. Another distinction is that when they undergo transition from the amorphous to the crystalline state, crystallization involves only certain areas—the large size of the molecules impedes a high degree of orderliness. It is difficult for the large and interlaced molecules to arrange themselves symmetrically in space.

The more symmetrical the particles themselves, the more symmetrically they are arranged and the smaller the bond between them in the liquid state, the more reason there is to expect that cooling the liquid will cause its crystallization. Actually, molten metals, the arrangement of whose atoms approximates close packing, readily crystallize, while molten silicates often pass into the vitreous state. Organic compounds containing hydroxyl groups, e.g., glycerol, unlike hydrocarbons do not, as a rule, crystallize on solidifying—the affect of the hydrogen bonds is too great.

APPENDICES

I. Determination of the ratio e/m for an electron. Let us consider a beam of electrons that passes between the plates of a plane capacitor (Fig. I.1). The force that acts on the electron in the electric field is equal to

$$f_{el} = eE = e\frac{V}{d} \tag{I.1}$$

where e = charge of electron
       E = field strength in the capacitor
       V = voltage across the plates
       d = distance between the plates
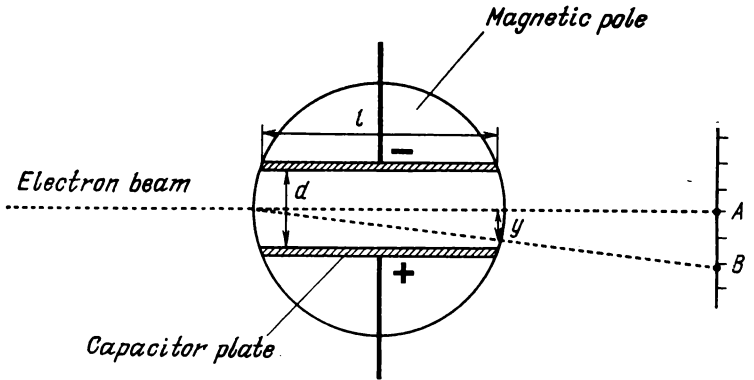
Fig. I.1. Layout for determining e/m_e

This force imparts acceleration to the electron in the direction perpendicular to the original direction of the electron beam

$$f_{el} = m_e a \tag{I.2}$$

where a = acceleration of electron
    m_e = mass of electron

It follows from equation (I.1) and (I.2) that

$$a = \frac{e}{m_e} \cdot \frac{V}{d}$$

For a period of time t during which the electron is between the plates, the beam is displaced by a distance y; the value of y is determined by the relation

$$y = \frac{1}{2} at^2 \tag{I.3}$$

Obviously, $t = l/v$
where l = length of plate
v = velocity of the electron
Hence,

$$y = \frac{1}{2} \frac{eVl^2}{m_e dv^2} \tag{I.4}$$

The distance y can be determined from the distance AB on the screen.

However, equation (I.4) contains the velocity of the electron v which is as yet unknown. It can be found from the deviation of the electron in a magnetic field. It is convenient to use such a field that would compensate for the deviation of the electron in the electric field so that the direction of the electron beam remains unchanged; then

$$f_{el} = f_{magn} \tag{I.5}$$

where f_{magn} = force of the magnetic field acting on the electron.

Current $i = ev$ corresponds to the moving electron. Hence, according to electrodynamics, the magnetic field will act on the electron moving perpendicular to the field with a force

$$f_{magn} = iH = evH \tag{I.6}$$

where H = intensity of the magnetic field.

From equations (I.6), (I.5) and (I.1) it follows that

$$evH = e\frac{V}{d}$$

or

$$v = \frac{V}{dH}$$

In this way in equation (I.4) the only value remaining unknown is e/m_e which can now be determined.

II. Characteristics of wave motion. Interference and diffraction of waves. The wave process is characterized by the following parameters: the *wavelength* λ, its *amplitude* a (Fig. II.1), and the *rate of propagation* u. Since in a unit of time the wave covers a distance equal to u, the number of waves that fit into the distance u is equal

to u/λ; this value, equal to the number of vibrations per unit of time, is called *frequency* and is denoted as ν; hence,

$$\nu = \frac{u}{\lambda}$$

Since the frequency of electromagnetic vibrations for visible and ultraviolet radiation is very great, it is usually more convenient to use the value $\bar{\nu}$, the *wave number*

$$\bar{\nu} = \frac{1}{\lambda}$$

As can be seen, ν is equal to $\bar{\nu}$ multiplied by the constant u (i.e., ν is directly proportional to $\bar{\nu}$ and wave number is thus a measure of frequency). The wave number is the number of waves per centimetre.
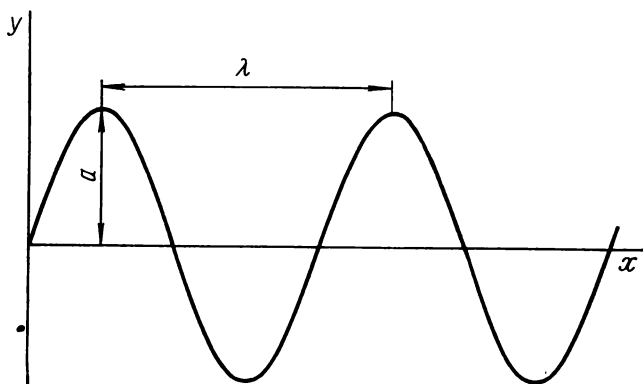
Fig. II.1. Wave parameters

Figure II. 2 shows the wavelengths of different kinds of electromagnetic radiation and the energies of the quanta of radiation (per *mole*) corresponding to different wavelengths.

The phenomenon known as *interference* is the effect produced when a train of waves is reinforced or weakened by another one (i.e., when intensification or extinction takes place). Reinforcement is observed when the waves are *in phase*, i.e., when the rises and falls of both waves coincide. On the contrary, when the rise of one wave coincides with the fall of the other one (the waves are *out-of-phase*), the waves cancel each other out, i.e., extinction takes place.

Diffraction is the phenomenon that occurs when waves meet obstacles; it is due to the separation of the wave into several groups of waves that interfere with each other. Such an obstacle may be a

diffraction grating (Fig. II.3) with a great number of clear slits equidistant from each other and of a size that is of the same order as that of the wavelength.

Infrared rays

Visible light

Ultraviolet rays

X-rays

γ-rays

Radio waves

10^6 10^3 1 10^{-3} 10^{-6} 10^{-9} 10^{-12}

λ, cm

10^{-9} 10^{-6} 10^{-3} 1 10^3 10^6 10^9

E, kcal/mole

Rotation of molecules

Vibrations of atoms in molecules

Transitions of electrons in inner shells

Nuclear processes

Transitions of electrons in outer shells of atoms and molecules
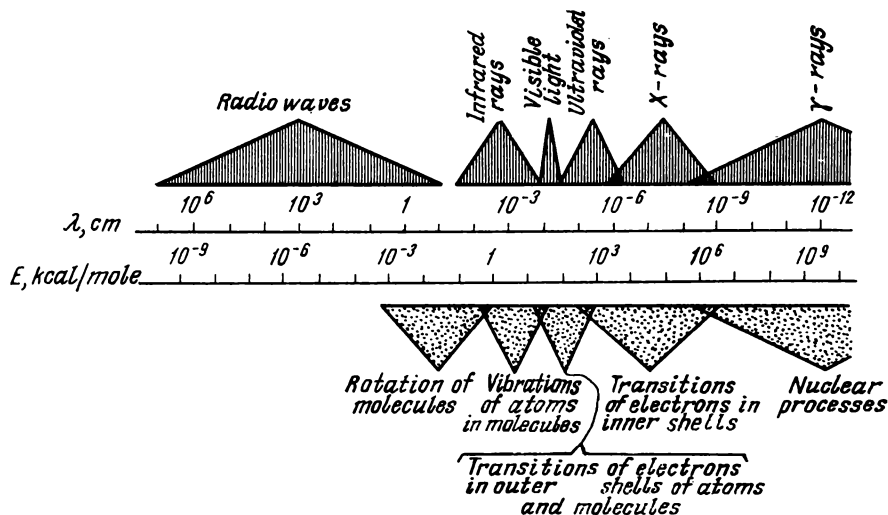
Fig. II.2. Wavelengths and energies of different kinds of electromagnetic radiation

$Sin\,\theta = 3\lambda/d$
$Sin\,\theta = 2\lambda/d$
$Sin\,\theta = \lambda/d$
$Sin\,\theta = 0$
$Sin\,\theta = \lambda/d$
$Sin\,\theta = 2\lambda/d$
$Sin\,\theta = 3\lambda/d$

θ

Screen

Radiation source   Diffraction grating
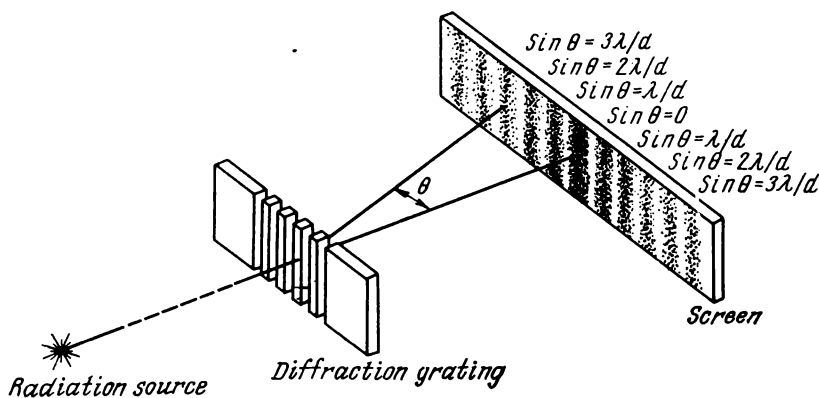
Fig. II.3. Schematic drawing of formation of diffraction pattern when radiation passes through a diffraction grating

Since the wave can pass the grating only through the clear slits, each slit becomes an independent source of waves which propagate in all directions and interfere with each other. As seen in Fig. II.4, from the point of view of simple geometry, it follows that the waves

are in phase in the directions defined by the relation

$$\sin \theta = \frac{n\lambda}{d}$$

where $n = 1, 2, 3, \ldots$
        θ = angle between the given direction and the line perpendicular to the grating
        λ = wavelength
        d = distance between the clear slits of the grating
   Intensification of the waves occurs in the directions that satisfy this relation. On the contrary, in directions defined by similar rela-
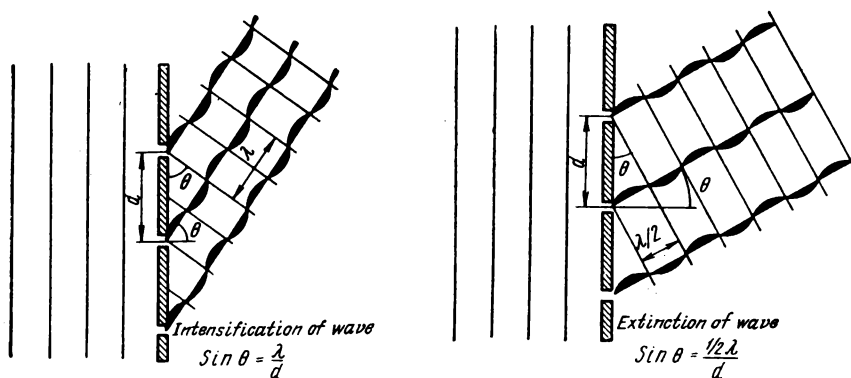
Fig. II.4. Interference of waves on passing through a diffraction grating

tions containing half-integer values of n ($n = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$), the waves are out-of-phase as a result of which extinction of the waves occurs.
   The *diffraction pattern* is observed on a screen placed in front of the grating. A diffraction pattern (the periodic change in illumination along the screen) is shown schematically in Fig. II.3. It is evident that the wavelength λ can readily be determined by measuring the angle θ if the distance between the clear slits in the grating is known.
   The diffraction pattern can be observed not only when the wave passes through a grating, but also when it is reflected from the latter.
   Diffraction gratings for visible light ($\lambda = 4000\text{-}7600$ Å) are produced by incising on a glass plate (with the aid of a diamond point) very many parallel lines close to each other; there are 1000 and more lines per 1 mm of length. Naturally occurring crystals are used as diffraction gratings for X-rays. The particles in crystals are arranged in a strictly definite order and the distances between the layers of the atoms are of the same order as the wavelengths of X-rays.

III. Construction of the Schrödinger equation. The equation for a monochromatic electromagnetic wave is

$$\frac{\partial^2 a}{\partial x^2} + \frac{\partial^2 a}{\partial y^2} + \frac{\partial^2 a}{\partial z^2} + \left(\frac{2\pi}{\lambda}\right)^2 a = 0 \qquad \text{(III.1)}$$

where a = amplitude
  λ = wavelength

To obtain the Schrödinger equation, in this relation a is substituted by the ψ-*function* and λ by its value as determined from the de Broglie relation $\lambda = h/p$, where p = momentum of the particle ($p = mv$); thus we obtain

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^4} + \frac{\partial^2 \psi}{\partial z^2} + \frac{4\pi^2}{h^2} p^2 \psi = 0 \qquad \text{(III.2)}$$

The kinetic energy of the particle E_k is related to the momentum by the equation

$$E_k = \frac{p^2}{2m}$$

Hence,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m E_k}{h^2} \psi = 0 \qquad \text{(III.3)}$$

The resulting equation does not take into account the potential energy of the particle; it is the equation for the motion of a free particle. When a particle moves in a potential field, its total energy E is equal to the sum of the kinetic energy and the potential energy U which depends on the coordinates x, y, and z

$$E = \frac{p^2}{2m} + U(x, y, z) \qquad \text{(III.4)}$$

Hence,

$$p^2 = 2m[E - U(x, y, z)] \qquad \text{(III.5)}$$

By substituting the value of p^2 from equation (III.5) into equation (III.2) we obtain

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}[E - U(x, y, z)]\psi = 0$$

or

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + U(x, y, z)\psi = E\psi$$

IV. Polarization of light. Light is t ansverse electromagnetic vibrations. This means that the electric and magnetic fields vibrate perpendicularly to the direction of propagation of the waves. These vibrations are in different planes passing through the axis of the light beam (Fig. IV.1).

The light emitted by different sources (sun, candle, electric lamp, etc.) is not polarized, that is, the vibrations are in all possible planes.

Light is said to be polarized if the vibrations of the field are in a single plane. The plane of the vibrations of the magnetic field is called the plane of polarization.

Polarized light can be produced by different methods. One extensively employed method makes use of the optical properties of crystals.

When light is passed through a crystal in a direction which does not coincide with its optical axis, the light ray is split into two polarized rays issuing from the crystal at a certain angle to one another
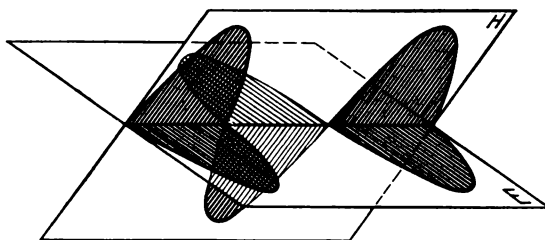
Fig. IV.1. Vibrations of electric and magnetic fields in electromagnetic wave

(Fig. IV.2)[1]. This is because the refraction indices in the crystal are different for vibrations taking place in different planes. This is very pronounced in crystals of the mineral calcite ($CaCO_3$), the angle between the rays being 6.5°. Large transparent crystals of this mineral, known as Iceland spar, are used for obtaining polarized light.
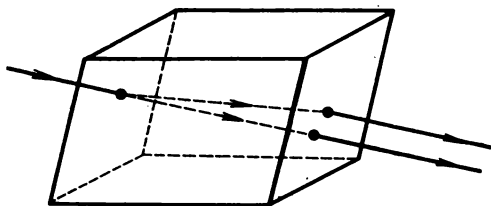
Fig. IV.2. Passage of light ray through crystal of Iceland spar

In order to produce polarized light one of the rays issuing from the crystal must be separated from the other. The optical system known as a *Nicol prism* is often used for this purpose.

The Nicol prism (Fig. IV.3) is a crystal of Iceland spar sawn in half along the diagonal and cemented with a substance whose refractive index is greater than that of Iceland spar. In this prism one of the rays undergoes complete internal reflection and is diverted to the lateral face which is painted black to absorb the light. The

---

[1] This phenomenon is not observed in crystals of the cubic system.

second ray falls on the joint at a different angle and passes through the prism. Thus by passing light through a Nicol prism we obtain a beam of polarized light. If a second Nicol prism is placed in the path of this ray and rotated 90° about its axis, the polarized light will not pass through. Thus by means of a second Nicol prism—the *analyzer*—it is possible to determine the direction of the plane of

Fig. IV.3. Nicol prism
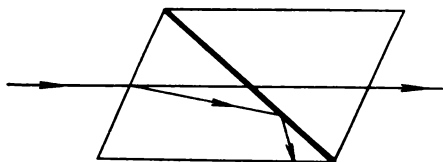
polarization of the light. When examining optically active substances, the test substance is placed between two Nicol prisms and the angle through which the plane of polarization is rotated is determined.

V. Derivation of relationship describing electron diffraction by molecules. To obtain a relationship expressing the intensity of an
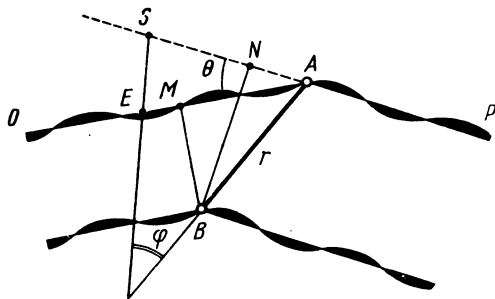
Fig. V.1. Scattering of waves by a molecule

electron stream scattered through a certain angle θ to the initial direction of the electron beam, we shall consider the diffraction of electrons by a diatomic molecule consisting of atoms A and B, whose nuclei are at a distance r apart.

Since the wave properties of electrons are manifested in their diffraction, the electron stream in the given case can be considered a beam of wavelength λ. Mark and Wierl (Germany) who were the first to apply electron diffraction for the study of molecules employed unchanged the theory of X-ray scattering previously formulated by Debye.

Let a plane wave fall on molecule AB (Fig. V.1). When the wave impinges on atoms it is scattered in all possible directions, and the

scattered waves interfere with one another. Let us consider the inter-
ference of the scattered waves in a direction making a certain angle
θ with the initial direction of the electron beam OA.

As in the example with the diffraction grating (see Appendix II)
the intensification or damping depends on the *phase difference* ρ
which is connected with the *path difference* δ of the rays according to
the relationship

$$\rho = \frac{2\pi\delta}{\lambda} \tag{V.1}$$

As can be seen from Fig. V.1

$$\delta = AM - AN$$

where AM and AN are projections of the section AB, equal to r,
on the directions of the incident and scattered rays.

If sections AE and AS, equal to r, are laid off on the above dire-
ctions, and a straight line is drawn through points S and E, it will
form angle φ with the line AB. By means of this auxiliary constru-
ction, δ can be expressed through r and angles θ and φ. Actually,
the difference between the projections of AB on directions OA and
AP can be replaced by the difference between the projections on the
direction AB, of sections equal to AB which are laid off on directions
OA and AP. Then δ is equal to the difference between the projections
of AE and AS on AB. But since the difference between the proje-
ctions of two sides of a triangle on any direction is equal to the pro-
jection of the third side on the same direction, δ will be equal to
the projection of ES on AB, i.e., ES cos φ. It is evident that

$$ES = 2r \sin \frac{\theta}{2}$$

whence

$$\delta = 2r \sin \frac{\theta}{2} \cos \varphi$$

It follows that the phase difference of waves moving in the dire-
ction AP will be expressed by the relationship

$$\rho = \frac{4\pi r}{\lambda} \sin \frac{\theta}{2} \cos \varphi$$

or

$$\rho = sr \cos \varphi \tag{V.2}$$

where

$$s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \tag{V.3}$$

The amplitudes ψ_A and ψ_B of waves scattered by atoms A and B
depend on the intensity of the interaction of the incident waves with
the atoms. In the given case, where we are examining the diffra-

ction of fast electrons, the amplitudes can be considered proportional to the nuclear charges Z. The intensity of the electron stream is proportional to the square of the amplitude of the resulting wave (we are considering de Broglie waves, and the electron density is determined by the quantity ψ^2).

When waves interfere, vector addition of their amplitudes takes place (Fig. V.2). Angle ρ between the vector directions is equal to the phase difference.

It follows from Fig. V.2 that the square of the amplitude of the wave resulting from interference is expressed by the relationship

$$\psi_{res}^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B \cos \rho \qquad (V.4)$$

Fig. V.2. Vector addition of amplitudes
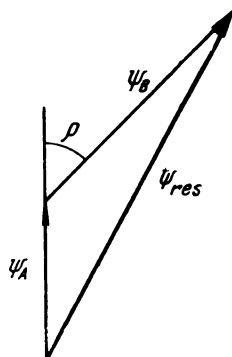
Since the intensity of the electron stream I is proportional to ψ^2, while $\psi_A \sim Z_A$ and $\psi_B \sim Z_B$ ($\sim$ is the proportionality sign), we can write

$$I \sim Z_A^2 + Z_B^2 + 2Z_AZ_B \cos \rho \qquad (V.5)$$

In order to make the following operations less cumbersome we shall consider only that part of the total intensity of the electron stream which is dependent on ρ. For it we can write

$$I \sim Z_A Z_B \cos \rho$$

It is necessary, however, to take account of the fact that phase difference ρ which we have calculated depends on the position of the molecule relative to the electron stream. Any arrangement of the molecules in a gas is possible, and therefore in order to find the actual intensity of the electron stream the mean value of $\cos \rho$ must be calculated for all possible positions of the molecules.

The position of the molecule relative to the incident wave when the value of angle θ is fixed can be determined by the angle φ. Therefore, we must calculate the mean value of $\cos \rho$ for all possible values of φ from 0 to π. It is determined by the relationship

$$\overline{\cos \rho} = \frac{\int \cos \rho \, d\rho}{\int d\rho} \qquad (V.6)$$

in which the integrals must be taken within such limits that angle φ ranges from 0 to π.

We integrate. According to (V.2)

$$d\rho = -sr \sin \varphi \, d\varphi$$

Therefore,

$$\int d\rho = - \int_0^\pi sr \sin \varphi \, d\varphi = \Big|_0^\pi sr \cos \varphi = -2sr$$

$$\int \cos \rho \, d\rho = - \int_0^\pi \cos (sr \cos \varphi) \, sr \sin \varphi \, d\varphi$$

We calculate the last integral, putting $\cos \psi = u$; then $du = -\sin \varphi \, d\varphi$, and consequently

$$- \int_0^\pi \cos (sr \cos \varphi) \, sr \sin \varphi \, d\varphi = \int_0^\pi \cos (sru) \, sr \, du = \Big|_0^\pi \frac{sr \sin (sru)}{sr} =$$

$$= \Big|_0^\pi \sin (sr \cos \varphi) = [-\sin sr - \sin sr] = -2 \sin sr$$

It follows that the mean value of $\cos \rho$ will be

$$\overline{\cos \rho} = \frac{\sin sr}{sr} \tag{V.7}$$

and the expression for the intensity of the scattered electrons will have the form

$$I \sim Z_A Z_B \frac{\sin sr}{sr} \tag{V.8}$$

For a polyatomic molecule containing n atoms of two species, l and m, we must carry out a vectorial summation of the amplitudes of the de Broglie waves for the electrons scattered by each atom. This is achieved by constructing the appropriate polygon of vectors in exactly the same way as the triangle in Fig. V.2 was constructed. The line closing the polygon gives the resulting amplitude. In this case the total intensity of the scattered electrons is expressed by the relationship

$$I \sim \sum_1^n {}_l \sum_1^n {}_m Z_l Z_m \frac{\sin sr}{sr} \tag{V.9}$$

Summation is carried out for all interatomic distances, including $r = 0$, when the neighbour of the atom under consideration is taken to be this atom itself; in that case $(\sin sr)/sr = 1$. Thus, as the result of such summation there appear the members Z_l^2 and Z_m^2 which were omitted for the time being when expression (V.8) was derived.

The theory set forth here is concerned only with *coherent* (elastic) electron scattering by molecules, in which the molecules do not pass into an excited state. But during the bombardment of molecules

by fast electrons, *incoherent* (inelastic) scattering of the electrons also takes place, in which the electrons give up part of their energy to the molecules, transferring them to an excited state. In this case wavelength λ of the de Broglie waves of the electrons incident on the molecules changes. Incoherent scattering gives a solid background without maxima, which quickly attenuates as parameter s increases. The actual curve of the change in the intensity of scattered electrons

Fig. V.3. Distribution of intensity of electron stream scattered by Br_2 molecules

1—coherent scattering (curve displaced upward); *2*—incoherent scattering; *3*—summation curve
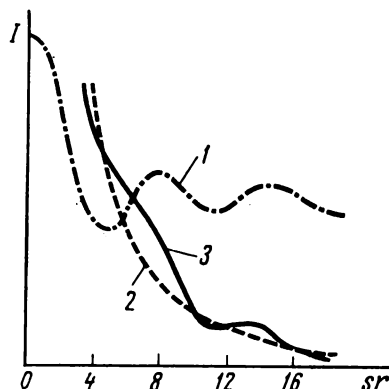
is determined by the sum of the coherent and incoherent scattering. Such summation for electrons scattered by Br_2 molecules is shown in Fig. V.3.

When electron diffraction pictures are interpreted visually, incoherent scattering need not be taken into account since the eye senses disturbances in the regular decrease in the blackening of the photographic plate and easily perceives maxima and minima corresponding to the curve of coherent scattering.

VI. Moment of inertia. Imagine that a material point rotates about an axis (Fig. VI.1). The velocity of a moving body is the derivative of the distance traversed with respect to time

$$v = \frac{ds}{dt} \qquad (VI.1)$$

In the case of rotary motion the element of the distance ds can be expressed as the product of the radius r of the circle along which the material point is moving by the value of the angle $d\varphi$ corresponding to the distance ds travelled

$$ds = r \, d\varphi \qquad (VI.2)$$

Then instead of (VI.1) we can write

$$v = r \frac{d\varphi}{dt} \qquad (VI.3)$$

The magnitude $d\varphi/dt$, denoted by the letter ω, is the *angular velocity*. Thus

$$v = r\omega \qquad\qquad (VI.4)$$

The kinetic energy of a moving body is defined by the equation

$$E_k = \frac{mv^2}{2}$$

Taking account of (VI.4) we have

$$E_k = \frac{mr^2\omega^2}{2} = \frac{I\omega^2}{2} \qquad\qquad (VI.5)$$

The magnitude $I = mr^2$ is called the *moment of inertia*. Equation (VI.5) relates to a material point. The moment of inertia of a body
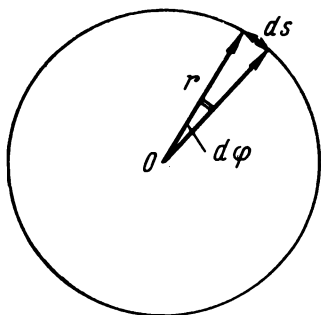
Fig. VI.1. Diagram for equation (VI.2)
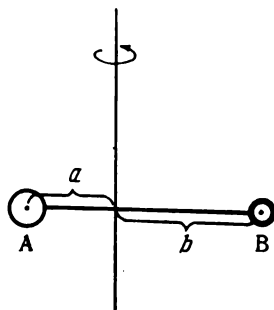
Fig. VI.2. Rotation of diatomic molecule

is the sum of the moments of inertia of the material points composing the body

$$I = \sum m_i r_i^2 \qquad\qquad (VI.6)$$

We next find the relationship between the energy of rotary motion

$$F_{rot} = \frac{mv^2}{2},$$

the angular momentum $M = mvr$ and the moment of inertia $I = mr^2$. Since

$$M^2 = m^2 v^2 r^2$$

it is evident that

$$E_{rot} = M^2/2mr^2$$

Thus

$$E_{rot} = M^2/2I \qquad\qquad (VI.7)$$

Let us find an expression for the moment of inertia of a diatomic molecule consisting of atoms A and B whose nuclei are at a distance r apart (Fig. VI.2).

Free rotation of the molecule will take place about an axis passing through the centre of mass perpendicular to the line connecting the atomic nuclei. Let the distances of the nuclei from the axis of rotation be a and b (Fig. VI.2). During rotation the following relationship should be met

$$m_A a = m_B b \qquad\qquad\qquad (VI.8)$$

where m_A and m_B are the masses of atoms A and B. Furthermore,

$$a + b = r \qquad\qquad\qquad (VI.9)$$

By solving the set of Equations (VI.8) and (VI.9), we find expressions for a and b

$$a = \frac{r m_B}{m_A + m_B} ; \qquad b = \frac{r m_A}{m_A + m_B} \qquad\qquad (VI.10)$$

In accordance with (VI.6) the moment of inertia of molecule AB will be

$$I = m_A a^2 + m_B b^2$$

Substituting the expressions for a and b, we obtain

$$I = [m_A m_B /(m_A + m_B)] \, r^2 \qquad\qquad (VI.11)$$

The magnitude m_{AB}^*, defined by the relationship

$$m_{AB}^* = m_A m_B /(m_A + m_B) \qquad\qquad (VI.12)$$

is called the *reduced mass*. Thus

$$I = m_{AB}^* r^2 \qquad\qquad\qquad (VI.13)$$

VII. Expressions for wave functions of hybrid orbitals.

sp-hybridization

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_s + \psi_{p_x}); \qquad \psi_2 = \frac{1}{\sqrt{2}} (\psi_s - \psi_{p_x})$$

sp²-hybridization

$$\psi_1 = \frac{1}{\sqrt{3}} \left(\psi_s + \sqrt{2}\, \psi_{p_x} \right)$$

$$\psi_2 = \frac{1}{\sqrt{3}} \left(\psi_s - \frac{\sqrt{2}}{2} \psi_{p_x} + \frac{\sqrt{6}}{2} \psi_{p_y} \right)$$

$$\psi_3 = \frac{1}{\sqrt{3}} \left(\psi_s - \frac{\sqrt{2}}{2} \psi_{p_x} - \frac{\sqrt{6}}{2} \psi_{p_y} \right)$$

sp³-hybridization

$$\psi_1 = \frac{1}{2} (\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}); \qquad \psi_2 = \frac{1}{2} (\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z})$$

$$\psi_3 = \frac{1}{2} (\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z}); \qquad \psi_4 = \frac{1}{2} (\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z})$$

VIII. Electron spin and magnetic properties of matter. If a magnet with 'magnetic charges' at the ends equal to q is placed in a magnetic field, a pair of forces (a couple) will act on it, that strives to position the magnet along the lines of force of the magnetic field (Fig. VIII.1). The moment of the forces M that turns the magnet is equal to

$$M = qlH \sin \varphi \qquad\qquad (\text{VIII.1})$$

where l = length of magnet

H = magnetic field strength

φ = angle formed by the magnet and the lines of force of the field

The product $ql = \mu_{magn}$ is called the *magnetic moment*.

As is known from the course of general physics, on a current-carrying circuit in a magnetic field, there also act a pair of forces
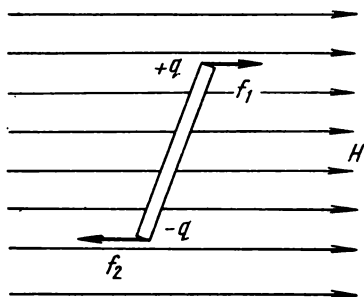
Fig. VIII.1. Interaction of magnet
and field
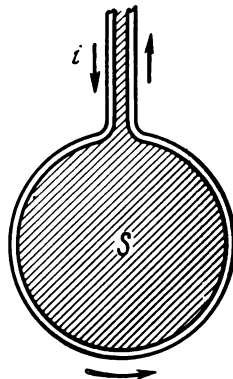
Fig. VIII.2. Current-carrying circuit

that strive to place it perpendicular to the field. Therefore, the circuit has a magnetic moment; it can be shown that in the given case (Fig. VIII.2)

$$\mu_{magn} = iS \qquad\qquad (\text{VIII.2})$$

where i = current

S = area of the circuit

The magnetic moment is a vector directed perpendicular to the plane of the circuit. The motion of a charged particle along a closed path is similar to that of the current in the circuit; it also gives rise to a magnetic moment. If, in accordance with the Bohr theory, it is assumed that the electron moves in an orbit, the *orbital magnetic moment of the electron* can be calculated with the aid of equation

(VIII.2). For the first Bohr orbit the magnetic moment is equal to

$$\mu_{magn}^{\circ} = \frac{1}{2} \frac{e\hbar}{m_e c} \qquad \text{(VIII.3)}$$

where e = charge of electron

$\hbar$ = Planck's constant divided by 2π

m_e = mass of electron

c = velocity of light

μ_{magn}° characterizes the *value of the projection of the orbital magnetic moment of the electron*; it is equal to $0.927 \cdot 10^{-20}$ erg/gauss and is called the *Bohr magneton*.

The projection of the orbital magnetic moment of the electron on the direction of the magnetic field is equal to the product of the Bohr magneton and the magnetic quantum number m. It is evident that when m is equal to zero, the projection under consideration is also equal to zero.

An electron has an *inherent magnetic moment* due to its spin. The magnitude of the projection of this magnetic moment is equal to one Bohr magneton; it can have a positive or negative sign depending on the direction of the spin in space. This projection cannot be equal to zero.

The composition of magnetic moments of electrons in a molecule is carried out by the rule of addition of vectors. *When all the electrons of a molecule are paired, the resultant magnetic moment is equal to zero.*

The presence or absence of a resultant magnetic moment in a molecule can easily be determined by the interaction of the given substance with a non-uniform magnetic field. *If the molecules of the substance have a magnetic moment, the substance is said to be paramagnetic; it is attracted by the magnetic field. In the absence of a magnetic moment in the molecules, the substance will be diamagnetic; it is repelled by the magnetic field.* The resultant magnetic moment of the molecules can be determined by the intensity of the interaction of the substance with the magnetic field.

Oxygen is a paramagnetic substance. On approaching a pole of a strong magnet to the surface of liquefied oxygen, it is readily noticed that oxygen is attracted to the magnet. Determinations have shown that the magnetic moment of the O_2 molecule corresponds to the presence of two unpaired electrons.

IX. Calculation of the absorption spectra of polymethylene dyes. As was pointed out on p. 194, the π-electrons in] a chain of carbon atoms containing conjugated double bonds, which can be denoted $—(CH = CH)_m—$, are not localized, but can move freely along the chain. The conditions of movement of an electron in such a polymethylene chain (the $—CH=$ radical is called methylene or methene) correspond quite closely to the model of the unidimensional

potential well (see p. 39-43). By means of this model it is possible to calculate fairly accurately the absorption spectra of a number of compounds represented by the general formulae

(A)

and

(B)
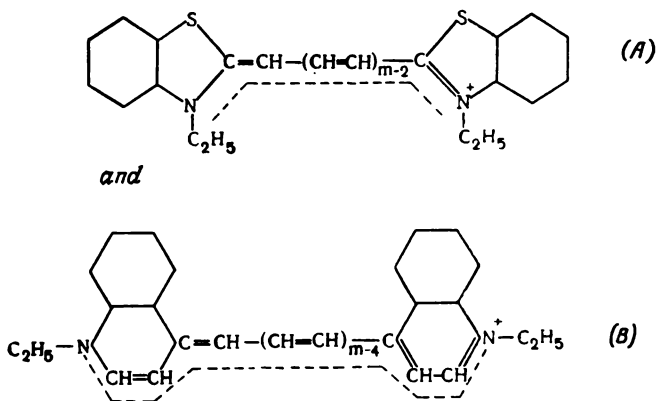
The path along which the electron can travel is indicated by a dotted line.

The energy of an electron in a unidimensional potential well is expressed by the relationship

$$E = \frac{n^2 h^2}{8 m_e a^2}$$

In the above compounds the number of delocalized π-electrons is equal to 2 m. In the unidimensional potential well these electrons will occupy m first energy levels, for which n is equal to 1, 2, ..., m; on each energy level there will be two electrons with opposite spins.

Since all the energy levels for which $n \leqslant m$ will be filled, the transfer of energy to a molecule occupying a level where $n = m$ will cause its transition to the next level for which $n = m + 1$. The molecule will absorb quanta corresponding to the energy of the given transition

$$E = E_{m+1} - E_m$$

Wavelength λ of the radiation corresponding to this energy can be calculated by means of the relationships

$$E = h\nu; \quad \nu = \frac{c}{\lambda}$$

Dimension a of the potential well is equal to the length of the chain of atoms along which the electron can move. If the distance between the carbon atoms in the polymethylene chain is taken to be 1.40 Å and the ends of the 'well' are considered to be at a distance of one

bond length beyond the nitrogen atoms, the calculation gives the results cited in Table IX.1. It can be seen that the calculated values of λ are quite close to the observed absorption maxima for compounds of the specified types.

Table IX.1

Wavelengths of Radiation Absorbed by Compounds A and B

m	Wavelength of maximum absorption; experimental values, Å		Wavelength calculated from potential well model, Å
	compound A	compound B	
2	4250	—	3280
3	5600	—	4540
4	6500	5900	5800
5	7600	7100	7060
6	8700	8200	8330
7	9900	9300	9600

X. Solution of homogeneous sets of linear equations. Sets of equations of the type

$$
\left.
\begin{aligned}
a_{11}x_1 + a_{12}x_2 + \ldots + a_{1n}x_n &= 0 \\
a_{21}x_1 + a_{22}x_2 + \ldots + a_{2n}x_n &= 0 \\
\cdots \cdots \cdots \cdots \cdots \cdots \\
a_{n1}x_1 + a_{n2}x_2 + \ldots + a_{nn}x_n &= 0
\end{aligned}
\right\}
$$

where x_1, x_2, . . ., x_n are unknowns and a_{11}, a_{12} . . . are coefficients the first subscript corresponds to the number of the equation, and) the second, to the number of the term) are said to be *homogeneous*.

For such systems two types of solutions are possible. In the first place it is clear that all the equations will be satisfied if all the unknowns are equal to zero: $x_1 = 0$, $x_2 = 0$, . . ., $x_n = 0$. This is called a *zero* or *trivial solution*, and it is always possible. If a set of equations has no other solution, the equations are said to be *incompatible*.

There are also sets of equations for which a non-trivial solution is possible. For such a solution to be possible, the *determinant* composed of the coefficients must be equal to zero. This is expressed as follows:

$$
\begin{vmatrix}
a_{11}a_{12} \ldots a_{1n} \\
a_{21}a_{22} \ldots a_{2n} \\
\cdot \cdot \cdot \cdot \cdot \cdot \cdot \\
a_{n1}a_{n2} \ldots a_{nn}
\end{vmatrix} = 0
$$

Next let us see what is meant by a determinant. Let there be a table composed of magnitudes of some kind, for example

$$\begin{pmatrix} a & b & c \\ d & e & f \\ g & h & n \end{pmatrix}$$

A table consisting of magnitudes arranged in the form of rows and columns is called a *matrix*. The magnitudes forming a matrix are called its *elements*. If the number of rows is equal to the number of columns, the matrix is *square*.

A determinant is a quantity calculated from the values of the elements of a square matrix according to a certain rule. A determinant is denoted by drawing vertical lines on both sides of the corresponding matrix.

If a matrix consists of four elements, the determinant is the difference of the products of the elements forming the diagonals, for example

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

Before considering the calculation of more complex determinants, we must introduce the concept of the *minor*. The minor is a determinant obtained from a given matrix by crossing out a line and a column containing some chosen element.

Now we can formulate a rule for calculating any determinant. To find the value of the determinant each element of the first line must be multiplied by the corresponding minor and the products added algebraically, writing the product with the plus sign if the element is odd (1st, 3rd, etc.) and with the minus sign if it is even. If necessary, values of the minors can be calculated in the same way. Thus, in the long run, any determinant is expressed by the algebraic sum of the products of its elements. As an example we can take the calculation of the determinant used in the treatment of the butadiene molecule by the Hückel method:

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} =$$

$$= x^2 \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - x \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} - 1 \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} + 1 \begin{vmatrix} 0 & 1 \\ 0 & x \end{vmatrix} =$$

$$= x^2 (x^2 - 1) - xx - x^2 + 1 = x^4 - x^2 - x^2 - x^2 + 1 = x^4 - 3x^2 + 1$$

VALUES OF UNITS OF MEASURE
AND PHYSICAL CONSTANTS USED
IN THE BOOK IN THE SI SYSTEM OF UNITS

$$1 \text{ Å} = 10^{-10} \text{ m}$$
$$1 \text{ g} = 10^{-3} \text{ kg}$$
$$1 \text{ kcal} = 4.184 \times 10^3 \text{ J}$$
$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$
$$1 \text{ erg} = 10^{-7} \text{ J}$$
$$\text{Electron charge } e = 1.602 \times 10^{-19} \text{ C}$$
$$\text{Velocity of light } c = 2.998 \times 10^8 \text{ m/s}$$
$$\text{Planck's constant } h = 6.625 \times 10^{-34} \text{ J·s}$$
$$\text{Bohr magneton } \mu^{\circ}_{magn} = 9.273 \times 10^{-24} \text{ a·m}^2$$

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MENDELEEV'S PERIODIC

Periods	Series				G R O	
		I	II	III	IV	V
I	1	(H)				
II	2	Li 3 $\frac{1}{2}$ 6.939	Be 4 $\frac{2}{2}$ 9.0122	5 $\frac{3}{2}$ B 10.811	6 C $\frac{4}{2}$ 12.01115	7 N $\frac{5}{2}$ 14.0067
III	3	Na 11 $\frac{1}{8}$ 22.9898	Mg 12 $\frac{2}{8}$ 24.305	13 Al $\frac{3}{8}$ 26.9815	14 Si $\frac{4}{8}$ 28.086	15 P $\frac{5}{8}$ 30.9738
IV	4	K 19 $\frac{1}{8}$ 39.102	Ca 20 $\frac{2}{8}$ 40.08	Sc 21 $\frac{2}{9}$ 44.956	Ti 22 $\frac{2}{10}$ 47.90	V 23 $\frac{2}{11}$ 50.942
	5	29 Cu 63.546	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216
V	6	Rb 37 85.47	Sr 38 87.62	Y 39 88.905	Zr 40 91.22	Nb 41 92.906
	7	47 Ag 107.868	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75
VI	8	Cs 55 132.905	Ba 56 137.34	La 57 138.91		
				Ce 58 140.12	Pr 59 140.907	Nd 60 144.24
				Tb 65 158.924	Dy 66 162.50	Ho 67 164.930
					Hf 72 178.49	Ta 73 180.948
	9	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980
VII		Fr 87 [223]	Ra 88 [226]	Ac 89 [227]		
				Th 90 232.038	Pa 91 [231]	U 92 238.03
	10			Bk 97 [247]	Cf 98 [251]	Es 99 [254]
				Ku 104 [260]		105
	11					

SYSTEM OF THE ELEMENTS

U   P   S

VI	VII	VIII			0
	1 H 1 1.00797				**He** 2 4.0026
8 O 16.9994	**9 F** 18.9984				**Ne** 10 20.179
16 S 32.064	**17 Cl** 35.453				**A** 18 39.948
Cr 24 51.996	**Mn 25** 54.9380	**Fe 26** 55.847	**Co 27** 58.9332	**Ni 28** 58.71	
34 Se 78.96	**35 Br** 79.904				**Kr 36** 83.80
Mo 42 95.94	**Tc 43** [99]	**Ru 44** 101.07	**Rh 45** 102.905	**Pd 46** 106.4	
52 Te 127.60	**53 I** 126.9044				**Xe 54** 131.30

Pm 61 [147]	**Sm 62** 150.35	**Eu 63** 151.96	**Gd 64** 157.25
Er 68 167.26	**Tm 69** 168.934	**Yb 70** 173.04	**Lu 71** 174.97
W 74 183.85	**Re 75** 186.2	**Os 76** 190.2	**Ir 77** 192.2

	0
84 Po [210]	**85 At** [210]
	Rn 86 [222]

Np 93 [237]	**Pu 94** [244]	**Am 95** [243]	**Cm 96** [247]
Fm 100 [257]	**Md 101** [258]	**No 102** [255]	**Lw 103** [258]