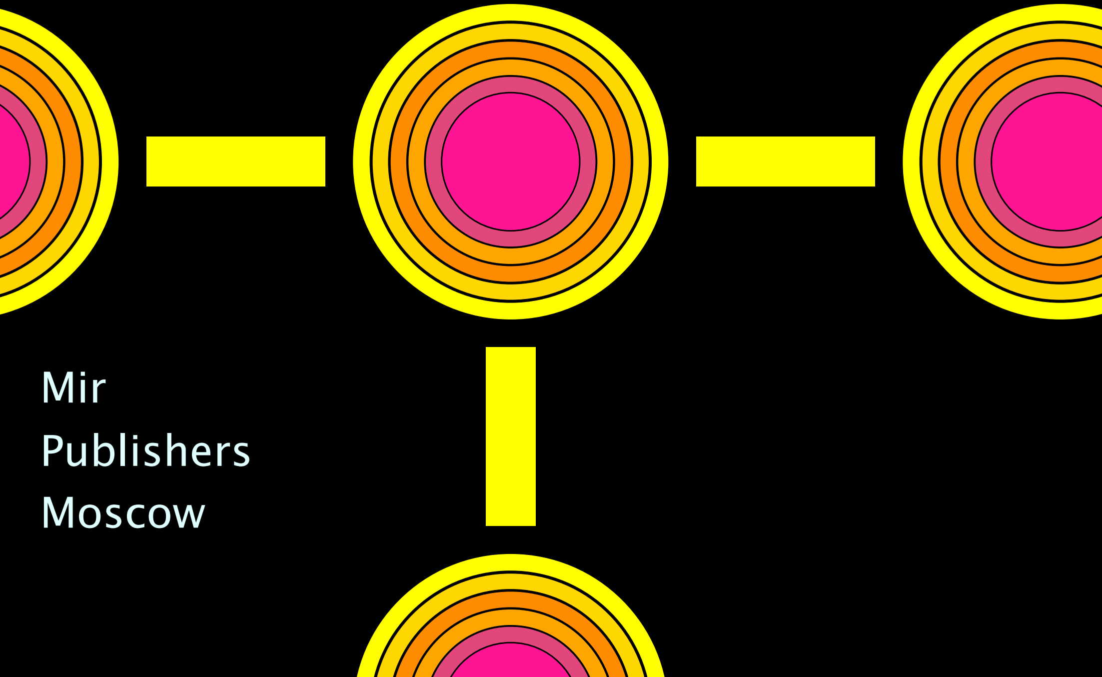
General Chemistry

N. L. Glinka

Volume

I



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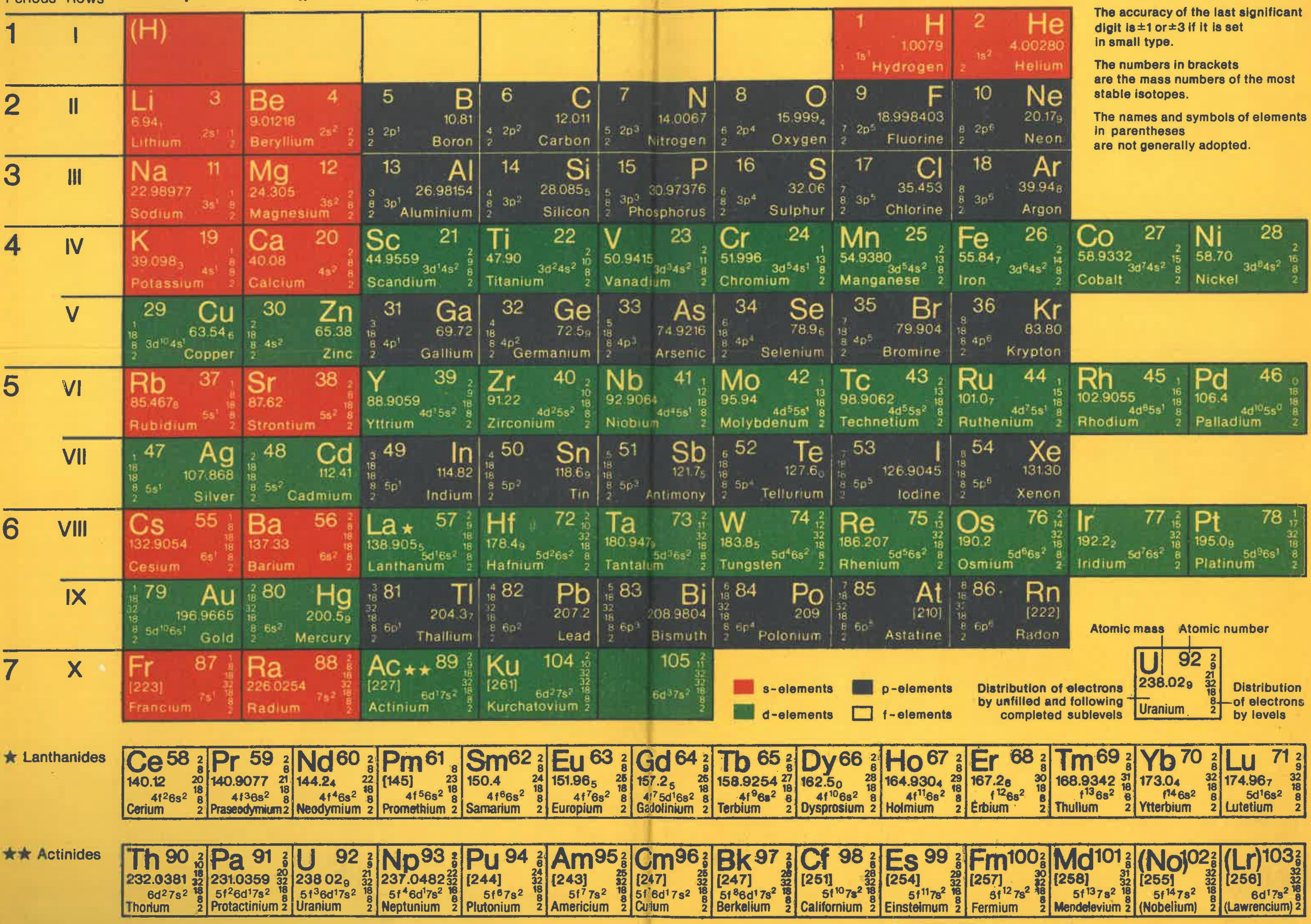
Moscow

Nikolai Glinka, after graduating from the Moscow University in 1908, conducted research for several years under the guidance of N. D. Zelinksy. He preferred teaching to research, however, and took his doctorate in that field. He taught chemistry in Podolsk for twelve years and was then transferred to Moscow in 1924 by the People's Commissariat of Education. In 1940, he was appointed Head of the Department of Inorganic and General Chemistry at the All-Union Polytechnical Correspondence Institute, a post he held to the end of his life. He died in 1965 at the age of 82.

Veniamin Rabinovich, the editor of the revised edition of **General Chemistry** graduated from the Leningrad State University in 1940. He is a Candidate of Sciences (Chemistry) and an associate professor at the A. I. Gertsen Pedagogical Institute, Leningrad. He is the author of over 50 scientific works, mainly on the thermodynamics of electrolyte solutions. His other activities include the publication of reference literature: he is the deputy editor in chief and a co-author of the fundamental seven volume **Chemist's Handbook** (in Russian), and the editor and a co-author of a **Concise Chemical Reference Book** (in Russian).

Mendeleev's Periodic Table of the Elements

Groups of elements ⟶



Periods	Rows	I	II	III	IV	V	VI	VII	VIII		
1	I	(H)						**H** 1 1.0079 $1s^1$ Hydrogen 1	**He** 2 4.00280 $1s^2$ Helium 2		
2	II	**Li** 3 6.94_1 $2s^1$ Lithium 1 2	**Be** 4 9.01218 $2s^2$ Beryllium 2 2	**B** 5 10.81 $2p^1$ Boron 3 2	**C** 6 12.011 $2p^2$ Carbon 4 2	**N** 7 14.0067 $2p^3$ Nitrogen 5 2	**O** 8 15.999_4 $2p^4$ Oxygen 6 2	**F** 9 18.998403 $2p^5$ Fluorine 7 2	**Ne** 10 20.17_9 $2p^6$ Neon 8 2		
3	III	**Na** 11 22.98977 $3s^1$ Sodium 1 8 2	**Mg** 12 24.305 $3s^2$ Magnesium 2 8 2	**Al** 13 26.98154 $3p^1$ Aluminium 3 8 2	**Si** 14 28.085_5 $3p^2$ Silicon 4 8 2	**P** 15 30.97376 $3p^3$ Phosphorus 5 8 2	**S** 16 32.06 $3p^4$ Sulphur 6 8 2	**Cl** 17 35.453 $3p^5$ Chlorine 7 8 2	**Ar** 18 39.94_8 $3p^6$ Argon 8 8 2		
4	IV	**K** 19 39.098_3 $4s^1$ Potassium 1 8 8 2	**Ca** 20 40.08 $4s^2$ Calcium 2 8 8 2	**Sc** 21 44.9559 $3d^14s^2$ Scandium 2 9 8 2	**Ti** 22 47.90 $3d^24s^2$ Titanium 2 10 8 2	**V** 23 50.9415 $3d^34s^2$ Vanadium 2 11 8 2	**Cr** 24 51.996 $3d^54s^1$ Chromium 1 13 8 2	**Mn** 25 54.9380 $3d^54s^2$ Manganese 2 13 8 2	**Fe** 26 55.84_7 $3d^64s^2$ Iron 2 14 8 2	**Co** 27 58.9332 $3d^74s^2$ Cobalt 2 15 8 2	**Ni** 28 58.70 $3d^84s^2$ Nickel 2 16 8 2
	V	**Cu** 29 63.54_6 $3d^{10}4s^1$ Copper 1 18 8 2	**Zn** 30 65.38 $4s^2$ Zinc 2 18 8 2	**Ga** 31 69.72 $4p^1$ Gallium 3 18 8 2	**Ge** 32 72.5_9 $4p^2$ Germanium 4 18 8 2	**As** 33 74.9216 $4p^3$ Arsenic 5 18 8 2	**Se** 34 78.9_6 $4p^4$ Selenium 6 18 8 2	**Br** 35 79.904 $4p^5$ Bromine 7 18 8 2	**Kr** 36 83.80 $4p^6$ Krypton 8 18 8 2		
5	VI	**Rb** 37 85.467_8 $5s^1$ Rubidium 1 8 18 8 2	**Sr** 38 87.62 $5s^2$ Strontium 2 8 18 8 2	**Y** 39 88.9059 $4d^15s^2$ Yttrium 2 9 18 8 2	**Zr** 40 91.22 $4d^25s^2$ Zirconium 2 10 18 8 2	**Nb** 41 92.9064 $4d^45s^1$ Niobium 1 12 18 8 2	**Mo** 42 95.94 $4d^55s^1$ Molybdenum 1 13 18 8 2	**Tc** 43 98.9062 $4d^55s^2$ Technetium 2 13 18 8 2	**Ru** 44 101.0_7 $4d^75s^1$ Ruthenium 1 15 18 8 2	**Rh** 45 102.9055 $4d^85s^1$ Rhodium 1 16 18 8 2	**Pd** 46 106.4 $4d^{10}5s^0$ Palladium 0 18 18 8 2
	VII	**Ag** 47 107.868 $5s^1$ Silver 1 18 18 8 2	**Cd** 48 112.41 $5s^2$ Cadmium 2 18 18 8 2	**In** 49 114.82 $5p^1$ Indium 3 18 18 8 2	**Sn** 50 118.6_9 $5p^2$ Tin 4 18 18 8 2	**Sb** 51 121.7_5 $5p^3$ Antimony 5 18 18 8 2	**Te** 52 127.6_0 $5p^4$ Tellurium 6 18 18 8 2	**I** 53 126.9045 $5p^5$ Iodine 7 18 18 8 2	**Xe** 54 131.30 $5p^6$ Xenon 8 18 18 8 2		
6	VIII	**Cs** 55 132.9054 $6s^1$ Cesium 1 8 18 18 8 2	**Ba** 56 137.33 $6s^2$ Barium 2 8 18 18 8 2	**La**★ 57 138.905_5 $5d^16s^2$ Lanthanum 2 9 18 18 8 2	**Hf** 72 178.4_9 $5d^26s^2$ Hafnium 2 10 32 18 8 2	**Ta** 73 180.947_9 $5d^36s^2$ Tantalum 2 11 32 18 8 2	**W** 74 183.8_5 $5d^46s^2$ Tungsten 2 12 32 18 8 2	**Re** 75 186.207 $5d^56s^2$ Rhenium 2 13 32 18 8 2	**Os** 76 190.2 $5d^66s^2$ Osmium 2 14 32 18 8 2	**Ir** 77 192.2_2 $5d^76s^2$ Iridium 2 15 32 18 8 2	**Pt** 78 195.0_9 $5d^96s^1$ Platinum 1 17 32 18 8 2
	IX	**Au** 79 196.9665 $5d^{10}6s^1$ Gold 1 18 32 18 8 2	**Hg** 80 200.5_9 $6s^2$ Mercury 2 18 32 18 8 2	**Tl** 81 204.3_7 $6p^1$ Thallium 3 18 32 18 8 2	**Pb** 82 207.2 $6p^2$ Lead 4 18 32 18 8 2	**Bi** 83 208.9804 $6p^3$ Bismuth 5 18 32 18 8 2	**Po** 84 209 $6p^4$ Polonium 6 18 32 18 8 2	**At** 85 [210] $6p^5$ Astatine 7 18 32 18 8 2	**Rn** 86 [222] $6p^6$ Radon 8 18 32 18 8 2		
7	X	**Fr** 87 [223] $7s^1$ Francium 1 8 18 32 18 8 2	**Ra** 88 226.0254 $7s^2$ Radium 2 8 18 32 18 8 2	**Ac**★★ 89 [227] $6d^17s^2$ Actinium 2 9 18 32 18 8 2	**Ku** 104 [261] $6d^27s^2$ Kurchatovium 2 10 32 32 18 8 2	105 $6d^37s^2$ 2 11 32 32 18 8 2					

Atomic masses are given according to the International Table of 1977.

The accuracy of the last significant digit is ±1 or ±3 if it is set in small type.

The numbers in brackets are the mass numbers of the most stable isotopes.

The names and symbols of elements in parentheses are not generally adopted.

🟥 s-elements
⬛ p-elements
🟩 d-elements
☐ f-elements

Atomic mass
Atomic number

U 92 238.02_9 Uranium 2 9 21 32 18 8 2

Distribution of electrons by unfilled and following completed sublevels

Distribution of electrons by levels

★ Lanthanides

Ce 58	**Pr** 59	**Nd** 60	**Pm** 61	**Sm** 62	**Eu** 63	**Gd** 64	**Tb** 65	**Dy** 66	**Ho** 67	**Er** 68	**Tm** 69	**Yb** 70	**Lu** 71
140.12	140.9077	144.2_4	[145]	150.4	151.96_5	157.2_5	158.9254	162.5_0	164.930_4	167.2_6	168.9342	173.0_4	174.96_7
$4f^26s^2$	$4f^36s^2$	$4f^46s^2$	$4f^56s^2$	$4f^66s^2$	$4f^76s^2$	$4f^75d^16s^2$	$4f^96s^2$	$4f^{10}6s^2$	$4f^{11}6s^2$	$f^{12}6s^2$	$f^{13}6s^2$	$f^{14}6s^2$	$5d^16s^2$
Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
2 8 20 18 8 2	2 8 21 18 8 2	2 8 22 18 8 2	2 8 23 18 8 2	2 8 24 18 8 2	2 8 25 18 8 2	2 9 25 18 8 2	2 8 27 18 8 2	2 8 28 18 8 2	2 8 29 18 8 2	2 8 30 18 8 2	2 8 31 18 8 2	2 8 32 18 8 2	2 9 32 18 8 2

★★ Actinides

Th 90	**Pa** 91	**U** 92	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**(No)** 102	**(Lr)** 103
232.0381	231.0359	$238\ 02_9$	237.0482	[244]	[243]	[247]	[247]	[251]	[254]	[257]	[258]	[255]	[256]
$6d^27s^2$	$5f^26d^17s^2$	$5f^36d^17s^2$	$5f^46d^17s^2$	$5f^67s^2$	$5f^77s^2$	$5f^76d^17s^2$	$5f^86d^17s^2$	$5f^{10}7s^2$	$5f^{11}7s^2$	$5f^{12}7s^2$	$5f^{13}7s^2$	$5f^{14}7s^2$	$6d^17s^2$
Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteimum	Fermium	Mendelevium	(Nobelium)	(Lawrencium)
2 10 18 32 18 8 2	2 9 20 32 18 8 2	2 9 21 32 18 8 2	2 9 22 32 18 8 2	2 8 24 32 18 8 2	2 8 25 32 18 8 2	2 9 25 32 18 8 2	2 9 26 32 18 8 2	2 8 28 32 18 8 2	2 8 29 32 18 8 2	2 8 30 32 18 8 2	2 8 31 32 18 8 2	2 8 32 32 18 8 2	2 9 32 32 18 8 2

ИЗДАТЕЛЬСТВО • МИР •

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General Chemistry

N. L. Glinka

Volume I

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Second printing, 1986

На английском языке

PREFACE TO THE THIRD ENGLISH EDITION

Professor N. Glinka's textbook *General Chemistry* has been very popular in the Soviet Union and other countries for many years. During the author's life, it saw 12 editions in Russian and was repeatedly published in the languages of the peoples of the USSR. Many generations of students have studied chemistry from this text, secondary school graduates have used it in preparing for their entrance examinations to higher educational establishments, and specialists of non-chemical professions have often found answers to their questions in it. The popularity of the textbook can be attributed to the intelligent selection of the material and the clear logic of the order of presentation. The fourteenth Russian edition was the basis for the revised fourth English edition.

The time that has elapsed since the author's death, however, has required the introduction of appreciable amendments into the book. This necessity was due first of all to the extensive penetration of chemistry into many branches of the economy and its growing role in the training of specialists in a variety of professions. In addition, the volume of the factual material of chemistry has grown tremendously, which requires a new approach to its selection for a textbook. Finally, this period is characterized by the continuation of the process of the transformation of chemistry from an empirical science to a branch of science based on strictly scientific foundations, above all on the modern concepts of the structure of matter and on the theory of thermodynamics.

The required revision of the textbook was carried out in its sixteenth Russian edition (1973). The sections devoted to the structure of a substance, the fundamentals of chemical thermodynamics, solutions, and complex compounds were substantially expanded; greater attention was given to matters associated with oxidation-reduction processes and with the properties of metals and alloys; the material devoted to the chemistry of individual elements has been appreciably revised.

The textbook was revised by a group of authors including P. N. Sokolov, Cand. Sc. (Chem.), Prof. A. V. Markovich, D.Sc. (Chem.), Prof. A. I. Stetsenko, D.Sc. (Chem.), Associate Professors Z. Ya. Khavin, Cand.Sc. (Chem.), K. V. Kotegov, Cand.Sc. (Chem.), and V. A. Rabinovich, Cand.Sc. (Chem.), who was also responsible for editing the entire book. An additional revision of the book mainly due to the transition to SI units of physical quantities and the associated alterations in terminology was carried out in the 19th Russian edition (1977).

The present English text has been translated from the 21st Russian edition and has been divided into two volumes so as to facilitate work with the book. We hope that it will be met with interest by our readers.

V. A. Rabinovich

CONTENTS

INTRODUCTION

1. Matter and Its Motion

Chemistry is among the natural sciences studying the world surrounding us with all the wealth of its forms and the variety of phenomena occurring in it.

All of nature, the entire world exist objectively outside and independently of man's consciousness. The world is material; everything that exists is one form or another of moving matter that is always in a state of continuous motion, change, and development. Motion, being constant change, characterizes matter as a whole and each of its tiniest particles.

The forms of motion of matter are diverse. The heating and cooling of bodies, the emission of light, an electric current, chemical transformations, and vital processes are all different forms of motion of matter. Various forms of motion of matter may transform into other ones. For example, mechanical motion may transform into thermal motion, the latter into chemical motion, and chemical motion may transform into electrical motion. These transformations are witnesses of the unity and continuous relationships between qualitatively different forms of motion.

Notwithstanding all the diverse ways in which various forms of motion can transform into other ones, a fundamental law of nature—that of the eternity of matter and its motion, is accurately observed. This law governs all kinds of matter and all forms of its motion; no kind of matter and no form of motion can be obtained from nothing or converted into nothing. This is confirmed by the entire century-old experience of science.

The individual forms of motion of matter are studied by physics, chemistry, biology, and other branches of science. The general laws of nature's development, however, are dealt with by materialistic dialectics.

2. Substances and Their Changes. The Subject of Chemistry

Every individual kind of matter having definite physical properties in given conditions, for example water, iron, sulphur, lime, and oxygen, is called a **substance** in chemistry. For instance, sulphur is a substance consisting of light-yellow brittle crystals insoluble in water; the density of sulphur is 2.07 g/cm^3, and it melts at 112.8 °C. All these are characteristic physical properties of sulphur.

To establish the properties of a substance, it must be available in the purest possible state. Even a very small content of an impurity may sometimes result in a great change in some properties of a substance. For example, the presence of even hundredths of a per cent of iron or copper in zinc accelerates its reaction with hydrochloric acid hundreds of times (see Vol. 2, Sec. 82).

Substances are not encountered in the pure state in nature. Natural substances are mixtures sometimes consisting of a very great number of different substances. Natural water, for instance, always contains dissolved salts and gases. When one of the substances is present in a mixture in a predominating amount, the entire mixture usually bears its name.

Substances produced by chemical enterprises—**chemical products**—also contain a certain amount of impurities. Special symbols are used to indicate how pure they are. In the order of decreasing impurity content, there are distinguished commercial chemical products (com.), pure products (p.), analytically pure products (a.p.), chemically pure (c.p.), and specially pure (s.p.) products. Only a few products of grade s.p. are manufactured. The tolerated content of impurities in a chemical product of each of the above classes is established by special government or state standards (in the USSR by State All-Union Standards—GOST's).

A pure substance is always homogeneous. Mixtures may be homogeneous or heterogeneous. In the former, particles of the substances forming them cannot be detected directly or under a microscope owing to their negligibly small size. Such mixtures include mixtures of gases, many liquids, and some alloys.

Examples of heterogeneous mixtures are various minerals and rocks, soil, turbid water, and dusty air. The heterogeneity of a mixture cannot always be detected immediately; this can sometimes be done only by using a microscope. For example, blood at first sight seems to be a homogeneous red liquid, but when observed under a microscope it can be seen to consist of a colourless liquid in which red and white corpuscles are swimming.

We can see every day that substances experience various changes: a lead bullet flying out of a rifle's barrel becomes so greatly heated if it hits a stone that the lead melts, transforming into a liquid;

a steel object rusts in humid air; firewood burns in a stove leaving only a small heap of ashes; leaves that have fallen from trees gradually decay, turning into humus, and so on.

When a lead bullet melts, its mechanical motion transforms into thermal motion, but this transition is not attended by a chemical change of the lead—solid and molten lead are the same substance.

Matters are different when lead as a result of prolonged heating in air transforms into lead oxide (litharge). Here we get a new substance with other properties. New substances are also formed when steel rusts, firewood burns, and leaves decay.

Phenomena in which substances transform into other, new substances are called **chemical.** Such phenomena are studied by **chemistry.** *Chemistry is a science dealing with the transformations of substances. It studies the composition and structure of substances, how the properties of substances depend on their composition and structure, the conditions and ways in which substances transform into other ones.*

Chemical changes are always attended by physical ones. Consequently, chemistry is associated very closely with physics. It is also associated with biology because biological processes are attended by continuous chemical transformations. Chemical phenomena, however, do not come to physical processes, and biological phenomena to chemical and physical processes: each form of motion of matter has its own features.

3. The Importance of Chemistry. Chemistry in the National Economy of the USSR

Chemistry plays an exceedingly important role in modern life, especially in man's industrial activities. It is difficult to find a branch of industry not connected with the use of chemistry. Nature gives us only the starting raw material—wood, ore, petroleum, etc. By subjecting natural materials to chemical processing, we get various substances needed for agriculture, for manufacturing industrial articles, and for domestic use—fertilizers, metals, plastics, surface finishes, medicines, detergents, soda, and the like. To be able to chemically process natural materials, we must know the general laws of transformation of substances, and it is exactly chemistry that gives us this knowledge.

Tsarist Russia had no large-scale chemical industry. This greatly affected the state of the chemical science in the country because it had no material foundation for its development. Scientific research met with support on the part of the government only in rare cases. Notwithstanding their extremely unfavourable conditions of work, however, Russian scientists involved in chemistry made a major contribution to the world's chemical science.

The Great October Socialist Revolution provided all necessary conditions for the free development of science. Already in the first years of existence of the young Soviet republic, during the hard years of devastation and civil war, the government rendered tremendous aid to the science of chemistry: the first research institutes and laboratories were organized, and their number began to grow quite rapidly in the following years. The number of chemical educational establishments also increased many times. Scientific research encompassing all the branches of chemistry was developed on a large scale.

During the years of the prewar five-year periods, a powerful chemical industry was created virtually anew in the USSR. There were erected groups of mining and chemical enterprises, and plants producing mineral fertilizers, synthetic ammonia, synthetic rubber, plastics, etc. By 1941, the chemical industry exceeded the prerevolutionary level more than 20 times with respect to the amount of manufactured products.

The post-war years saw considerable expansion of the branches of the chemical industry producing nitrogen and potassium fertilizers, plastics, synthetic rubber, chlorine and its derivatives, and of those occupied in organic synthesis. The production of synthetic fibres, synthetic ethyl alcohol, organic agricultural pesticides, and other substances was set up.

The development of the chemical industry is one of the most important conditions for technical progress. The use of chemical materials makes it possible to increase the quantity of products manufactured and improve their quality. This is exactly why the plans for the Soviet Union's national economy provide for the priority rates of development of the chemical industry.

The development of the chemical industry will ensure constantly growing rates of **"chemization" of the national economy**—the constantly growing use of chemical materials and products in industry and agriculture, and also the widespread use of chemical methods of production in all the branches of the national economy.

1

THE ATOMIC AND MOLECULAR CONCEPT

The notion that a substance consists of individual very tiny particles—the **atomic hypothesis**—originated back in ancient Greece. The creation of a scientifically substantiated theory of atoms and molecules, however, became possible much later—in the 18th and 19th centuries, when physics began to be based on accurate experiments. In chemistry, quantitative methods of research were introduced by M. Lomonosov in the second half of the 18th century.

Mikhail Vasilyevich Lomonosov (1711-1765)

Mikhail Vasilyevich Lomonosov was born on November 8, 1711, in the village of Mishaninskaya near the large village of Kholmogory, Arkhangel'sk province, in a fisherman's family. After being taught to read and write by a countryman, Lomonosov soon read all the books he could get in his village. His tremendous inquisitiveness and passionate urge for knowledge made him leave his native village when nineteen. In the winter of 1730, Lomonosov started off for Moscow on foot and with almost no money. Upon his arrival, he succeeded in entering the Slav-Greek-Latin Academy, the only higher educational establishment in Moscow at that time.

His brilliant abilities and tenacious efforts allowed Lomonosov to complete the curriculum of seven years of the Academy in four. He was transferred to St. Petersburg to study at the Academy of Sciences as one of a group of the twelve best students.

In less than a year after arriving at St. Petersburg, Lomonosov was sent abroad to study metallurgy and mining. After returning home in 1741, he was appointed a junior scientific assistant at the Academy in the class of physics, and soon became a professor in chemistry and a member of the Russian Academy of Sciences.

Lomonosov belonged to the rare, exceptionally talented people whose scientific ideas are many decades ahead of their time. His tireless scientific and practical activities were distinguished by their striking breadth and diversity. As Academician S. Vavilov said, "What he alone achieved in the fields of physics, chemistry, astronomy, instrument-making, geology, geography, linguistics, and history could well enough be the activities of a whole Academy".

Lomonosov was the first to define chemistry as a science "dealing with the changes occurring in a mixed body". He conceived this science as a collection of chemical facts combined by a mathematical way of treatment and systematized on the basis of conceptions of the structure of matter. Accurate experiments with pure substances, employing "measures and weights", must be attended by a theoretical analysis of the results. Being decades ahead of his contemporaries, Lomonosov developed a corpuscular theory of the structure of matter anticipating the modern theory of atoms and molecules.

Lomonosov considered chemistry to be his "main profession", but he was also the first outstanding Russian physicist. He clearly envisaged the close relation between chemistry and physics; he considered that chemistry must be studied with the aid of physics, and that chemical analyses could be properly interpreted only on the basis of physical laws. Using physics to explain chemical phenomena, he laid the foundation of a new science—physical chemistry.

Lomonosov was not only a brilliant naturalist, but also a materialist philosopher. In dealing with nature's phenomena, he formed a materialistic approach to the fundamental question of philosophy—the relation of thought to being. As a result of Lomonosov's efforts and according to his project, in 1755 the first university in Russia—the Moscow University, was founded. It later became one of the centres of education and science in the country.

4. Law of Conservation of Mass

Lomonosov set up a chemical laboratory at the Academy of Sciences. In it, he studied how chemical reactions proceed, weighing the reactants and the products. This led him to establish the **law of conservation of mass (weight)**:

The mass (weight) of the substances entering into a reaction equals the mass (weight) of the substances formed as a result of the reaction.

Lomonosov first formulated this law in 1748, and confirmed it experimentally in 1756, roasting metals in sealed vessels.

Somewhat later (1789), the law of conservation of mass was established independently of Lomonosov by the French chemist A. Lavoisier. He showed that not only the total mass of the substances is conserved in chemical reactions, but also the mass of each of the elements which the reacting substances consist of.

Antoine Laurent Lavoisier (1743-1794)

Antoine Laurent Lavoisier, an outstanding French scientist, was born in Paris on August 26, 1743. Like Lomonosov, he consistently used the theoretical notions and methods of physics known in his time to solve the basic problems of chemistry. This allowed him to achieve very important scientific results.

A great merit of Lavoisier was the systematization of the enormous amount of factual data accumulated by chemistry. He worked out (together with three other French chemists) a rational chemical nomenclature, and accurately classified all the substances (elements and chemical compounds) known at that time.

In 1905, A. Einstein (see p. 68) showed that the mass of a body (m) and its energy (E) are related as follows:

$$E = mc^2$$

where c is the speed of light in vacuum, $c = 2.997\,925 \times 10^8\ \text{m}\cdot\text{s}^{-1}$ (or approximately $300\,000\ \text{km}\cdot\text{s}^{-1}$). **Einstein's equation** holds both for macroscopic bodies and for particles of the microworld (for example, electrons and protons). Energy is always liberated or absorbed in chemical reactions (see Sec. 54). Hence, when dealing with the mass of substances, we must take into account its increase or decrease corresponding to the absorption or liberation of energy in the given reaction. Owing to the enormous value of the quantity c^2, however, very small masses that are impossible to measure correspond to the energies that are liberated or absorbed in chemical reactions*. This is why the mass which is brought in or carried off by the energy in chemical reactions may be disregarded.

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* For example, when one mole of hydrogen chloride (36.461 g) forms from hydrogen and chlorine, the energy liberated corresponds to a mass of about 10^{-9} g.

5. Essence of the Atomic and Molecular Concept

Lomonosov laid the foundation of the science of atoms and molecules. In 1741 in one of his first works—"Elements of Mathematical Chemistry"—he presented the most important propositions of his corpuscular theory of the structure of matter.

According to Lomonosov, all substances are formed of very tiny "insensitive" particles that are physically indivisible and are capable of mutual cohesion. The properties of substances are due to the properties of these particles. Lomonosov distinguished two kinds of such particles: smaller ones—"elements", corresponding to atoms in today's interpretation of this term, and larger ones—"corpuscles", which are now known as molecules.

The composition of every corpuscle is the same as that of the entire substance. Chemically different substances also have corpuscles that differ in their composition. "Corpuscles are homogeneous if they consist of the same number of the same elements combined in the same way", and "corpuscles are heterogeneous if they consist of different elements combined in different ways or in different numbers".

A glance at the above definitions reveals that Lomonosov saw the reason why substances differ not only in the different composition of the corpuscles, but also in the different arrangement of the elements in a corpuscle.

Lomonosov stressed the fact that corpuscles move according to the laws of mechanics; without motion, corpuscles would not be able to collide with one another or act on one another in some other way to produce changes. Since all the changes in substances are the result of motion of corpuscles, chemical transformations must be studied not only by methods of chemistry, but also by those of physics and mathematics.

During the more than 200 years that have elapsed since Lomonosov's time, his ideas on the structure of matter were verified comprehensively, and their correctness was confirmed completely. At present, all our notions of the structure of matter, of the properties of substances, and of the nature of physical and chemical phenomena are based on the concept of atoms and molecules.

The cornerstone of the concept of atoms and molecules is the principle of **discreteness** (discontinuity of structure) of a substance: a substance is not something solid or continuous, but consists of individual very minute particles. The difference between substances is due to the difference between their particles; the particles of a single substance are identical, while those of different substances are different. The particles of a substance are in motion in all conditions; the higher the temperature of a body, the more intensive is this motion.

The particles of most substances are molecules. *A molecule is the smallest particle of a substance having its chemical properties.* Molecules, in turn, consist of atoms. *An atom is the smallest particle of an element having its chemical properties.* Molecules may consist of a different number of atoms. Thus, the molecules of the noble gases are monatomic, those of substances such as hydrogen and nitrogen are diatomic, those of water are triatomic, etc. The molecules of the most complex substances—the higher proteins and nucleic acids—are built up of hundreds of thousands of atoms. Atoms can combine with one another not only in different proportions, but also in different ways. Therefore, while the number of chemical elements is comparatively small, the number of different substances is very great.

Students often cannot immediately understand why a molecule of a given substance does not have its physical properties. To clarify this matter, let us consider several physical properties of substances, for example the melting and boiling points, the heat capacity, mechanical strength, hardness, density, and electrical conductance.

Properties such as the melting and boiling points, the mechanical strength, and the hardness are determined by the strength of the bond between the molecules in the given substance in its given state of aggregation. Therefore, the application of such concepts to an individual molecule has no sense. Density is a property characterizing an individual molecule and one that can be calculated. The density of a molecule, however, is always greater than that of a substance (even in the solid state) because there is always a free space between the molecules in any substance. Properties such as the electrical conductance and heat capacity are determined not by the properties of the molecules, but by the structure of a substance as a whole. To convince ourselves that this is true, it is sufficient to remember that these properties change quite greatly with a change in the state of aggregation of a substance, whereas the molecules do not experience deep changes. Thus, the concepts of some physical properties cannot be applied to individual molecules, and of others can be applied, but these properties themselves differ in their magnitude for a molecule and a substance as a whole.

The particles forming a substance are not always molecules. Many substances in the liquid and solid state, for example most salts, have an ionic structure instead of a molecular one. Some of the substances have an atomic structure. The structure of solids and liquids will be considered in greater detail in Chapter 5. Here we shall only indicate that the carriers of the chemical properties in substances having an ionic or atomic structure are not molecules, but the combinations of ions or atoms forming the given substance.

6. Elementary Substance and Chemical Element

One of the first chemists who indicated the need to distinguish between the concepts of an **elementary (simple) substance** and a **chemical element** was Dmitri Mendeleev.

Indeed, every elementary substance is characterized by definite physical and chemical properties. When an elementary substance enters into a chemical reaction and forms a new substance, it loses most of its properties. For example, when iron combines with sulphur, it loses its metallic lustre, ductility, magnetic properties, etc. Consequently, iron sulphide does not contain iron as we know it in the form of an elementary substance. But since metallic iron can again be obtained from iron sulphide with the aid of chemical reactions, chemists say that the composition of iron sulphide includes the **element** iron, understanding by this term the material which metallic iron consists of. Like iron, sulphur too is in iron sulphide not in the form of the brittle yellow combustible substance sulphur, but in the form of the **element** sulphur. In exactly the same way, hydrogen and oxygen forming water are contained in the latter not as gaseous hydrogen and oxygen with their characteristic properties, but in the form of the **elements** hydrogen and oxygen. If these elements, however, are in the "free state", i.e. are not combined chemically with another element, they form elementary substances.

We may define *a chemical element* to be *a species of atoms characterized by a definite collection of properties**. When atoms of the same element combine with one another, they form elementary substances. A combination of atoms of different elements is either a mixture of elementary substances or a compound (a compound substance).

The difference between an elementary substance and an element becomes especially clear when we encounter a few elementary substances consisting of the same element.

Let us take a piece of phosphorus, for example. This is a white semitransparent substance melting at 44.2 °C and very poisonous. Phosphorus glows in air in the dark and may ignite spontaneously. It is an elementary substance and cannot be decomposed into other substances. If we heat phosphorus without the access of air, however, after a certain time its properties change very sharply: the phosphorus acquires a red-violet colour, stops glowing in the dark, becomes unpoisonous, and does not ignite spontaneously in the air. These novel properties do not vanish when heating is stopped. Thus, we undoubtedly have to do with a transformation of one substance into another one, but this is a special transformation: the substance we have taken has not decomposed, and nothing has been added to it. This makes us consider both substances, the initial one and the one

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* A definition of the concept "chemical element" based on the theory of the structure of atoms is given in Sec. 35.

obtained after heating, to be only different forms of existence of the same element phosphorus in the free state; the first of them is called white, and the second red phosphorus.

A proof of the fact that white and red phosphorus are indeed different forms of the same element and consist of identical atoms is their relation to oxygen: when heated in oxygen, both white and red phosphorus react with it to form the same substance—phosphoric anhydride. Hence, the element phosphorus can exist in the free state in the form of different elementary substances.

Like phosphorus, many other elements in the free state may also exist in the form of several different elementary substances.

The phenomenon of a chemical element existing in the form of several elementary substances is called **allotropy**. The different elementary substances formed by the same element are called **allotropic modifications** of this element. Allotropy in some cases is due to the fact that the molecules of the different allotropic modifications consist of a different number of atoms, and in others to the fact that their crystals have a different structure. For instance, white phosphorus consists of molecules P_4, whereas the crystals of red phosphorus have an absolutely different polymeric structure (see Vol. 2, Sec. 31).

The abundance of the elements on the Earth is far from being the same. Their occurrence in the Earth's crust is studied by **geochemistry**, a science that owes its development to a considerable extent to the works of the Soviet scientists V. Vernadsky and A. Fersman*.

Oxygen is the most abundant element in the Earth's crust (49.5%). The second place belongs to silicon (27%), next come aluminium, iron, calcium, sodium, potassium, magnesium, and hydrogen. These nine elements form over 98 per cent of the mass of the Earth's crust, so that less than two per cent fall to the share of all the remaining elements. These two per cent also include such elements widely employed in the national economy as copper, zinc, lead, nickel, sulphur, and phosphorus.

Fersman introduced the concept of **atomic percentage**, i.e. the content of atoms of the elements in the Earth's crust in per cent, to

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* Vladimir Ivanovich Vernadsky (1863-1945), Academician, State Prize winner, an outstanding mineralogist and geochemist, was one of the founders of geochemistry and its branch—biogeochemistry—studying the part played by organisms in geochemical processes. He devoted many years of his scientific activities to revealing the processes of mineral formation and studying the composition of the Earth's crust. Vernadsky's works on radioactive minerals and ores of scarce metals were the foundation for the development of the rare metal industry in the USSR.

Aleksandr Evgenyevich Fersman (1883-1945), Academician, Lenin and State Prize winner, was a pupil of Vernadsky. He was the author of a number of fundamental works in geochemistry. He conducted enormous work in the exploration and studying of the USSR's mineral wealth and discovered a number of deposits of valuable minerals.

characterize the occurrence of the elements in the Earth's crust. The atomic percentage and the percentage by mass differ for the same element. For example, hydrogen is third with respect to the number of its atoms in the Earth's crust (17%), but is only ninth (1%) with respect to mass.

7. Law of Definite Proportions. Law of Multiple Proportions

Lomonosov's profound ideas on the structure of matter were not understood by his contemporaries. In addition, experimental verification of these views of his was impossible at that time. This is why there was no progress in the theory of atoms and molecules in the second half of the 18th century. What was lacking for the final building up of this science was a knowledge of the laws determining the relationships between the amounts of substances reacting with one another and formed in chemical reactions. These laws were discovered only at the end of the 18th and the beginning of the 19th centuries.

The establishment of the law of conservation of mass resulted in the firm rooting of quantitative methods of research in chemistry beginning from the end of the 18th century. The quantitative composition of many substances was studied. This led to the establishment of the **law of definite proportions** (also called the **law of constant composition**):

> *The masses of the elements forming a given compound are always in a definite proportion that does not depend on how this compound was prepared.*

Many elements in combining with one another can form different substances each of which is characterized by a definite proportion of the masses of these elements. For instance, carbon forms two compounds with oxygen. One of them—carbon monoxide—contains 42.88% (mass) of carbon* and 57.12% (mass) of oxygen. The second compound—carbon dioxide—contains 27.29% (mass) of carbon and 72.71% (mass) of oxygen. In studying such compounds, J. Dalton** in 1803 established the **law of multiple proportions**:

> *If two elements form several chemical compounds with each other, then the masses of one of the elements corresponding to the same mass of the other element in these compounds are in a simple integral proportion.*

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* Here and below, we shall use to notation % (mass) to signify per cent by mass, and % (vol.) to signify per cent by volume.

** John Dalton (1766-1844) was a British scientist working in the field of physics, chemistry, and meteorology. When studying the properties of gases, he discovered the law of partial pressures of gases. His merits were especially great in the development of the atomic theory.

Dalton was an adherent of the atomic concept of the structure of matter. The discovery of the law of multiple proportions was a confirmation of this concept. The law was a direct indication of the fact that elements enter the composition of compounds only in definite portions. Let us calculate, for example, the mass of the oxygen combining with the same amount of carbon in the formation of carbon monoxide and carbon dioxide. For this purpose, we shall divide the quantities giving the content of oxygen and carbon in both oxides by one another. We shall find that there is exactly two times more oxygen per unit mass of the carbon in carbon dioxide than in carbon monoxide:

Compound	Carbon monoxide	Carbon dioxide
Carbon content, % (mass)	42.88	27.29
Oxygen content, % (mass)	57.12	72.71
Mass of oxygen per unit mass of carbon	1.33	2.66

The ability of elements to combine only in definite portions pointed to the discontinuous structure of a substance. Developing the atomic concept, Dalton introduced a notion of atoms and of relative atomic masses of elements close to the modern one. He adopted the mass of a hydrogen atom, which is the lightest one, as the unit of atomic mass. For the first time in the history of chemistry, he compiled a table of atomic masses including 14 elements.

The laws of definite proportions and multiple proportions follow from the atomic and molecular concepts. Substances having a molecular structure consist of identical molecules. It is therefore natural that the composition of such substances is constant. When several compounds are formed from two elements, the atoms of these elements combine with one another into molecules of a different, but definite composition. For example, a molecule of carbon monoxide is built up of one atom of carbon and one atom of oxygen, while a molecule of carbon dioxide includes one carbon atom and two oxygen atoms. It is obvious that the mass of the oxygen falling to the same mass of carbon is two times greater in the second of these compounds than in the first one.

Unlike the law of conservation of mass, whose correctness was completely confirmed by the discoveries made after its establishment, the laws of definite proportions and multiple proportions were found to be not so universal. In connection with the discovery of isotopes (Sec. 35), it was found that the ratio of the masses of the elements forming a given substance is constant only provided that the isotopic composition of these elements is constant. A change in the isotopic composition of an element is attended by a change in the mass composition of the compound. For instance, heavy water (Sec. 72) contains about 20% (mass) of hydrogen, whereas ordinary water contains only 11%. Here the law of definite proportions does not hold.

At the beginning of the 20th century, N. Kurnakov (see Vol. 2, Sec. 81), when studying metal alloys, discovered **compounds of varying composition.** In these compounds, for each unit of mass of a given element there may be a varying mass of another element. For example, in a compound formed by bismuth with thallium, there may be from 1.24 to 1.82 units of mass of bismuth per unit of mass of thallium.

In the thirties of the present century, it was found that compounds of varying composition are encountered not only among the compounds of metals with one another, but also among other solids, for example oxides, compounds of metals with sulphur, nitrogen, carbon, and hydrogen.

For many compounds of varying composition, the limits within which their composition may change have been found. Titanium dioxide TiO_2, for example, may contain from 0.65 to 0.67 unit of mass of oxygen per unit of mass of titanium, which corresponds to the formula $TiO_{1.9\text{-}2.0}$. It is quite natural that such formulas indicate not the composition of a molecule—compounds of varying composition have an atomic structure instead of a molecular one, but only reflect the limits of the composition of the relevant substance.

The limits of the possible change in composition vary for different compounds. They also vary with a change in the temperature.

If two elements form several compounds of varying composition with each other, then here the law of multiple proportions does not hold too. For example, titanium forms several oxides of varying composition with oxygen, the most important of them being $TiO_{1.46\text{-}1.56}$ and $TiO_{1.9\text{-}2.0}$. It is evident that in this and in similar cases the law of multiple proportions is not observed.

The law of multiple proportions is also not observed for substances whose molecules consist of a great number of atoms. For example, hydrocarbons are known having the formulas $C_{20}H_{42}$ and $C_{21}H_{44}$. The numbers of units of mass of hydrogen per unit mass of carbon in these and similar compounds form an integral ratio, but these numbers cannot be called small.

8. Law of Combining Volumes. Avogadro Law

The French scientist J. Gay-Lussac, the author of the well-known law of the thermal expansion of gases, performed the first quantitative investigations of reactions between gases. By measuring the volumes of gases entering into a reaction and formed as a result of a reaction, Gay-Lussac arrived at a conclusion known as the **law of combining volumes** or Gay-Lussac's chemical law:

> *When gases react, the volumes consumed and produced, measured at the same temperature and pressure, are in ratios of small whole numbers.*

For example, when two volumes of hydrogen react with one volume of oxygen (at a temperature above the boiling point of water), two volumes of water vapour are formed.

In 1811, the Italian physicist A. Avogadro explained the simple ratios between the volumes of gases observed in chemical reactions by establishing the following law:

> *Equal volumes of all gases at the same temperature and pressure contain the same number of molecules.*

This law (the Avogadro law) introduced into science the concept of **molecules** as of the tiniest particles of a substance. The concept of atoms as of the tiniest particles of an element remained in force. Avogadro especially stressed the fact that molecules of simple substances do not necessarily have to be identical with the relevant atoms; on the contrary, they usually consist of several atoms of the given element.

The Avogadro law made possible the conclusions on the number of atoms in molecules of gases. Particularly, it was assumed on its basis that molecules of gases such as hydrogen, chlorine, oxygen, and nitrogen consist of two atoms. This assumption explained the ratios between the volumes of gases established by Gay-Lussac.

The Avogadro law played a great role in establishing the atomic masses of elements and the molecular masses of compound substances (see Sec. 10).

9. Atomic and Molecular Masses. The Mole

A very important method of determining the molecular masses of gaseous substances is based on the Avogadro law. But before treating this method, we must indicate the units used to express molecular and atomic masses.

Originally, the mass of an atom of hydrogen, the lightest of all the elements, was adopted as the unit of mass in calculating atomic masses, and the masses of the atoms of the other elements were determined relative to it. But since the atomic masses of the majority of the elements are found from the composition of their oxygen compounds, the calculations were actually performed with respect to the atomic mass of oxygen, which was assumed to equal 16; the ratio between the atomic masses of oxygen and hydrogen was taken equal to 16 : 1. More accurate measurements later showed this ratio to be 15.874 : 1 or 16 : 1.0079. A change in the atomic mass of oxygen would result in a change in the atomic masses of most elements. It was therefore decided to leave an atomic mass of 16 for oxygen, adopting an atomic mass of 1.0079 for hydrogen.

Thus, a unit equal to 1/16 the mass of an oxygen atom and called the **oxygen unit** was adopted as the unit of atomic mass. It was subsequently found that natural oxygen is a mixture of isotopes (see Sec. 35), so that the oxygen unit characterizes the average value of the mass of the atoms of oxygen's natural isotopes. This unit was unacceptable for atomic physics, and in this branch of science, the unit of atomic mass was taken equal to 1/16 the mass of the oxygen atom ^{16}O. The result was the appearance of two scales of atomic masses—the **chemical** and the **physical** one. The existence of two atomic mass scales was very inconvenient for scientists.

In 1961, a single scale of relative atomic masses was adopted. It was based on the **atomic mass unit** (amu), which is 1/12 the mass of an atom of the carbon isotope ^{12}C. According to this scale, the relative atomic masses of oxygen and hydrogen equal 15.9994 and 1.0079 amu, respectively.

Thus, at present, *the relative atomic mass* (or simply *the atomic mass*) *of an element is defined as the mass of its atom expressed in atomic mass units.*

The mass of a molecule of any substance equals the sum of the masses of the atoms forming this molecule. Hence, the molecular mass equals the sum of the corresponding atomic masses. For example, the molecular mass of a hydrogen molecule consisting of two atoms is 2.0158 amu, and the molecular mass of water whose molecule contains two hydrogen atoms and one oxygen atom is $15.9994 + 2 \times 1.0079 = 18.0152$ amu. Hence, *the relative molecular mass* (or simply *the molecular mass*) *of an elementary substance or a compound is defined as the mass of its molecule expressed in atomic mass units.*

Until recent times, the terms "atomic weight" and "molecular weight" were used instead of the terms "atomic mass" and "molecular mass".

In addition to units of mass and volume, a unit of the amount of substance called the **mole** (mol) is used in chemistry.

The mole is the amount of a substance containing as many molecules, atoms, ions, electrons, or other elementary entities as there are carbon atoms in 0.012 kilogram of the carbon isotope ^{12}C.

When using the unit "mole", the elementary entity must be specified in each case exactly. For instance, we must distinguish between a mole of atoms H, a mole of molecules H_2, and a mole of ions H^+.

At present, the number of elementary entities contained in one mole of a substance (**Avogadro's number**) has been determined with a high accuracy. In practical calculations, it is taken equal to 6.02×10^{23}

The mass of one mole of a given substance is called its **molar mass.** The molar mass is usually expressed in g/mol. Since one mole of any substance contains the same number of elementary entities, then the molar mass of a substance (M, g/mol) is proportional to the mass of the corresponding elementary entity, i.e. to the relative molecular (or atomic) mass of the given substance (M_r, amu):

$$M = KM_r$$

where K is a constant of proportionality. It is the same for all substances.

It is not difficult to see that $K = 1$. Indeed, for the carbon isotope ^{12}C, we have $M_r = 12$ amu, while its molar mass (in accordance with the definition of the mole) is 12 g/mol. Consequently, the numerical values of M (g/mol) and M_r (amu) coincide, and therefore $K = 1$. It thus follows that *the molar mass of a substance expressed in grams has the same numerical value as its relative molecular (atomic) mass expressed in amu.* Thus, the molar mass of atomic hydrogen is 1.0079 g/mol, of molecular hydrogen is 2.0158 g/mol, and of molecular oxygen is 31.9988 g/mol.

According to the Avogadro law, the same number of molecules of any gas occupies the same volume in identical conditions. On the other hand, one mole of any substance contains (by definition) the same number of particles. Hence, it follows that *one mole of any substance in the gaseous state occupies the same volume at the same temperature and pressure.*

It is not difficult to calculate the volume occupied by one mole of a gas in **standard conditions**, i.e. at standard atmospheric pressure (101.325 kPa or 760 mmHg) and a temperature of 0 °C. For example, it has been experimentally established that the mass of one cubic decimetre (i.e. one litre) of oxygen in standard conditions is 1.43 grams. Consequently, the volume occupied in the same conditions by one mole of oxygen (32 g) is $32 : 1.43 = 22.4$ litres. We shall get the same number by calculating the volume of one mole of hydrogen, carbon dioxide, etc.

One mole of any gas in standard conditions occupies a volume of 22.4 litres. This volume is called the **molar volume** of a gas in standard conditions*.

10. Determining the Molecular Masses of Gaseous Substances

To determine the relative molecular mass of a substance (in amu), we usually find the molar mass of the substance (in g) numerically

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* The molar volume of an ideal gas in standard conditions is (22.4138 ± ± 0.0070) litres. The molar volumes of real gases vary and differ somewhat from the value 22.4138 litres. In the majority of cases, this difference tells only in the fourth and following significant figures. Consequently, for real gases, we should use either the value 22.4 litres, or (if a higher accuracy is required) the value of the molar volume of the gas being studied.

equal to it. If the substance is in the gaseous state, its molar mass can be found with the aid of Avogadro's law.

According to this law, equal volumes of gases taken at the same temperature and the same pressure contain the same number of molecules. It thus follows that the masses of equal volumes of two gases must relate to each other like their molecular masses or like their molar masses numerically equal to the molecular masses:

$$\frac{m_1}{m_2}=\frac{M_1}{M_2}$$

Here m_1 and m_2 are the masses, and M_1 and M_2 the molar masses of the first and second gases.

The ratio of the mass of a given gas to the mass of the same volume of another gas taken at the same temperature and the same pressure is called the **relative density of the first gas with respect to the second.**

For example, the mass of one litre of carbon dioxide is 1.98 g, and that of one litre of hydrogen in the same conditions is 0.09 g. Hence, the density of carbon dioxide relative to hydrogen is $1.98 : 0.09 = 22$.

Let us denote the relative density of a gas m_1/m_2 by the symbol d. Hence

$$d=\frac{M_1}{M_2}$$

whence

$$M_1 = dM_2$$

The molar mass of a gas equals its density relative to another gas multiplied by the molar mass of the second gas.

The relative densities of various gases are often determined with respect to hydrogen because it is the lightest of all gases. Since the molar mass of hydrogen is 2.0158 g/mol, then in this case the equation for calculating molar masses becomes

$$M_1 = 2.0158d$$

or, if we round off the molar mass of hydrogen to 2:

$$M_1 = 2d$$

When using this equation, for example, to find the molar mass of carbon dioxide whose density relative to hydrogen, as indicated above, is 22, we find

$$M_1 = 2 \times 22 = 44$$

The molar mass of a gas is also quite often calculated on the basis of its density relative to air. Although air is a mixture of several gases, we can nevertheless speak of the **mean molar mass of air** determined from its density relative to hydrogen. The molar mass of air found in this way is 29 g/mol.

Denoting the relative density of a gas being studied with respect to air through d_{air}, we get the following equation for calculating molar masses:

$$M_1 = 29d_{air}$$

The molar mass of a substance (and, therefore, its relative molecular mass too) can also be determined in a different way, using the concept of the molar volume of a substance in the gaseous state. For this purpose, we find the volume occupied in standard conditions by a definite mass of the given substance in the gaseous state, and then compute the mass of 22.4 litres of this substance in the same conditions. The quantity obtained is the molar mass of the substance (in g/mol).

Example. The volume occupied by 0.7924 g of chlorine at 0 °C and a pressure of 101.325 kPa is 250 ml. Calculate the relative molecular mass of the chlorine.

We find the mass of the chlorine contained in a volume of 22.4 l (22 400 ml):

$$m = \frac{22\,400 \times 0.7924}{250} \approx 71 \text{ g}$$

Consequently, the molar mass of chlorine is 71 g/mol, and its relative molecular mass is 71 amu.

The volumes of gases are usually measured in conditions other than the standard ones. The volume of a gas can be reduced to standard conditions with the aid of an equation combining Boyle's and Gay-Lussac's gas laws and expressing the **combined gas law**:

$$\frac{pV}{T} = \frac{p_0V_0}{T_0}$$

Here V is the volume of a gas at the pressure p and absolute temperature T, and V_0 is the volume of the gas at the standard pressure p_0 (101.325 kPa or 760 mmHg) and temperature T_0 (273 K)*.

The molar masses of gases can also be calculated by using an **equation of state of an ideal gas**—the Clapeyron-Mendeleev equation

$$pV = \frac{m}{M}RT$$

where p is the pressure of the gas, Pa; V is its volume, m^3; m is the mass of the substance, kg; M is its molar mass, kg/mol; T is the absolute temperature, K; and R is the **molar gas constant** equal to 8.314 J/(mol·K).

We can use the methods described above to find the molecular masses not only of gases, but also of all substances that pass into

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* More exactly, 273.15 K.

the gaseous state when heated (without decomposing). To do this, a sample of the substance being studied is transformed into a vapour, and its volume, temperature, and pressure are measured. The following calculations are performed in the same way as when determining the molecular masses of gases.

The molecular masses determined in these ways are not quite accurate because the gas laws considered above and the Clapeyron-Mendeleev equation are strictly true only at very low pressures (see Sec. 11). The molecular masses are calculated more accurately on the basis of the analysis of the relevant substance (see Sec. 14).

11. Partial Pressure of a Gas

To find the molecular masses of gases, it is very often necessary to measure the volume of a gas collected over water and therefore saturated with water vapour. When determining the gas pressure in this case, we have to introduce a correction for the partial pressure of the water vapour.

In ordinary conditions, gases mix with one another in any proportions. Each gas in a mixture is characterized by its own **partial pressure.** It is the pressure which the amount of the given gas present in the mixture would exert if it alone occupied the entire volume which the mixture occupied at the same temperature.

The law of partial pressures established by Dalton is as follows:

> *The pressure of a mixture of gases that do not react chemically with one another equals the sum of the partial pressures of each gas in the mixture.*

Assume that 570 ml of a gas at a temperature of 20 °C and a pressure of 104.1 kPa are collected over water. This pressure is composed of two quantities—the partial pressure of the gas itself and the pressure of the saturated water vapour. The latter at each temperature has a quite definite value; in particular, at 20 °C it is 2.34 kPa (see Table 8). Consequently, the partial pressure of the gas in this case is 104.1 — 2.34 = 101.76 kPa. When reducing the volume to standard conditions, we must use the partial pressure of the gas (101.76 kPa) in the equation instead of the total pressure of the gas mixture:

$$V_0 = \frac{pVT_0}{p_0T} = \frac{101.76 \times 570 \times 273}{101.325\,(273+20)} = 533 \text{ ml}$$

If we take no account of the correction for the pressure of the water vapour, then instead of the volume found we get

$$V_0 = \frac{104.1 \times 570 \times 273}{101.325\,(273+20)} = 546 \text{ ml}$$

The error is 13 ml, i.e. about 2.5 per cent, which is allowable only in tentative calculations.

All the gas laws considered above—Dalton's law, Gay-Lussac's law of combining volumes, and Avogadro's law are approximate laws. They are observed strictly at very low pressures when the mean distance between molecules is considerably greater than their own dimensions, and interaction of the molecules with one another is virtually absent. At the conventional moderate pressures, they are observed approximately, and at high pressures, great deviations from these laws are observed.

12. Equivalent. Law of Equivalents

It follows from the law of definite proportions that elements combine with one another in strictly definite quantitative proportions. This is why the concepts of equivalent and equivalent mass were introduced in chemistry.

At present *an equivalent of an element is defined to be an amount of it such that combines with one mole of hydrogen atoms or replaces the same number of hydrogen atoms in chemical reactions.* For example, in the compounds HCl, H_2S, NH_3, and CH_4, the equivalents of chlorine, sulphur, nitrogen, and carbon are 1, 1/2, 1/3, and 1/4 mole, respectively.

The mass of one equivalent of an element is called its **equivalent mass.** For instance, in the above examples, the equivalent masses of chlorine, sulphur, nitrogen, and carbon are respectively 34.45, $32/2 = 16$, $14/3 = 4.67$, and $12/4 = 3$ g/mol.

Equivalents and equivalent masses are usually found either from the data of compound analysis or from the results obtained in the displacement of one element by another. To determine the equivalent (or equivalent mass) of an element, we do not necessarily have to proceed from its compound with hydrogen. The equivalent (equivalent mass) can be calculated using the composition of a compound of the given element with any other one whose equivalent (equivalent mass) is known.

Example. The combination of 1.50 g of sodium with an excess of chlorine resulted in the formation of 3.81 g of sodium chloride. Find the equivalent mass of sodium (E_{Na}) and its equivalent if the equivalent mass of chlorine is known to be 35.45 g/mol.

It follows from the conditions of the example that sodium chloride contains $3.81 - 1.50 = 2.31$ g of chlorine per 1.50 g of sodium. Hence:

E_{Na} g/mol of sodium are equivalent to 35.45 g/mol of chlorine
1.50 g of sodium are equivalent to 2.31 g of chlorine

whence

$$E_{Na} = \frac{1.50 \times 35.45}{2.31} = 23.0 \text{ g/mol}$$

The molar mass of sodium atoms (numerically coinciding with the relative atomic mass of sodium) is 23.0 g/mol. Consequently, the molar and equivalent masses of sodium atoms are the same, whence the equivalent of sodium is one mole.

Many elements form several compounds with one another. It thus follows that the equivalent of an element and its equivalent mass may have different values depending on the composition of the compound they were calculated from. But in all such cases, the different equivalents (or equivalent masses) of the same element form a ratio of small integers. For example, the equivalent masses of carbon calculated on the basis of the composition of carbon dioxide and carbon monoxide are 3 and 6 g/mol, respectively. The ratio of these values is 1 : 2.

In addition to the concept of equivalent mass, it is sometimes convenient to use the concept of equivalent volume, i.e. the volume occupied in given conditions by one equivalent of the substance being considered. For example, in standard conditions, the equivalent volume of hydrogen is 11.2, and that of oxygen is 5.6 litres per mole.

The concept of equivalents and equivalent masses also extends to compound substances (compounds). *The equivalent of a compound substance is defined to be an amount of it such that reacts without any residue with one equivalent of hydrogen or in general with one equivalent of any other substance**.

The introduction of the concept "equivalent" into chemistry made it possible to formulate a law known as the **law of equivalents**:

> *Substances react with one another in amounts proportional to their equivalents.*

When solving some problems, it is more convenient to use a different formulation of the law of equivalents:

> *The masses (volumes) of substances reacting with one another are proportional to their equivalent masses (volumes).*

The branch of chemistry dealing with the quantitative composition of substances and the quantitative relations (mass, volume) between reacting substances is called **stoichiometry.** Accordingly, the calculations of the quantitative relationships between elements in compounds or between substances in chemical reactions (see Sec. 16) are called **stoichiometric calculations.** They are based on the laws of conservation of mass, of definite proportions, of multiple proportions, and also the gas laws—Gay-Lussac's law of combining volumes and the Avogadro law. The laws listed above are customarily considered to be the fundamental laws of stoichiometry.

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* The calculation of equivalents and equivalent masses of compound substances—acids, bases, salts—is treated in Sec. 16.

13. Determination of Atomic Masses. Valence

The Avogadro law allows us to find the number of atoms in a molecule of a simple gas. Investigation of the volume ratios in reactions with the participation of hydrogen, oxygen, nitrogen, and chlorine showed that the molecules of these gases are diatomic. Hence, by determining the relative molecular mass of any of these gases and dividing it by two, one could find directly the relative atomic mass of the corresponding element. It was established, for example, that the molecular mass of chlorine is 70.90. Hence, the atomic mass of chlorine is 70.90 : 2 or 35.45.

Another method of determining the atomic masses that came into greater favour was proposed in 1858 by the Italian scientist S. Cannizzaro. According to this method, the molecular mass of the greatest possible number of gaseous or highly volatile compounds of the given element is initially determined. Next the data of analysis are used to calculate the number of atomic mass units falling to the share of this element in a molecule of each of the compounds. The smallest of the numbers found is adopted as the required mass.

Let us explain this method by the following example. Table 1 gives the molecular masses of a number of carbon compounds and the carbon content in each of them in per cent (mass). The last column of the table indicates the mass of the carbon in a molecule of each compound computed from the molecular mass of the compound and the carbon content in it in per cent (mass).

Table 1

Molecular Masses of Selected Carbon Compounds and Carbon Content in Them

Compound	Molecular mass, amu	Carbon content, % (mass)	Mass of carbon in one molecule, amu
Carbon dioxide	44	27.27	12
Carbon monoxide	28	42.86	12
Acetylene	26	92.31	24
Benzene	78	92.31	72
Diethyl ether	74	64.86	48
Acetone	58	62.07	36

Inspection of the table shows that the smallest mass of carbon in a molecule of the compounds considered is 12 amu. It is thus obvious that the atomic mass of carbon cannot exceed 12 amu (for example, it cannot be 24 or 36 amu). Otherwise we would have to assume that molecules of carbon dioxide and carbon monoxide contain a fractional part of a carbon atom. We also have no grounds to consider that the atomic mass of carbon is less than 12 amu because we know of no molecules containing less than this amount of carbon. It is exactly this mass of carbon that passes from one molecule to another in chemical reactions without splitting. All the other masses of carbon are integral multiples of 12; consequently, 12 amu is the atomic mass of carbon.

Cannizzaro's method made it possible to find the atomic masses of only those elements that form a part of gaseous or highly volatile compounds. The majority of metals, however, do not form such compounds. For this reason, a different method was used at one time to find the atomic masses of metals. It is based on the relation between the atomic mass of an element and the specific heat capacity of the relevant elementary substance in the solid state.

In 1819, the French scientists P. Dulong and A. Petit, in determining the heat capacity of various metals, discovered that the product of the specific heat capacity of an elementary substance (in the solid state) and the molar mass of the atoms of the relevant element is approximately identical for most elements. The mean value of this quantity is 26 J/(mol·K). Since this product is the amount of heat needed to heat one mole of atoms of an element by one kelvin, it is called the **atomic heat capacity.** This relationship has been named the **Dulong and Petit law:**

> *The atomic heat capacity of most elementary substances in the solid state ranges from 22 to 29 J/(mol·K) [on an average about 26 J/(mol·K)].*

It follows from the Dulong and Petit law that by dividing 26 by the specific heat capacity of an elementary substance, which is easily found experimentally, we can determine the *approximate* value of the molar mass of the atoms of the relevant element and, consequently, the approximate value of the atomic mass of the element too.

The ways of finding the atomic masses considered above do not yield quite accurate results because, on the one hand, the accuracy of determining the molecular mass according to the density of the vapour rarely exceeds 1%, and, on the other, the Dulong and Petit law permits only the approximate value of the atomic mass to be determined. On the basis of the approximate values obtained in these ways, however, it is simple to find the accurate values of the atomic masses. For this purpose, we have to compare the found approximate value of the molar mass of an element's atoms with its equivalent mass. Such a comparison is useful because there is a relationship between the molar mass of an element's atoms and its equivalent mass that also includes the valence of the element. Let us consider the latter concept in somewhat greater detail.

Valence. The concept of valence was introduced in chemistry at the middle of the 19th century. The relationship between the valence of an element and its position in the periodic table was established by Mendeleev. He also introduced the concept of varying valence. The concept of valence was substantiated physically with the development of the theory of the structure of atoms and molecules.

Valence is a complicated concept. This is why there are several definitions of valence expressing the different aspects of this concept. The following definition can be considered as the most general one: *the valence of an element is the ability of its atoms to combine with other atoms in definite proportions.*

Originally the valence of a hydrogen atom was adopted as the unit of valence. The valence of another element can be expressed by the number of hydrogen atoms which one atom of this other element combines with or substitutes. The valence determined in this way is called the valence in hydrogen compounds or the hydrogen referred valence: thus, in the compounds HCl, H_2O, NH_3, and CH_4, the hydrogen referred valence of chlorine is one, of oxygen is two, of nitrogen is three, and of carbon is four.

The valence of oxygen, as a rule, is two. Therefore, knowing the composition or formula of an oxygen compound of an element, we can determine its valence as the double number of oxygen atoms which one atom of the given element can attach. The valence determined in this way is called the valence of the relevant element in oxygen compounds, or the oxygen referred valence, or the oxidation number: thus, in the compounds N_2O, CO, SiO_2, and SO_3, the oxygen referred valence of nitrogen is one, of carbon is two, of silicon is four, and of sulphur is six.

Most elements have different valences in hydrogen and in oxygen compounds: for example, the hydrogen referred valence of sulphur is two (H_2S), while its oxygen referred valence is six (SO_3). In addition, most elements display a different valence in different compounds. For instance, carbon forms two oxides with oxygen: carbon monoxide CO and carbon dioxide CO_2. The valence of carbon in the monoxide is two, and in the dioxide four. The above examples show that, as a rule, the valence of an element cannot be characterized by a single number.

In addition to the hydrogen referred and oxygen referred valence, the ability of atoms of a given element to combine with one another or with atoms of other elements can be expressed in other ways, for example, by the number of chemical bonds formed by an atom of the given element (covalence, see Sec. 39), or by the number of atoms directly surrounding a given atom (the coordination number, see p. 170 and Vol. 2, Sec. 89). We shall acquaint our reader with these and related concepts after studying the theory of the structure of the atom.

There is a simple relationship between the valence of an element in a given compound, the molar mass of its atoms, and its equivalent mass that directly follows from the atomic theory and the definition of the concept "equivalent mass". Assume, for example, that the hydrogen referred valence of an element is unity. This signifies that one mole of atoms of the given element can combine with or replace one mole of hydrogen atoms, i.e. one hydrogen equivalent. Consequently, the equivalent mass of this element equals the molar mass of its atoms. But if the valence of an element is two, the molar mass of its atoms and its equivalent mass will no longer be the same: the equivalent mass will be one-half of the molar mass. For example, the equivalent mass of oxygen (8 g/mol) is one-half of the molar mass of its atoms (16 g/mol) because one mole of oxygen atoms combines with two moles of hydrogen atoms, i.e. with two hydrogen equivalents; hence, $16/2 = 8$ g of oxygen fall to the share of 1.0079 g of hydrogen. The equivalent mass of aluminium, whose valence is three, is one-third of the molar mass of its atoms, etc.

Thus, *the equivalent mass of an element equals the molar mass of its atoms divided by the valence of the element in the given compound.* This relation can be written as follows:

$$\text{Equivalent mass} = \frac{\text{Molar mass of atoms}}{\text{Valence}}$$

or

$$\text{Valence} = \frac{\text{Molar mass of atoms}}{\text{Equivalent mass}}$$

The valence determined by the latter relationship is called the **stoichiometric valence** of the relevant element. By using this relationship, we can easily establish the exact value of the atomic mass of an element if we know its approximate value and the exact value of the equivalent mass. For this purpose, we first find the stoichiometric valence of the element by dividing the approximate value of the molar mass of the element's atoms by the equivalent mass. Since the stoichiometric valence is always expressed by an integral number, then the quotient obtained is rounded off to the nearest integer. By next multiplying the equivalent mass by the valence, we get the exact value of the molar mass of the element's atoms numerically coinciding with the atomic mass of the element.

Example. The equivalent mass of indium is 38.273 g/mol; the specific heat capacity of this metal is 0.222 J/(g·K). Find the atomic mass of indium.

Using the Dulong and Petit law, we first approximately find the molar mass of indium atoms:

$$26 : 0.222 = 117 \text{ g/mol}$$

Next, we find the valence of indium by dividing this approximate value by the equivalent mass:

$$117 : 38.273 \approx 3$$

We obtain the molar mass of indium atoms by multiplying the equivalent mass by the valence:

$$38.273 \times 3 = 114.82 \text{ g/mol}$$

Consequently, the atomic mass of indium is 114.82 amu.

14. Chemical Symbols

The symbols of the chemical elements in use today were introduced into science in 1813 by J. Berzelius. He proposed to designate the elements by the initial letters of their Latin names. For example, oxygen (*Oxygenium*) is designated by the letter O, sulphur (*Sulfur*) by the letter S, and hydrogen (*Hydrogenium*) by H. When the names of several elements begin with the same letter, one of the following letters is added to the first one for all of such elements except one. For instance, the symbol of carbon (*Carboneum*) is C, of calcium (*Calcium*) is Ca, of copper (*Cuprum*) is Cu.

Chemical symbols are not only abbreviated names of the elements. They also stand for definite amounts (or masses) of them, i.e. each symbol signifies either one atom of the relevant element, or one mole of its atoms, or a mass of the element equal (or proportional) to the molar mass of this element. For instance, C stands either for one atom of carbon, or one mole of carbon atoms, or 12 units of mass (usually 12 g) of carbon.

The formulas of substances also indicate not only the composition of the relevant substances, but also their amount and mass. Each formula signifies either one molecule of the substance, or one mole of the substance, or the mass of the substance equal (or proportional) to its molar mass. For example, H_2O means either one molecule of water, or one mole of water, or 18 units of mass (usually 18 g) of water.

Elementary substances are also designated by formulas showing the number of atoms which a molecule of the relevant elementary substance consists of. For example, hydrogen has the formula H_2. If the atomic composition of a molecule of an elementary substance is not known exactly or if the substance consists of molecules containing a different number of atoms, and also if the substance has an atomic or metallic structure instead of a molecular one, the elementary substance is designated by the symbol of the element. For example, the elementary substance phosphorus is designated by the formula P because, depending on the conditions, phosphorus may consist of molecules containing different numbers of atoms, or have a polymeric structure.

The formula of a substance is established from the results of its analysis. For example, according to the results of analysis data, glucose contains 40.00% (mass) of carbon, 6.72% (mass) of hydrogen, and 53.28% (mass) of oxygen. Consequently, the ratio of the masses of carbon, hydrogen, and oxygen is 40.00 : 6.72 : 53.28. Let the required formula of glucose be $C_xH_yO_z$, where x, y, and z are the numbers of atoms of carbon, hydrogen, and oxygen in a molecule. The atomic masses of these elements are 12.01, 1.01, and 16.00 amu, respectively. Therefore, a molecule of glucose contains $12.01x$ amu of carbon, $1.01y$ amu of hydrogen, and $16.00z$ amu of oxygen. The ratio of these masses is $12.01x : 1.01y : 16.00z$. But we have already found this ratio proceeding from the results of analysis of glucose. Hence,

$$12.01x : 1.01y : 16.00z = 40.00 : 6.72 : 53.28$$

According to the properties of a proportion,

$$x : y : z : = \frac{40.00}{12.01} : \frac{6.72}{1.01} : \frac{53.28}{16.00}$$

or $x : y : z = 3.33 : 6.65 : 3.33 = 1 : 2 : 1$.

Consequently a glucose molecule contains two hydrogen atoms and one oxygen atom per carbon atom. This condition is satisfied by the formulas CH_2O, $C_2H_4O_2$, $C_3H_6O_3$, etc. The first of these formulas—CH_2O—is known as the **simplest** or **empirical formula.** A molecular mass of 30.02 amu corresponds to it. To find out the **true** or **molecular formula,** we must know the molecular mass of the given substance. Glucose when heated decomposes without transforming into a gas. But its molecular mass can be determined in the ways described in Chap. 7; it is 180 amu. By comparing this molecular mass with that corresponding to the simplest formula, it is evident that the formula of glucose is $C_6H_{12}O_6$.

Having acquainted ourselves with how chemical formulas are derived, we can readily understand how the exact values of molecular masses are established. We have already mentioned that the existing ways of determining molecular masses do not give quite accurate results in the majority of cases. But if we know at least the approximate molecular mass and fractional composition of a substance, we can establish its formula expressing the atomic composition of a molecule. Since the mass of a molecule equals the sum of the masses of the atoms forming it, by summating the masses of the atoms in a molecule, we shall find its mass in amu, i.e. the molecular mass of the substance. The accuracy of the molecular mass found will correspond to the accuracy with which the substance was analysed.

15. Most Important Classes of Inorganic Substances

All substances are divided into elementary ones and compounds. Elementary substances consist of one element, while compounds consist of two or more elements. Elementary substances, in turn, are divided into metals and non-metals, previously called metalloids*. The latter classification is based on the difference in the physical properties of the relevant elementary substances.

Metals are distinguished by their characteristic "metallic" lustre, ductility, malleability, can be rolled into sheets or drawn into a wire, and are good conductors of heat and electricity. At room temperature, all metals (except for mercury) are in the solid state.

Non-metals do not have the lustre characteristic of metals, are brittle, and are very poor conductors of heat and electricity. Some of them are gaseous in conventional conditions.

Compounds are divided into organic and inorganic ones. The name organic is usually applied to the compounds of carbon**; all the remaining compounds are called inorganic (sometimes mineral).

Of the inorganic compounds, chemistry most often has to do with oxides, bases, acids, and salts. These basic classes of inorganic compounds are studied in detail in secondary school. We shall therefore give only the most important information about them in this book.

Oxides are compounds of elements with oxygen. With respect to their chemical properties, they are divided into salt-forming and non-salt-forming or indifferent. Salt-forming oxides, in turn, are divided into basic, acidic, and amphoteric ones. Bases correspond to basic oxides, and acids to acidic ones. Hydrates displaying both acidic and basic properties correspond to amphoteric oxides. Amphoteric phenomena are considered in Sec. 87. Indifferent oxides form neither acids nor bases.

Examples of basic oxides are calcium oxide CaO and magnesium oxide MgO. Calcium oxide reacts with water to form calcium hydroxide $Ca(OH)_2$:

$$CaO + H_2O = Ca(OH)_2$$

Magnesium oxide dissolves in water very slightly. A base corresponds to it, however—magnesium hydroxide $Mg(OH)_2$, which can be obtained from magnesium oxide indirectly.

Examples of acidic oxides are sulphur trioxide SO_3 and silicon dioxide SiO_2. The former of them reacts with water to form sulphuric acid H_2SO_4:

$$SO_3 + H_2O = H_2SO_4$$

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* The name "metalloids" was introduced into chemistry by Berzelius (1808) to denote elementary substances of a non-metallic nature. At present this term is customarily used to denote a few intermediate non-metallic elements such as arsenic that have some of the chemical properties of a metal.

** The simplest carbon compounds (CO, CO_2, H_2CO_3 and carbonates, HCN and cyanides, carbides, and some others) are usually treated in the course of inorganic chemistry.

Silicon dioxide does not react with water, but silicic acid H_2SiO_3 corresponds to it. The acid can be obtained from SiO_2 indirectly.

Acidic oxides can be obtained from acids by removing water from the latter. These oxides are therefore also called **acid anhydrides** or simply **anhydrides.**

Indifferent oxides include, for example, nitrogen monoxide NO. There is neither an acid nor a base corresponding to this oxide.

Two nomenclatures of oxides are in use at present: the newer **Stock** or **Roman numeral system** recommended by the International Union of Pure and Applied Chemistry (IUPAC), and the **classical system.** According to the Roman numeral system, all oxygen compounds of elements (except peroxides—see below) are called **oxides.** When an element can exhibit more than one oxidation number (or valence), Roman numerals are used to indicate the oxidation number in the particular oxide. Thus, CaO is called calcium oxide, while Cu_2O and CuO are called copper(I) oxide and copper(II) oxide. Oxides of the composition EO_2 or EO_3 are also called dioxides and trioxides, respectively.

According to the classical system*, if an element forms only one oxide, the latter is called simply an oxide. Thus, CaO is called calcium oxide. If a given element forms two or more oxides, Greek prefixes are used to indicate the number of atoms of the first element and of oxygen in the oxide, namely:

Number	1	2	3	4	5	6	7	8	...
Prefix	mono	di	tri	tetra	penta	hexa	hepta	octa	...

The *mono-* prefix is not used for the first element. Examples are SO_2—sulphur dioxide, Cu_2O—dicopper oxide, CuO—copper monoxide, Fe_2O_3—diiron trioxide, and Fe_3O_4—triiron tetroxide.

In a third system that is virtually obsolete at present, but is still encountered in some of the older chemistry books, an *-ic* ending is used on the name of the metal (or element) for the highest oxidation state and an *-ous* ending for the lowest. Also, the Latin name is used for iron (ferric and ferrous), copper (cupric and cuprous), tin (stannic and stannous), and lead (plumbic and plumbous). For example, in this system, CuO is called cupric oxide, and Cu_2O is called cuprous oxide.

There are substances—compounds of elements with oxygen—that only formally belong to the class of oxides. These substances include, particularly, metal peroxides, for example barium peroxide BaO_2. Such substances in their nature are salts of a very weak acid—hydrogen peroxide (see Vol. 2, Sec. 3). Salt-like compounds also include substances such as Pb_2O_3 and Pb_3O_4 (see Vol. 2, Sec. 74, last paragraph).

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* This system is preferred not only for oxides, but in general when naming binary covalent compounds formed between two non-metals.

Bases consist of a metal and monovalent hydroxyl groups* OH whose number equals the valence of the metal. Examples of bases are sodium hydroxide NaOH and copper(II) hydroxide $Cu(OH)_2$.

The most important chemical property of bases is their ability to form salts with acids. For example, when the compounds listed above react with hydrochloric acid, we get chloride salts of the corresponding metals—sodium or copper(II) chlorides:

$$NaOH + HCl = NaCl + H_2O$$

$$Cu(OH)_2 + 2HCl = CuCl_2 + 2H_2O$$

Bases are classified according to their solubility in water and according to their strength. With respect to solubility, bases are divided into soluble ones, or **alkalies**, and insoluble ones. The most important alkalies are sodium hydroxide NaOH, potassium hydroxide KOH, and calcium hydroxide $Ca(OH)_2$. With respect to their strength, bases are divided into strong and weak ones (Sec. 84). Strong bases include all the alkalies except for ammonium hydroxide. According to the IUPAC nomenclature, compounds containing the hydroxide group —OH are called **hydroxides**. For metals with a varying valence, the valence of the metal in the particular compound is indicated in parentheses. Thus, $Ca(OH)_2$ is calcium hydroxide, $Fe(OH)_2$ is iron(II) hydroxide, and $Fe(OH)_3$ is iron(III) hydroxide.

The latter two compounds were previously known as ferrous hydroxide and ferric hydroxide, respectively.

Acids consist of hydrogen capable of being substituted by a metal, and an acid residue. The number of hydrogen atoms equals the valence of the acid residue. Examples of acids are hydrochloric HCl, sulphuric H_2SO_4, nitric HNO_3, and acetic CH_3COOH acids.

The most important property of acids is their ability to form salts when reacting with bases. For instance, when acids react with sodium hydroxide, the sodium salts of these acids are produced:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

$$NaOH + HNO_3 = NaNO_3 + H_2O$$

Acids are classified according to their strength, their basicity, and the presence of oxygen in the acid. With respect to strength, acids are divided into strong and weak ones (Sec. 84). The most important strong acids are nitric, sulphuric, and hydrochloric acids.

The **basicity** of an acid is defined to be the number of hydrogen atoms in a molecule of the acid capable of being displaced by a

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* The concept of valence is applied not only to elements, but also to groups of atoms in chemical compounds that participate like a single whole in chemical reactions. The most important of such groups in inorganic chemistry are the hydroxyl group OH, acid residues, and the ammonium group NH_4.

metal with the formation of a salt. Hydrochloric and acetic acids are examples of monobasic acids, sulphuric acid is a dibasic one, orthophosphoric acid H_3PO_4 is a tribasic one.

With respect to the presence of oxygen in them, acids are divided into **oxyacids** (containing oxygen), and **hydracids** (containing no oxygen). Nitric and sulphuric acids are oxyacids, hydrochloric acid HCl and hydrosulphuric acid H_2S are hydracids.

The names of acids come from the element (or group) forming the acid. According to the recommendations of the IUPAC, hydracids are named as binary and pseudobinary compounds of hydrogen, for instance, hydrogen chloride, hydrogen sulphide, and hydrogen cyanide. According to the classical system still found in many books, the root of the name of the element forming the acid is sandwiched between the prefix *hydro-* (or *hydr-*) and the suffix *-ic* followed by the word acid. For instance, HCl is named *hydro*chlor*ic* acid, H_2S is *hydro*sulphur*ic* acid, HCN is *hydro*cyan*ic* acid. The names of oxyacids are also formed from the name of the relevant element. The latter, however, may exist in different oxidation states (have different valences), and there may be an acid corresponding to each state. Various prefixes and suffixes are used to denote these conditions, namely, the prefixes *hypo-* and *per-*, and the suffixes *-ous* and *-ic*. When an element has only a single oxidation state, the suffix *-ic* is used, for instance bor*ic* acid H_3BO_3. When there are two oxidation states, the suffix *-ic* denotes the higher one and the suffix *-ous* the lower one. Examples are sulphur*ic* acid H_2SO_4 and sulfur*ous* acid H_2SO_3. When there are three oxidation states, the sequence is the prefix *hypo-* and the suffix *-ous* for the lowest state, and the suffixes *-ous* and *-ic* for the higher two. Examples are *hypo*phosphor*ous* acid H_3PO_2, phosphor*ous* acid H_3PO_3, and phosphor*ic* acid H_3PO_4. Examples of the names of oxyacids for an element with four oxidation states are *hypo*chlor*ous* acid HClO, chlor*ous* acid $HClO_2$, chlor*ic* acid $HClO_3$, and *per*chlor*ic* acid $HClO_4$. In addition, several acids differing in the number of molecules of water may correspond to the same oxide (i.e. to the same oxidation state). In this case, the prefixes *ortho-*, *pyro-*, and *meta-* are used in the order of decreasing hydration. Examples are *ortho*phosphoric acid H_3PO_4, containing three molecules of water per molecule of diphosphorus pentoxide P_2O_5, *pyro*phosphoric acid $H_4P_2O_7$, containing two molecules of water per molecule of P_2O_5, and *meta*phosphoric acid, containing one molecule of water per molecule of P_2O_5. The prefix *ortho-* is sometimes omitted. For instance, H_3PO_4 is sometimes called phosphoric acid instead of orthophosphoric acid. According to the latest IUPAC recommendations, pyro-acids are generally regarded as the simplest cases of isopolyacids. The trivial name pyrophosphoric acid may be retained for $H_4P_2O_7$, although diphosphoric acid is preferable.

The above nomenclature of acids is not strict. Apart from the indicated prefixes and suffixes, others are also used. In addition, a number of acids have historically established names.

The products of the displacement of hydrogen in an acid by a metal or the OH group in a base by an acid residue are **salts.** Upon complete substitution, **neutral (normal)** salts are obtained, and upon incomplete substitution either acid or basic salts. An **acid salt** is obtained when the hydrogen of an acid is only partly displaced by a metal. A **basic salt** is obtained when the OH groups of a base are only partly displaced by an acid residue. It is quite obvious that an acid salt can only be formed by an acid whose basicity is two or higher, and a basic salt by a metal whose valence is two or higher.

Examples of salt formation:

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O$$

$CaSO_4$ is a normal salt—calcium sulphate;

$$KOH + H_2SO_4 = KHSO_4 + H_2O$$

$KHSO_4$ is an acid salt—potassium hydrogen sulphate (also called potassium bisulphate or potassium acid sulphate);

$$Mg(OH)_2 + HCl = MgOHCl + H_2O$$

MgOHCl is a basic salt—magnesium chloride hydroxide (also called magnesium hydroxychloride).

Salts formed by two metals and one acid are called **double salts,** and those formed by one metal and two acids—**mixed salts.** An example of a double salt is aluminium-potassium alum, or potassium-aluminium sulphate $KAl(SO_4)_2$. An example of a mixed salt is CaClOCl (or $CaOCl_2$)—the calcium salt of hydrochloric (HCl) and hypochlorous (HOCl) acids.

The same salt may have different names. For example, KNO_3 is known as saltpetre or potassium nitrate. At present, most chemists prefer the international (Latin) nomenclature for salts. In this nomenclature, the name of a salt reflects the name of the metal and the root of the Latin name of the acid residue. The Latin name of the acid and acid residue usually originates from the Latin name of the element forming the acid. The name of a salt of a hydracid has the suffix *-ide*, and of an oxyacid—the suffixes *-ate* for the higher valence of the acid-forming element and *-ite* for the lower valence. When the prefixes *hypo-* and *per-* are used for acids, they are retained in the names of the relevant salts. Thus, salts of hydrochloric acid are called chlor*ides*, of hydrosulphuric acid—sulph*ides*, of sulphuric acid—sulph*ates*, of sulphurous acid—sulph*ites*, of perchloric acids—*per*chlor*ates*, and of hypochlorous acid—*hypo*chlor*ites*.

For salts formed by metals with a varying valence, the valence of the metal is indicated in parentheses as in oxides or bases: thus, $FeSO_4$ is iron(II) sulphate, $Fe_2(SO_4)_3$ is iron(III) sulphate. The name of an acid salt includes the word *hydrogen* indicating the presence of unsubstituted hydrogen atoms. When the number of unsubstituted hydrogen atoms is two or more, it is denoted by using the Greek prefixes *di-*, *tri-*, etc. For instance, Na_2HPO_4 is called sodium hydrogen phosphate, while NaH_2PO_4 is sodium dihydrogen phosphate. Similarly, a basic salt is characterized by the inclusion of the word *hydroxide* in its name, which indicates the presence of unsubstituted OH groups. For example, $AlOHCl_2$ is called aluminium chloride hydroxide, $Al(OH)_2Cl$ is aluminium chloride dihydroxide. Below are given the names of salts of some of the most important acids:

Acid		Name of relevant normal salt
Name	Formula	
Aluminic	H_3AlO_3	Aluminates
Arsenic	H_3AsO_4	Arsenates
Arsenous	H_3AsO_3	Arsenites
Boric (orthoboric)	H_3BO_3	Borates (orthoborates)
Carbonic	H_2CO_3	Carbonates
Chloric	$HClO_3$	Chlorates
Chromic	H_2CrO_4	Chromates
Diphosphoric (pyrophosphoric)	$H_4P_2O_7$	Diphosphates (pyrophosphates)
Hydrobromic	HBr	Bromides
Hydrochloric	HCl	Chlorides
Hydrocyanic	HCN	Cyanides
Hydrofluoric	HF	Fluorides
Hydroiodic	HI	Iodides
Hypochlorous	HOCl	Hypochlorites
Metaphosphoric	HPO_3	Metaphosphates
Nitric	HNO_3	Nitrates
Nitrous	HNO_2	Nitrites
Perchloric	$HClO_4$	Perchlorates
Permanganic	$HMnO_4$	Permanganates
Phosphoric (orthophosphoric)	H_3PO_4	Phosphates (orthophosphates)
Phosphorous (phosphonic)	H_3PO_3	Phosphites
Silicic	H_2SiO_3	Silicates
Sulphuric	H_2SO_4	Sulphates
Sulphurous	H_2SO_3	Sulphites

16. Chemical Calculations

An exceedingly important corollary of the atomic and molecular concept is the possibility of conducting chemical calculations. The latter are based on the fact that the composition of individual substances can be expressed by chemical formulas, while the reaction between substances occurs according to chemical equations.

Calculations According to Formulas. A chemical formula can give us a lot of information about the relevant substance. First, it shows the elements which the given substance consists of and the number of atoms of each element a molecule contains. Second, it permits us to compute a number of quantities characterizing the substance in question. Indicated below are the most important of these calculations.

The **molecular mass of a substance** is calculated from its formula as the sum of the atomic masses of the atoms in a molecule of the substance.

The **equivalent mass of a substance** is calculated from its molar mass. The equivalent mass of an acid equals its molar mass divided by the basicity of the acid. The equivalent mass of a base equals its molar mass divided by the valence of the base-forming metal. The equivalent mass of a salt equals its molar mass divided by the product of the valence of the metal and the number of its atoms in a molecule.

Examples

HNO_3. Molar mass—63 g/mol. Equivalent mass = 63 : 1 = 63 g/mol.

H_2SO_4. Molar mass—98 g/mol. Equivalent mass = 98 : 2 = 49 g/mol.

$Ca(OH)_2$. Molar mass—74 g/mol. Equivalent mass = 74 : 2 = 37 g/mol.

$Al_2(SO_4)_3$. Molar mass—342 g/mol. Equivalent mass = 342 : (2 × 3) = = 57 g/mol.

Like the equivalent mass of an element, the equivalent mass of a compound may have several values if it is capable of entering into different types of reactions. For instance, the acid salt $NaHSO_4$ can react with sodium hydroxide or barium hydroxide:

$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O$$

$$NaHSO_4 + Ba(OH)_2 = BaSO_4\downarrow + NaOH + H_2O$$

The same amount of the salt reacts in the first case with one mole of a base formed by a monovalent metal (i.e. with one equivalent of the base), and in the second case with one mole of a base formed by a divalent metal (i.e. with two equivalents of the base). Therefore, in the first case, the equivalent mass of the $NaHSO_4$ equals the molar mass of the salt (120 g), and in the second, the molar mass divided by two (60 g).

Percentage Composition of a Compound. The composition of a compound is usually expressed in per cent by mass. Let us compute, for example, the magnesium content in magnesium carbonate $MgCO_3$. To do this, we shall calculate the molecular mass of this compound. It is $24.3 + 12 + 3 \times 16 = 84.3$ amu. Adopting this value as 100%, we find the content of magnesium: $x = 24.3 \times 100/84.3 = 28.8\%$ (mass).

Mass of One Litre of Gas at 0 °C and Standard Atmospheric Pressure (101.325 kPa or 760 mmHg). One mole of any gas in standard conditions occupies a volume of 22.4 litres. Hence, the mass of one litre of a gas in the same conditions equals the molar mass of this gas divided by 22.4.

Volume Occupied by a Given Mass of a Gas. If a gas is at 0 °C and standard atmospheric pressure, we can perform the calculations proceeding from the molar volume of the gas (22.4 l/mol). If the gas is at a different pressure and temperature, then its volume is calculated by the Clapeyron-Mendeleev equation

$$PV = \frac{m}{M} RT$$

(for the notation see Sec. 10). It is not difficult to perform the reverse calculations by this equation—calculate the mass of a given volume of a gas.

Calculations According to Equations. The atomic and molecular concept teaches that a chemical reaction consists in transformation of particles of the **reactants** into particles of the **products.** Knowing the composition of the reactant and product particles, we can express any reaction by a **chemical equation.** After writing the equation of a reaction, we must make the number of atoms in its left-hand side equal that in the right-hand one. The formulas of the substances are not changed. Equation is achieved only by properly choosing the coefficients before the formulas of the reactants and products.

Sometimes the complete equation of a reaction is replaced with its scheme indicating only what substances enter into the reaction and what products are obtained. In such cases, the equality sign is usually replaced with an arrow. For example, the reaction of combustion of hydrogen sulphide is shown schematically as follows:

$$H_2S + O_2 \rightarrow H_2O + SO_2$$

Chemical equations are used for performing various calculations associated with reactions. We remind our reader that every formula in an equation of a chemical reaction signifies one mole of the relevant substance. Consequently, knowing the molar masses of the reaction participants and the coefficients in the equation, we can find the quantitative relationships between the substances entering into a reaction and formed as its result. For instance, the equation

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

shows that two moles of sodium hydroxide react with one mole of sulphuric acid to form one mole of sodium sulphate and two moles of water. The molar masses of the reaction participants are $M(NaOH) = 40$ g/mol; $M(H_2SO_4) = 98$ g/mol; $M(Na_2SO_4) = 142$ g/mol, and $M(H_2O) = 18$ g/mol. We can therefore read the equation of the reaction being considered as follows: 80 g of sodium hydroxide react with 98 g of sulphuric acid to form 142 g of sodium sulphate and 36 g of water*.

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* The masses of the reactants can naturally be expressed not only in grams, but also in other units such as kilograms and tonnes; this, however, will lead to no quantitative changes in the proportion of the individual substances.

If gaseous substances participate in a reaction, its equation also indicates the relationships between the volumes of the gases.

Example. How many litres of oxygen taken in standard conditions are used for the combustion of one gram of ethyl alcohol C_2H_5OH?

The molecular mass of ethyl alcohol is $12 \times 2 + 1 \times 5 + 16 + 1 = 46$ amu. Hence, the molar mass of the alcohol is 46 g/mol. According to the equation of the reaction of alcohol combustion

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$$

three moles of oxygen are used in the combustion of one mole of the alcohol. In other words, $22.4 \times 3 = 67.2$ litres of oxygen are used in the combustion of 46 g of the alcohol. Consequently, for the combustion of one gram of ethyl alcohol, we need $67.2 \times 1/46 = 1.46$ litres of oxygen taken in standard conditions.

2

MENDELEEV'S PERIODIC LAW

The discovery of the periodic law was the most important event in chemistry after the atomic and molecular concept took shape. Made in 1869 by the outstanding Russian scientist Dmitri Mendeleev, this discovery was the cornerstone of a new epoch in chemistry and determined the ways of its development for many decades in advance. On the basis of the periodic law, Mendeleev classified the chemical elements in the form of a periodic table. This played a very important role in studying the properties of the chemical elements and in the further development of the concept of the structure of matter.

Attempts to systematize the chemical elements were also undertaken before Mendeleev presented his periodic law. But their only aim was to classify the elements, and they did not go further than combination of the individual elements into groups on the basis of the similarity of their chemical properties. Each element was considered as something solitary, having no relation to the other elements.

17. Mendeleev's Periodic Law

Mendeleev, unlike his predecessors, was firmly convinced that a regular relationship must exist between all the chemical elements combining them into a single whole, and arrived at the conclusion that systematization of the elements must be based on their relative atomic mass.

Indeed, upon arranging all the elements in the order of increasing atomic masses, Mendeleev discovered that elements similar to one another in a chemical respect occur at regular intervals and that many properties of the elements arranged in this order periodically repeat.

This remarkable relationship was formulated by Mendeleev in the following **periodic law**:

> *The properties of simple bodies, as well as the forms and properties of the compounds of the elements, are periodic functions of the atomic weights of the elements.**

To illustrate this law, let us write out the first 20 elements in the order of their increasing atomic mass.

Under the symbol of each element, we shall write its rounded-off atomic mass and the formula of its oxide corresponding to the maximum oxygen referred valence:

H	**He**	**Li**	**Be**	**B**	**C**	**N**
Hydrogen	Helium	Lithium	Beryllium	Boron	Carbon	Nitrogen
1	4	6.9	9	10.8	12	14
H_2O	-	Li_2O	BeO	B_2O_3	CO_2	N_2O_5
O	**F**	**Ne**	**Na**	**Mg**	**Al**	**Si**
Oxygen	Fluorine	Neon	Sodium	Magnesium	Aluminium	Silicon
16	19	20.2	23	24.3	27	28.1
—	F_2O	-	Na_2O	MgO	Al_2O_3	SiO_2
P	**S**	**Cl**	**Ar**	**K**	**Ca**	
Phosphorus	Sulphur	Chlorine	Argon	Potassium	Calcium	
31	32.1	35.5	39.9	39.1	40.1	
P_2O_5	SO_3	Cl_2O_7	-	K_2O	CaO	

An exception has been made in this series only for potassium, which ought to stand before argon. We shall see on a later page that this exception is completely justified by the modern theory of structure of the atom.

Without stopping to consider hydrogen and helium, let us investigate the sequence in which the properties of the other elements change.

Lithium is a monovalent metal that decomposes water very vigorously to form an alkali. Next comes beryllium, also a metal, but a divalent one, that decomposes water slowly at ordinary temperatures. Beryllium is followed by boron, a trivalent element with slightly expressed non-metallic properties, but which displays some properties of a metal. After this comes carbon—a tetravalent non-metal. Then come nitrogen—an element with quite sharply expressed properties of a non-metal, oxygen—a typical non-metal, and, finally, the seventh element fluorine, the most active of the non-metals belonging to the group of halogens.

Thus, the metallic properties, vividly pronounced in lithium, gradually weaken as we pass from one element to another, giving way to non-metallic properties, which are the most pronounced in fluorine. An increase in the atomic mass is also attended by an increase in the oxidation number beginning with lithium. It grows by unity for each consecutive element (the only exception from this regularity is fluorine whose oxidation number is unity; this is asso-

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* We remind our reader that the term "atomic weight" was used before the term "relative atomic mass" was introduced.

ciated with the features of the structure of the fluorine atom that will be treated in following chapters).

If the changes in the properties were to continue in the same direction, fluorine would be followed by an element with still more vividly expressed non-metallic properties. Actually, however, the element following fluorine—neon, is a noble gas that does not combine with other elements and displays neither metallic nor non-metallic properties.

Neon is followed by sodium—a monovalent metal similar to lithium. It returns us, as it were, to the series already considered. Indeed, after sodium comes magnesium—an analogue of beryllium; next is aluminium, which, although a metal and not a non-metal like boron, is also trivalent and displays certain properties of non-metals. The series is continued by silicon—a tetravalent non-metal similar in many respects to carbon, pentavalent phosphorus similar to nitrogen in its chemical properties, sulphur—an element with sharply expressed non-metallic properties, chlorine—a very vigorous non-metal belonging, like fluorine, to the group of halogens, and, finally, by argon, another noble gas.

If we study the change in the properties of the remaining elements, we shall find that in general it occurs in the same order as in the first sixteen (omitting hydrogen and helium) elements: argon is again followed by the monovalent alkaline metal potassium, next is the divalent metal calcium similar to magnesium, etc.

Thus, *the change in the properties of the chemical elements with increasing atomic mass does not occur continuously in the same direction, but is periodic.* After a definite number of elements, we return, as it were, to the initial properties, after which, to a certain degree, the properties of the preceding elements repeat themselves in the same sequence, but with certain qualitative and quantitative distinctions.

18. The Periodic Table of Elements

Series of elements within which the properties change consecutively like, for example, the series of eight elements from lithium to neon or from sodium to argon were called **periods** by Mendeleev. If we write these two periods one under the other with sodium under lithium and argon under neon, we get the following arrangement of elements:

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

Such an arrangement brings into the same vertical columns elements having similar properties and the same valence, for example lithium and sodium, beryllium and magnesium.

Mendeleev divided all the elements into periods and arranged one period under the other with elements similar in properties and the compounds they form in the same vertical column. He called the resulting table the **periodic system of elements by groups and series.** The table in use today, supplemented with the elements discovered after Mendeleev's time, is given at the beginning of the book. It consists of ten horizontal rows and eight vertical columns, or **groups** in which similar elements are arranged one under another.

Let us first give our attention to the arrangement of the elements in the horizontal rows. The first row contains only two elements—hydrogen and helium. These two elements form the first period. The second and third rows consist of elements we have already considered and form two periods of eight elements each. They both begin with an alkali metal and terminate in a noble gas. All three periods are known as **short periods.**

The fourth row also begins with an alkali metal—potassium. With a view to how the properties in the two preceding rows change, we could expect them to change here in the same sequence, with the seventh element in the row being a halogen again, and the eighth one a noble gas. Matters are different, however. Instead of a halogen, we find manganese in this position—a metal forming both basic and acidic oxides of which only the higher one Mn_2O_7 is similar to the corresponding chlorine oxide (Cl_2O_7). Manganese in this row is followed by three more metals—iron, cobalt, and nickel, which are very similar to one another. And only the next, fifth row, which begins with copper, terminates in the noble gas krypton. The sixth row again begins with the alkali metal rubidium, and so on. The properties of the elements after argon repeat more or less completely only after eighteen elements, and not after eight as in the second and third rows. These eighteen elements form the fourth, **long period** consisting of two rows.

The fifth long period includes the next two rows—the sixth and seventh ones. This period begins with the alkali metal rubidium and terminates in the noble gas xenon.

In the eighth row, lanthanum is followed by fourteen elements called the **rare-earth metals** or **lanthanides**, which are extremely similar to lanthanum and to one another. Owing to this similarity, resulting from the specific nature of the structure of their atoms (see Sec. 32), the lanthanides are commonly placed outside the general table, indicating only in the box for lanthanum their position in the table.

Since the noble gas radon following xenon is only at the end of the ninth row, then the eighth and ninth rows also form one long period—the sixth one containing thirty two elements.

Not all the properties of the elements change as consistently in the long periods as they do in the second and third ones. Here a certain periodicity in the change in the properties is also observed within the periods themselves. For instance, the maximum oxidation state first uniformly grows when passing from one element to another, but then, after reaching its highest value at the middle of the period, it drops to two, after which it again grows to seven at the end of the period. In this connection, the long periods are each divided into two parts (two rows).

The tenth row forming the seventh—meanwhile incomplete—period contains nineteen elements, of which the first and last thirteen ones have been obtained only comparatively recently by artificial means. The fourteen elements following actinium are similar to the latter in the structure of their atoms. They are therefore placed, under the name of **actinides** (or **heavy rare-earth elements**) outside the general table, like the lanthanides.

The vertical columns of the table, or its groups, accommodate elements having similar properties. Therefore each vertical group is, as it were, a natural family of elements. The table contains altogether eight such groups. Their numbers are indicated at the top of the table by Roman numerals.

Elements belonging to the first group form oxides with the general formula R_2O, second-group elements form the oxides RO, third-group ones—the oxides R_2O_3, and so on. Thus, the highest oxidation number of the elements of each group corresponds, with a few exceptions, to the number of the group.

When comparing the elements belonging to the same group, it is not difficult to see that beginning with the fifth row (the fourth period), each element exhibits the greatest resemblance not to the element directly below or above it, but to an element separated from it by one box. For example, in the seventh group, bromine does not directly adjoin chlorine and iodine, but is separated from chlorine by manganese, and from iodine by technetium; the similar elements selenium and tellurium in the sixth group are separated by molybdenum that greatly differs from them; rubidium in the first group has a great resemblance to cesium in the eighth row, but has only a slight resemblance to silver directly below it, and so on.

The explanation is that the fourth row marks the beginning of the long periods each consisting of two rows arranged one above the other*. Since within a period the metallic properties weaken in the direction from left to right, it is obvious that in each long period they manifest themselves more strongly in the elements of the upper (even) row than in those of the lower (odd) row. To indicate the difference between the rows, the elements of the first rows of the long periods are written in the left of their boxes in the table, and the elements of the second rows in the right.

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* Some authors prefer the long period form of the periodic table, in which the elements of each of the fourth and following periods are written in a single row, thus forming 18 vertical columns. This version is less compact, however, than the one]we are describing in the present chapter.

Thus, beginning with the fourth period, each group in the periodic table can be divided into two subgroups: an "even" one including the elements of the upper rows, and an "odd" one formed by the elements of the lower rows. As regards the elements of the short periods, which Mendeleev called **representative,** in the first and second groups they are closer in their properties to the elements of the even rows and are written in the left of their boxes, and in the other groups they are closer to the elements of the odd rows and are written in the right of their boxes. Therefore, the representative elements are generally combined with the elements of the even or odd rows resembling them into a **main** subgroup, or **subgroup A,** while the other subgroup is called a **secondary** one, or **subgroup B.**

In constructing the periodic table, Mendeleev was guided by the principle of arranging the elements according to their increasing atomic masses. Inspection of the table shows, however, that this principle was violated in three cases. Thus, argon (its atomic mass is 39.948 amu) is before potassium (39.098 amu), cobalt (58.9332 amu) is before nickel (58.70 amu), and tellurium (127.60 amu) is before iodine (126.9045 amu). Here Mendeleev divert-

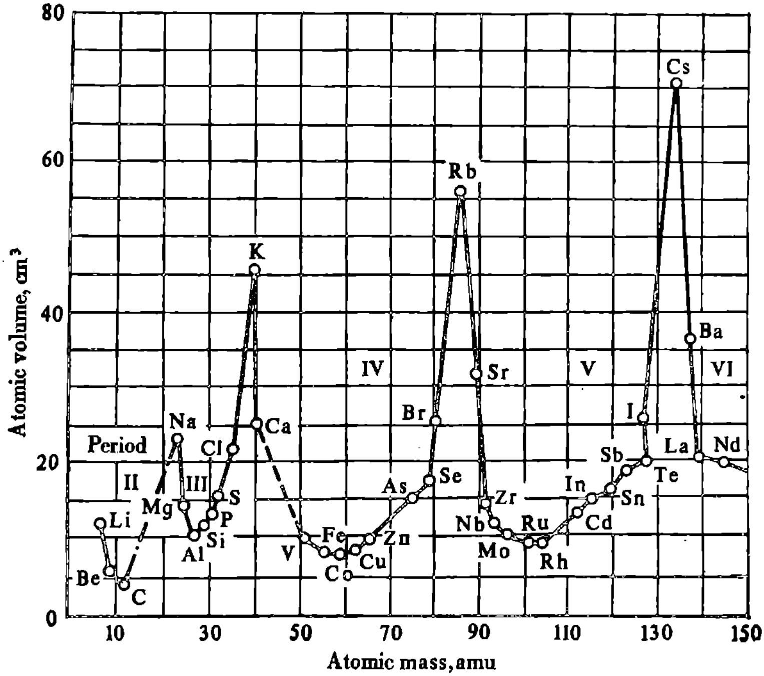
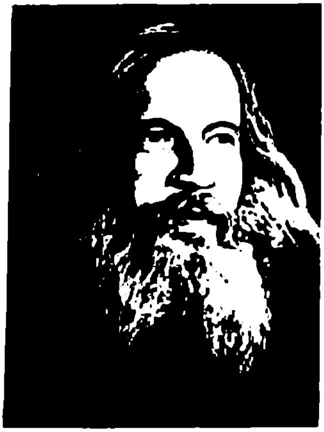


Fig. 1. Atomic volumes of elements against their atomic masses

ed from the procedure he had adopted with a view to the properties of these elements, which required exactly such a sequence of their arrangement. He did not thus attach exclusive significance to the atomic mass and when establishing the place of an element in the



Dmitri Ivanovich Mendeleev (1834-1907)

Dmitri Ivanovich Mendeleev was born on February 8, 1834 in the town of Tobolsk (Siberia) in the family of the director of the town's secondary school. After graduating from the Tobolsk secondary school, he entered the Petersburg Pedagogical Institute, which he graduated from in 1855 with a gold medal.

After receiving his master's degree in 1859 for the thesis "On Specific Volumes", Mendeleev went abroad on a two-year scientific commission. Upon returning to Russia, he was elected a professor first of the Petersburg Technological Institute, and two years later of the Petersburg University, where he conducted scientific research and instruction activities for 33 years.

In 1892, Mendeleev was appointed the Scientific Director of the Bureau of Standard Weights and Measures, which on his initiative was reorganized in 1893 into the Central Chamber of Weights and Measures (at present it is the All-Union Mendeleev Scientific Research Institute of Metrology).

An outstanding result of Mendeleev's creative activities was his discovery in 1869, i.e. when 35 years old, of the periodic law and the compilation of the periodic table of elements. The most important of his other works are "Investigation of Aqueous Solutions According to Their Specific Gravity", his Doctor's thesis "On the Combination of Alcohol with Water", and "The Concept of Solutions as Associations". The basic representations of the chemical or hydrate theory of solutions developed by Mendeleev are an important part of the modern science of solutions.

Special mention must be made of Mendeleev's notable book "The Fundamentals of Chemistry", in which for the first time in history all of inorganic chemistry was set out from the viewpoint of the periodic law.

Organically combining theory and practice, Mendeleev during his entire life devoted a lot of time to the development of his country's industry.

table, he regarded the entire collection of its properties. All later investigations showed that Mendeleev's arrangement of the elements in the periodic table is absolutely correct and corresponds to the structure of the atoms (for greater detail see Chap. 3).

Thus, the properties of the elements, their atomic mass, valence (oxidation number), and chemical nature vary in a definite sequence in the periodic table both in the horizontal periods and in the vertical groups. Hence, the position of an element in the table is determined by its properties, and, conversely, an element having a definite set of properties corresponds to each position. Knowing the position of an element in the table, we can therefore quite accurately indicate its properties.

Not only the chemical properties of the elements, but also very many physical properties of elementary substances vary periodically if we consider them as a function of the atomic mass. The periodicity of the change in the physical properties of elementary substances manifests itself very vividly, for instance, when their atomic volumes are compared*.

The curve in Fig. 1. shows how the atomic volume of the elements varies with increasing atomic mass: the alkali metals have the greatest atomic volumes.

Many other physical constants of elementary substances also change in a similar periodic manner.

19. Significance of the Periodic Table

The periodic table of elements greatly affected the subsequent development of chemistry. It was not only the first natural classification of the chemical elements showing that they form a harmonious system and are closely related to one another, but was also a powerful tool for further research.

When Mendeleev compiled his table on the basis of the periodic law he had discovered, many of the elements were still unknown. One of them was the element scandium belonging to the fourth period. Titanium followed calcium with respect to its atomic mass, but it could not be arranged in the table directly after calcium because it would be in the third group, whereas titanium forms the higher oxide TiO_2. Its other properties also show that it must be arranged in the fourth group. Mendeleev therefore left a vacant box between calcium and titanium. For the same reason, two vacant boxes were left in the fourth period between zinc and arsenic, which are now occupied by gallium and germanium. Vacancies were also left in other rows. Mendeleev was not only convinced that hitherto unknown elements must exist that would fill these vacancies, but

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* The **atomic volume** is the volume occupied by one mole of atoms of an elementary substance in the solid state of aggregation.

also predicted the properties of such elements with a view to their position among the other elements in the periodic table. He named the one that was to occupy the box in the table between calcium and titanium eka-boron (because its properties should be similar to those of boron). The two elements for which vacancies remained in the table between zinc and arsenic were called eka-aluminium and eka-silicon.

During the next fifteen years, Mendeleev's predictions were brilliantly confirmed: all three predicted elements were discovered. First, the French chemist Lecoq de Boisbaudran discovered gallium, which had all the properties of eka-aluminium; soon after this L. Nilson in Sweden discovered scandium having the properties of eka-boron, and, finally, in another few years in Germany C. Winkler discovered the element which he named germanium and which was identical to eka-silicon.

To show the astonishing accuracy of Mendeleev's predictions, let us compare the properties of eka-silicon which he predicted in 1871 with those of germanium discovered in 1886:

Properties of eka-silicon	Properties of germanium
Eka-silicon Es—a fusible metal capable of volatilizing at a high temperature	Germanium Ge—a gray metal melting at 936 °C and volatilizing at a higher temperature
Atomic mass—close to 72	Atomic mass equal to 72.59
Density—about 5.5 g/cm^3	Density at 20 °C equal to 5.35 g/cm^3
EsO_2 should be readily reduced	GeO_2 is readily reduced by coal or hydrogen to the metal
Density of EsO_2—close to 4.7 g/cm^3	Density of GeO_2 at 18 °C is 4.703 g/cm^3
$EsCl_4$ is a liquid boiling at about 90 °C; its density is close to 1.9 g/cm^3	$GeCl_4$ is a liquid boiling at 83 °C; its density at 18 °C is 1.88 g/cm^3

The discovery of gallium, scandium, and germanium was an outstanding triumph of the periodic law.

The periodic table was also of great significance in establishing the valence and atomic masses of several elements. Thus, the element beryllium for a long time was considered to be an analogue of aluminium, and its oxide was assumed to have the formula Be_2O_3. On the basis of the composition in per cent and the assumed formula of beryllium oxide, its atomic mass was considered to equal 13.5. The periodic table showed that it has only one position for beryllium, namely, above magnesium, so that its oxide must have the formula BeO. This gave the atomic mass of beryllium equal to nine. This conclusion was soon confirmed by determinations of the atomic mass of beryllium according to the density of the vapour of its chloride.

In exactly the same way, the periodic table gave an impetus to the correction of the atomic masses of some elements. For example, cesium was previously assumed to have an atomic mass of 123.4. In arranging the elements in the table, however, Mendeleev found that cesium according to its properties must be in subgroup A of the first group (subgroup IA) under rubidium and will therefore have an atomic mass of about 130. The latest determinations show that the atomic mass of cesium is 132.9054 amu.

Today too, the periodic law remains the guiding star and dominating principle of chemistry. It is exactly on its basis that the last decades have seen the artificial preparation of the **transuranium elements** arranged in the periodic table after uranium. One of them—element No. 101, first obtained in 1955—was named **mendelevium** in honour of the eminent Russian scientist.

The discovery of the periodic law and the systematization of the chemical elements were of tremendous significance not only for chemistry, but also for philosophy, for our entire world outlook. Mendeleev showed that the chemical elements form a harmonious system whose cornerstone is a fundamental law of nature. This was an expression of the tenet of materialistic dialectics on the mutual relationship and the mutual conditionality of nature's phenomena. Unveiling the relationship between the properties of chemical elements and the amount of matter in their atoms, the periodic table was a brilliant confirmation of one of the general laws of nature's development—the law of the transition of quantity into quality.

The subsequent development of science made it possible, on the basis of the periodic law, to cognize the structure of matter much deeper than was possible in Mendeleev's time. The theory of the structure of the atom developed in the 20th century, in turn, gave a new, deeper insight into the periodic law and the periodic table of elements. Mendeleev's prophetic words "The periodic law is not in danger of destruction, but only superstructure and development are promised" were brilliantly confirmed.

3

STRUCTURE OF THE ATOM. DEVELOPMENT OF THE PERIODIC LAW

For a long time, the opinion that atoms are indivisible, i.e. contain no simpler constituent parts, dominated in science. Atoms were also considered to be unchangeable: an atom of a given element could never transform into an atom of another one.

The end of the 19th century saw the establishment of a number of facts pointing to the complex composition of atoms and to the possibility of their mutual transformations. Among them is, first of all, the discovery of the electron by the British physicist J. J. Thomson in 1897.

An electron is an elementary particle having the smallest negative electric charge existing in nature (1.602×10^{-19} C). The mass of an electron is 9.1095×10^{-28} g, i.e. almost 1/2000 the mass of a hydrogen atom. It was found that electrons can be separated from any element: for instance, they are current carriers in metals, are detected in a flame, are emitted by many substances when heated, illuminated, or subjected to X-ray irradiation. It thus follows that electrons are contained in the atoms of all the elements. But electrons are charged negatively, whereas atoms have no electric charge, they are electrically neutral. Consequently, atoms must contain other, positively charged particles in addition to electrons. In other words, *atoms are complex formations built up of smaller structural units.*

A major role in establishing the intricate nature of the atom and decoding its structure was played by the discovery and study of radioactivity.

20. Radioactivity

The name radioactivity was given to the phenomenon of the emission by certain elements of radiation capable of penetrating through a substance, ionizing air, and of causing photographic plates to darken*. This phenomenon was first discovered (in 1896) in uranium

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* A more accurate definition of the radioactivity concept is given in Sec. 36.

compounds by the French physicist A. Becquerel. Soon after this, Marie Curie-Sklodowska found that thorium compounds also possess radioactivity. In 1898, together with her husband, the French physicist Pierre Curie, she discovered two new radioactive elements in uranium ores, which according to her suggestion were named **polonium** (from the Latin *Polonia*—Poland) and **radium** (from the Latin *radius*—ray). The new elements were found to be much more powerful sources of radioactive radiation than uranium and thorium.

Marie Curie-Sklodowska
(1867-1934)

Marie Curie-Sklodowska was born in Warsaw on November 7, 1867. In her youth, she took an active part in the revolutionary movement as a member of a circle organized by pupils of her father, a teacher of mathematics and physics in a secondary school. After graduating from the Paris University, Sklodowska together with Pierre Curie began to study radioactivity. For her outstanding discoveries in this field, she was awarded the degree of Doctor of Science (physics). After her husband's death (in 1906), Curie-Sklodowska continued her scientific activities involving the investigation of the radioactive elements. In 1910, she was the first to obtain metallic radium. She was awarded the Nobel prize twice (in chemistry and in physics). Since 1926, she was an honorary member of the USSR Academy of Sciences.

Investigations of the Curies and of the British physicist Ernest Rutherford showed that radioactive radiation is not homogeneous: a magnetic field causes it to divide into three beams, one of which does not change its original direction, while the other two deviate in opposite directions.

The rays that do not deviate in a magnetic field and, consequently, carry no electric charge, were called **gamma rays**. They are electromagnetic radiation similar to X-rays and having a very high penetrability.

The deflection of the other two beams under the action of a magnetic field indicates that these beams consist of electrically charged particles. The opposite directions of the observed deflections witness that one beam contains negatively charged particles (this kind of radiation was named **beta rays**), while the other (**alpha rays**) contains positively charged particles. The beta rays were found to be a stream of rapidly moving electrons. This was another confirmation of the fact that electrons are among the particles which atoms consist of.

The positively charged alpha rays were found to consist of particles whose mass equals that of a helium atom, and whose charge in absolute value is double that of an electron. Rutherford proved by direct experiments that these particles are charged helium atoms. He placed a thin-walled fused glass tube containing a small amount of radium into a larger tube from which the air was then evacuated. The alpha rays penetrated through the thin walls of the inner tube, but were retained by the thick walls of the outer tube, so that the alpha particles remained in the space between the two tubes. Spectral analysis indicated the presence of helium in this space.

The results of the experiment signified that radium atoms in the process of radioactive emission disintegrate (decay), transforming into atoms of other elements, particularly into helium atoms. It was later shown that another product of radium decay is the element radon. The latter is also radioactive and belongs to the noble gas family. Similar conclusions were arrived at in studying other radioactive elements.

Ernest Rutherford (1871-1937)

Ernest Rutherford, one of the most eminent scientists in the field of radioactivity and atomic structure, was born on August 30, 1871, in Nelson (New Zealand). He was a professor of physics at the Montreal University (Canada), from 1907 in Manchester, and from 1919 in Cambridge and London.

Beginning from 1900, Rutherford studied the phenomena of radioactivity. He discovered the three kinds of rays emitted by radioactive substances; presented (together with Frederick Soddy) a theory of radioactive decay; proved the formation of helium in many radioactive processes; discovered the atomic nucleus, and developed the nuclear model of the atom, thus laying the foundation of the modern science of the structure of the atom. In 1919, he was the first to achieve artificial transmutation of some stable elements by bombarding them with alpha particles. In 1908, he was awarded the Nobel prize. He was elected an honorary member of the USSR Academy of Sciences.

21. Nuclear Model of the Atom

The study of radioactivity confirmed the complexity of the composition of atoms. The problem appeared of revealing the structure of an atom.

According to the model proposed in 1903 by J. J. Thomson, an atom consists of a positive charge uniformly distributed over the entire volume of the atom and electrons vibrating inside this charge. To verify Thomson's hypothesis and establish more accurately the internal structure of an atom, E. Rutherford ran a series of experiments involving the scattering of alpha particles by thin metal plates (gold foil). The setup of such an experiment is shown in Fig. 2. Source *S* of alpha rays was placed in lead capsule *C* with a borehole drilled in it in order to obtain a pencil of alpha particles flying in a definite direction. Upon reaching screen *Sc* coated with zinc sulphide, the alpha particles cause it to glow. Microscope *M* made it possible to see and count the separate flashes on the screen produced by the individual alpha particles. Thin gold foil *F* was placed between the radiation source and the screen. The flashes on the screen allowed the experimenter to assess the scattering of the alpha particles, i.e. their deflection from the original direction when passing through the foil.

Most of the alpha particles were found to pass through the foil without changing their direction, although the thickness of the foil was hundreds of thousands of atomic diameters. But a certain fraction of the alpha particles was nevertheless deflected through small angles, while from time to time the particles sharply changed the direction of their motion, and some of them even rebounded from the foil as if they had encountered a massive obstacle. Such sharp deflections of the alpha particles could be observed by moving the screen with the microscope along arc *A*.

It followed from the results of these experiments that the predominating part of the space occupied by an atom of a metal contains no heavy particles—only electrons can be there. We know that the mass of an alpha particle is almost 7500 times greater than that of an electron, so that a collision with the latter cannot virtually affect

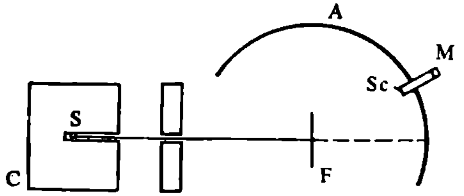

Fig. 2. Setup of alpha particle scattering experiment

the direction of motion of the alpha particle. Cases of sharp deflection and even rebounding of the alpha particles, however, signify that an atom contains a heavy nucleus in which the predominating part of the entire mass of the atom is concentrated. This nucleus occupies a very small volume—it is exactly for this reason that the alpha particles collide so rarely with it—and must have a positive charge. The latter is why the nucleus repels the positively charged alpha particles.

On the basis of these considerations, Rutherford in 1911 proposed the following model of the structure of an atom, which is known as the **nuclear model of the atom.** An atom consists of a positively charged nucleus in which the predominating part of the atom's mass is concentrated, and of electrons orbiting around it. The positive charge of the nucleus is neutralized by the total negative charge of the electrons, so that the atom as a whole is electrically neutral. The centrifugal force produced owing to rotation of the electrons around the nucleus is balanced by the force of electrostatic attraction of the electrons to the oppositely charged nucleus. The size of the nucleus is very small in comparison with that of an atom as a whole: the diameter of an atom is of the order of 10^{-8} cm, whereas the diameter of the nucleus is of the order of 10^{-13} to 10^{-12} cm.

An increase in the charge of an atomic nucleus is attended by stronger repulsion of an alpha particle from it. Hence cases of great deflections of the alpha particles passing through the foil from their original course will be encountered more often. Therefore, experiments involving the scattering of alpha particles make it possible not only to detect an atomic nucleus, but also to determine its charge. It already followed from Rutherford's experiments that *the charge of a nucleus* (expressed in units of electron charge) *numerically equals the atomic number (serial number) of the element in the periodic table.* This was confirmed by H. Moseley, who in 1913 found a simple relationship between the wavelengths of definite lines of the X-ray spectrum of an element and its atomic number, and by J. Chadwick, who in 1920 determined with a great accuracy the charges of the atomic nuclei of a number of elements according to the scattering of alpha particles.

The physical meaning of the atomic number of an element in the periodic table was ascertained: *the atomic number was found to be a very important constant of an element expressing the positive charge of its atom's nucleus.* It can be seen from the electrical neutrality of an atom that the number of electrons orbiting about the nucleus also equals the atomic number of the element.

This discovery was a new substantiation of the arrangement of the elements in the periodic table. At the same time, it also eliminated an apparent contradiction in Mendeleev's table—the position of some of the elements with a greater atomic mass ahead of elements with a smaller atomic mass (tellurium and iodine, argon and potassium, cobalt and nickel). It was found that there is no contradiction here because the place of an element in the table is determined by the charge of the atomic nucleus. It was established experimentally that the charge of a tellurium atom is 52, and that of an iodine atom 53. This is why tellurium, notwithstanding its greater atomic mass, must be ahead of iodine. In exactly the same way, the charges of the nuclei of argon and potassium, nickel and cobalt completely correspond to the sequence of arrangement of these elements in the table.

Thus, the charge of the atomic nucleus is the basic quantity determining the properties of an element and its position in the periodic table. Consequently, Mendeleev's periodic law can be formulated at present as follows:

> *The properties of the elements and the simple substances and compounds they form are in a periodic relation to the charge of the nucleus of the atoms of the elements.*

The determination of the atomic numbers of the elements according to the charges of the nuclei of their atoms made it possible to establish the total number of positions in the periodic table between hydrogen, whose atomic number is 1, and uranium (its atomic number is 92), which at that time was considered to be the last member of the periodic table of elements. When the theory of the structure of the atom was created, positions 43, 61, 72, 75, 85, and 87 were vacant, which pointed to the possibility of undiscovered elements existing. And indeed, in 1922 the element **hafnium** was discovered, which occupied position 72, next in 1925 **rhenium** was discovered, occupying position 75. The elements that ought to occupy the remaining four vacancies in the table were found to be radioactive and have never been discovered in nature. They were obtained, however, artificially. These new elements were named **technetium** (atomic number 43), **promethium** (61), **astatine** (85), and **francium** (87). At present, all the boxes of the periodic table between hydrogen and uranium are filled. But the periodic table itself is not completed, which is witnessed by the discovery of the transuranium elements (for greater detail see Sec. 37).

22. Atomic Spectra

The nuclear model developed by Rutherford was a major step in cognizing the structure of the atom. The main features of this model—the presence in an atom of a positively charged heavy nucleus surrounded by electrons—stood the test of time and were confirmed by a great number of experiments. Rutherford's model, however, in some respects contradicted firmly established facts. We shall note two of these contradictions.

First, Rutherford's theory could not explain the stability of the atom. An electron orbiting about a positively charged nucleus ought to emit electromagnetic energy in the form of light waves like an oscillating electric charge. But, in emitting light, the electron would lose part of its energy, which would result in the violation of equilibrium between the centrifugal force associated with the rotation of the electron and the force of electrostatic attraction of the electron to the nucleus. To restore equilibrium, the electron must move closer to the nucleus. Thus, an electron continuously emitting electromagnetic energy and moving along a spiral will approach the nucleus. After exhausting all of its energy, it should "fall" onto the nucleus, and the atom will stop existing. This conclusion contradicts the real properties of atoms, which are stable formations and can exist without decay for an exceedingly long time.

Second, Rutherford's model led to improper conclusions on the nature of atomic spectra. We remind our reader that when light emitted by a glowing solid or liquid body is passed through a glass or quartz prism, a **continuous spectrum** is observed on a screen placed after the prism. The visible part of this spectrum is a coloured band containing all the colours of the rainbow*. The explanation of this phenomenon is that the radiation of a glowing solid or liquid body consists of electromagnetic waves of every possible frequency. Waves of different frequencies are refracted differently by the prism and impinge on different parts of the screen.

A spectrum can be produced with the aid of a **diffraction grating** instead of a prism. The grating is a glass plate whose surface contains an array of very close thin parallel lines (up to 1500 lines per mm). Light passing through such a grating is decomposed and forms a spectrum similar to that obtained with the aid of a prism. Diffraction

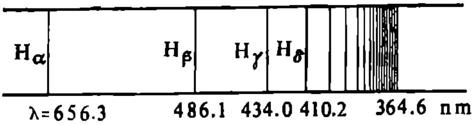

Fig. 3. Schematic view of atomic spectrum of hydrogen in the visible region (the adopted symbols for the separate lines and wavelengths are indicated in the figure)

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* The spectrum also extends beyond the limits of the frequencies corresponding to visible light—into the **ultraviolet** (higher frequencies) and **infrared** (lower frequencies) regions.

is a property of any wave motion and is one of the basic proofs of the wave nature of light.

The radiation emitted by solids or liquids always produces a continuous spectrum. The radiation emitted by glowing gases and vapours, unlike that emitted by solids and liquids, contains only definite wavelengths. Consequently, instead of a continuous band on the screen, we get a number of individual coloured lines separated by dark spaces. The number and arrangement of these lines depend on the kind of the incandescent gas or vapour. For instance, potassium vapour produces a spectrum consisting of three lines—two red and one violet; the spectrum of calcium vapour contains several red, yellow, and green lines, and so on. Such spectra are known as **line** ones. Figure 3 shows as an example a schematic view of the atomic spectrum of hydrogen in the visible and near ultraviolet region. The circumstance that the atoms of every element produce a quite definite spectrum characteristic only of this element, the intensity of the corresponding spectral lines being higher, the greater the content of the element in the sample taken, is widely used for determining the qualitative and quantitative composition of substances and materials. This method of investigation is called **spectral analysis.**

As indicated above, an electron revolving about a nucleus should approach the latter, continuously changing its speed. The frequency of the light it emits depends on the speed of its rotation and, consequently, should also change continuously. This signifies that the emission spectrum of an atom should be continuous, but this, as we have seen, does not correspond to actual facts. Thus, Rutherford's theory could explain neither the existence of stable atoms nor the presence of line spectra of atoms.

An appreciable step in the development of the atomic structure concept was made by Niels Bohr, who in 1913 proposed a theory combining the nuclear model of the atom with the **quantum theory of light.**

23. The Quantum Theory of Light

In 1900, Max Planck* showed that the ability of a heated body to emit radiation can be properly described quantitatively only by assuming that *radiant energy is emitted and absorbed by bodies not continuously, but discretely, i.e. in separate portions—quanta.* The energy E of each portion is related to the frequency of radiation

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* **Max Planck** (1858-1947) was a prominent German physicist and a Nobel Prize winner. His main works are devoted to thermodynamics and thermal radiation. The notion of the quantum nature of the emission and absorption of energy introduced by Planck played a very important role in the development of modern science.

ν by an expression known as the Planck equation

$$E = h\nu$$

The proportionality constant h—the **Planck constant**—is a universal constant equal to 6.626×10^{-34} J·s.

Planck himself assumed for a long time that the emission and absorption of light in quanta is a property of the emitting bodies, and not of the radiation itself, which is capable of having any energy and could therefore be absorbed continuously. In 1905, however, Albert Einstein, analysing the phenomenon of the **photoelectric effect,** arrived at the conclusion that electromagnetic (radiant) energy exists only in the form of quanta and that, consequently, radiation is a stream of indivisible material "particles" (**photons**) whose energy is determined by the Planck equation.

By the photoelectric effect is meant the emission of electrons by a metal under the action of the light falling on it. This phenomenon was studied in detail in 1888-1890 by Aleksandr Stoletov*. A setup for measuring the photoelectric effect is shown schematically in Fig. 4. If we place the setup in a vacuum and apply a negative potential to plate M, no current will be observed in the circuit because the space between the plate and the screen contains no charged particles capable of carrying an electric current. But when the plate is illuminated by a light source, the galvanometer detects the appearance of a current (called a **photoelectric current**) whose carriers are the electrons ejected by the light from the metal.

It was found that a change in the intensity of illumination is attended only by a change in the number of electrons emitted by the metal, i.e. in the photoelectric current. But the maximum kinetic energy of each electron flying out of the metal does not depend on the intensity of illumination; it changes only when the frequency of the light falling on the metal changes. It is exactly with an

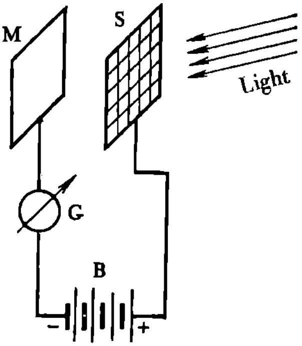

Fig. 4. Setup for observing the photoelectric effect:
M—plate of the metal being studied; S—metal screen; B—source of direct electric voltage; G—galvanometer

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* **Aleksandr Grigoryevich Stoletov** (1839-1896) was a prominent Russian physicist, a professor at the Moscow University. He studied the magnetic properties of iron, which was of great theoretical and practical interest. He established the fundamental laws of the photoelectric effect, and showed the possibility of the direct conversion of luminous energy into electrical. In his philosophical works, he showed himself to be a convinced materialist.

increase in the wavelength (i.e. with diminishing of the frequency*) that the energy of the electron emitted by the metal decreases. Then, at a definite wavelength for each metal, the photoelectric effect vanishes and does not manifest itself even at a very high intensity of illumination. For instance, when illuminated with red or orange light, sodium does not display the photoelectric effect and begins to emit electrons only at a wavelength less than 590 nm (yellow light). The photoelectric effect is detected in lithium at still smaller wavelengths beginning with 516 nm (green light), while the ejection of electrons from platinum under the action of visible light does not occur at all, and begins only when platinum is irradiated with ultraviolet light.

These properties of the photoelectric effect are absolutely unexplainable from the standpoints of the classical wave theory of light, according to which the effect should be determined (for a given metal) only by the amount of energy absorbed by the surface of the metal in unit time, but should not depend on the kind of radiation falling on the metal. These same properties, however, receive a simple and convincing explanation if we consider that the radiation consists of separate portions, photons, having quite definite energies.

Indeed, an electron in a metal is bound to the atoms of the metal so that a definite energy must be spent to eject it. If a photon has the required store of energy (the energy of a photon is determined by the frequency of radiation!), then the electron will be ejected, and the photoelectric effect will be observed. When a photon interacts with a metal, it gives up its energy to an electron completely because a photon cannot decompose into parts. The energy of the photon will be partly used to break the bond of the electron with the metal, and partly to impart the kinetic energy of motion to the electron. Therefore, the maximum kinetic energy of an electron knocked out of a metal cannot be greater than the difference between the energy of a photon and the energy binding the electron to the atoms of the metal. Consequently, an increase in the number of photons falling on the surface of a metal in unit time (i.e. an increase in the intensity of illumination) will be attended only by a growth in the number of electrons ejected from the metal. The result will be a greater photoelectric current, but the energy of each electron will not grow. If the energy of a photon, however, is less than the minimum energy needed for the ejection of an electron, the photoelectric effect will not be observed, no matter what number of electrons falls on the metal, i.e. no matter what the intensity of illumination is.

The quantum theory of light developed by Einstein was able to explain not only the properties of the photoelectric effect, but also the laws of the chemical action of light, the temperature dependence

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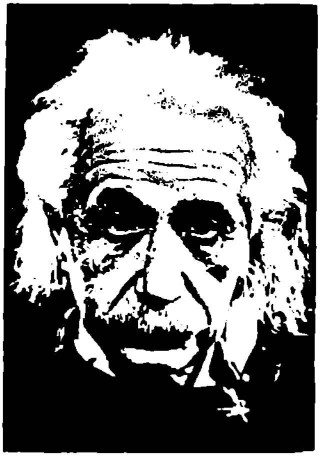
* We remind our reader that the wavelength of light λ and its frequency ν are related by the expression $\lambda\nu = c$, where c is the speed of light.

of the heat capacity of solids, and a number of other phenomena. It was also exceedingly useful in the development of the modern concept of the structure of atoms and molecules.



Albert Einstein (1879-1955)

Albert Einstein, an outstanding physicist, was born on March 14, 1879, in Ulme (Germany); from 14 years old he lived in Switzerland. He worked as a secondary school teacher, a patent examiner; from 1909 he was a professor of the Zurich University (Switzerland), from 1914 to 1933 a professor of the Berlin University. In 1933, as a protest against the Hitlerite regime, he gave up his German citizenship and his title of member of the Prussian Academy of Sciences. From 1933 to his death in 1955, he was a professor of the Institute of Fundamental Research at Princeton, New Jersey (USA).

In 1905, Einstein presented the special, and by 1916 the general, theory of relativity that laid the foundation of today's notions of space, gravitation, and time. He conducted basic research in the field of the quantum theory of light. A number of his important works are devoted to the theory of Brownian motion, magnetism, and other questions of theoretical physics. In 1921, he was awarded the Nobel prize. From 1927 he was an honorary member of the USSR Academy of Sciences.

It follows from the quantum theory of light that a photon is indivisible: it interacts as a whole with an electron of a metal, ejecting it from a plate. It also interacts as a whole with the light-sensitive substance of a photographic film, causing it to darken at a definite point, and so on. In this sense, a photon behaves like a particle, i.e. displays **corpuscular properties**. A photon, however, also has **wave properties**: this manifests itself in the wave nature of light propagation, and in the ability of a photon to take part in interference and diffraction. A photon differs from a particle in the classical meaning of this term in that its exact position in space, like the exact position of any wave, cannot be indicated. But it also differs from a "classical" wave in its inability to divide into parts. Combining both corpuscular and wave properties, a photon, strictly speaking, is neither a particle nor a wave—it has **wave-particle duality**.

24. Structure of an Atom's Electron Shell According to Bohr

As we have already indicated, Niels Bohr proceeded from the nuclear model of the atom in his theory. On the basis of the thesis of the quantum theory of light on the intermittent, **discrete** nature of radiation and on the linear nature of atomic spectra, he arrived at the conclusion that the energy of the electrons in an atom cannot change continuously, but changes in jumps, i.e. **discretely.** This is why only definite "allowed" energy states of the electrons are possible in an atom rather than any states. In other words, the energy states of the electrons in an atom are **quantized.** The transition from one allowed state to another is performed in a jump and is attended by the emission or absorption of a quantum of electromagnetic radiation.

Bohr formulated the basic propositions of his theory in the form of **postulates** (a postulate is a statement accepted without proof) given below:

1. An electron can revolve about a nucleus not in any random orbit, but only in certain definite circular orbits. The latter were called **stationary orbits.**
2. When travelling in a stable orbit, an electron emits no electromagnetic energy.
3. Emission occurs when an electron makes a transition (jumps) from one stationary orbit to another. This is attended by the emission or absorption of a quantum of electromagnetic radiation whose energy equals the difference between the energy of the atom in the final and that in the initial states.

The latter statement requires explanations. The energy of an electron orbiting about a nucleus depends on the radius of the orbit. An electron has the lowest energy when it is in the orbit closest to the nucleus (this is the **normal** or **ground** state of an atom). To transfer an electron to an orbit farther from the nucleus, the electron's attraction to the positively charged nucleus must be overcome, which requires the expenditure of energy. This process takes place when a quantum of light is absorbed. Accordingly, the energy of the atom increases upon such a transition, and it passes over into an **excited state.** The transition of an electron in the reverse direction, i.e. from a farther orbit to one closer to the nucleus, results in diminishing of the atom's energy. The released energy will be liberated in the form of a quantum of electromagnetic radiation. If we denote the initial energy of an atom when an electron is in an orbit farther from the nucleus by E_{in}, and the final energy of the atom for the orbit closest to the nucleus by E_{f}, then the energy of a quantum emitted when an electron makes the transition will equal the difference

$$E = E_{\text{in}} - E_{\text{f}}$$

Taking into account the Planck equation

$$E = h\nu$$

we get

$$h\nu = E_{\text{in}} - E_f$$

whence

$$\nu = \frac{E_{\text{in}} - E_f}{h}$$

The last equation allows us to calculate the possible frequencies (or wavelengths) of the radiation that can be emitted or absorbed by an atom, i.e. to *calculate* the spectrum of the atom.

Bohr's postulates sharply contradict the propositions of classical physics. From the viewpoint of classical mechanics, an electron can revolve in any orbits, while classical electrodynamics does not permit the motion of a charged particle in a circular orbit without radiation. But these postulates were justified by the remarkable results obtained by Bohr in calculating the spectrum of the hydrogen atom.

It must be noted here that Bohr's work appeared at a time (1913) when the atomic spectra of many elements had been studied and spectral analysis had already found widespread applications. Thus, the noble gases were discovered with the aid of spectral analysis; helium was first discovered in the Sun's spectrum, and only later on the Earth. It was clear that atomic spectra are, as it were, "identification cards" of the elements. The language of these cards, however, remained unclear. Only a few empirical rules were established that described the arrangement of the lines in atomic spectra.

Bohr's theory not only explained the physical nature of atomic spectra to be the result of transition of an atom's electrons from one set of stationary orbits to others, but also for the first time allowed calculation of the spectra. Bohr's calculation of the spectrum of the simplest atom—the hydrogen atom—gave brilliant results: the computed position of the spectral lines in the visible part of the spectrum coincided excellently with their actual position in the spectrum (see Fig. 3). These lines were found to correspond to a transition of an electron from the more remote orbits to the second one from the nucleus.

Bohr did not limit himself to an explanation of the known properties of the hydrogen spectrum, but on the basis of his theory predicted the existence and location of spectral series of hydrogen that were unknown at that time. These series are in the ultraviolet and infrared regions of the spectrum and are associated with a transition of an electron to the orbit closest to the nucleus and to orbits farther from the nucleus than the second one. All these spectral series were later discovered experimentally and agreed remarkably with Bohr's calculations.

The calculation of the hydrogen atom spectrum was a brilliant achievement of Bohr's theory.

Niels Bohr (1885-1962)

Niels Bohr, a prominent Danish physicist, was born in 1885. In 1911-1912, he worked in Rutherford's laboratory; from 1916 he was a professor at the Copenhagen University, and from 1920 to his death he headed the Institute of Theoretical Physics of this university.

Bohr was the head of a major scientific school in the field of theoretical physics and the author of the original quantum theory of the structure of the atom (1913-1916) that was the point of departure of today's quantum mechanical theory of the structure of the atom. In 1913, he established the principle of correspondence between classical and quantum concepts. He was also the author of works devoted to a theoretical explanation of Mendeleev's periodic law and to the theory of the atomic nucleus. In 1922, he was awarded the Nobel prize. From 1929, he was a foreign member of the USSR Academy of Sciences.

The triumph of Bohr's theory cannot nevertheless be considered complete. It suffered from an intrinsic contradiction that Bohr himself recognized: together with the postulates contradicting the laws of mechanics and electrodynamics, in Bohr's theory these laws were used to calculate the forces acting on an electron in an atom. A number of questions associated with Bohr's postulates themselves also remained unclear, for example: where is an electron in the process of its transition from one orbit to another? It follows from the theory of relativity that no physical process can propagate with a speed exceeding that of light. Therefore, the transition of an electron to a new orbit separated by a certain distance from the original one does not occur instantaneously, but lasts a certain time. During this time, the electron must be somewhere between the initial and the final orbit. But it is exactly such intermediate states that are "forbidden" by the theory because it is postulated that an electron can be only in stationary orbits.

Finally, notwithstanding the refinements introduced into Bohr's theory by the German physicist A. Sommerfeld and other scientists (account was taken of the possibility of the electrons in an atom travelling not only in circular, but also in elliptical orbits arranged differently in space), this theory could not explain some important spectral characteristics of many-electron atoms and even of the hydrogen atom. For instance, the reason why the lines in the atomic spectrum of hydrogen have different intensities remained unclear.

Bohr's theory was nevertheless an important step in the development of the concepts of the atomic structure. Like Planck's and Einstein's hypothesis of light quanta (photons), it showed that the laws of nature holding for large bodies—objects of the **macroworld**—cannot be extended automatically to negligibly small objects of the **microworld** such as atoms, electrons, and photons. This is exactly why the problem appeared of developing a new physical theory suitable for an uncontradictory description of the properties and behaviour of objects of the microworld. For macroscopic bodies, the conclusions of this theory must coincide with those of classical mechanics and electrodynamics (the so-called **correspondence principle** advanced by Bohr).

This problem was solved in the twenties of the 20th century after the appearance and development of a new branch of theoretical physics—**quantum** or **wave mechanics.**

25. Initial Concepts of Quantum Mechanics

Quantum mechanics developed along the path of generalizing the concepts of the wave-particle duality of the photon and extending them to all the objects of the microworld, and first of all to electrons.

The particle properties of the photon are expressed by the Planck equation

$$E = h\nu$$

according to which the photon is indivisible and exists as a discrete formation. The wave properties of the photon, on the other hand, are expressed in the equation

$$\lambda\nu = c$$

relating the wavelength λ of electromagnetic oscillation to its frequency ν and the speed of propagation c. The use of the wavelength concept here assumes that the photon has wave properties.

These equations yield an expression relating the particle characteristic of a photon E to its wave characteristic λ:

$$E = \frac{hc}{\lambda}$$

But a photon having the energy E also possesses a certain mass m in accordance with the Einstein equation (see Sec. 4):

$$E = mc^2$$

It follows from the last two equations that

$$mc^2 = \frac{hc}{\lambda}$$

whence

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

The product of the mass of a body and its velocity is called the **momentum** of the body. Denoting the momentum of a photon by p, we finally get

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

We must stress once more that the above equation has been derived by assuming that a photon has both wave and particle properties.

In 1924, Louis de Broglie* assumed that wave-particle duality is a property of electrons in addition to photons. Consequently, an electron must display wave properties, and, like a photon, it must obey the last equation, which is often called the **de Broglie equation**. Hence, for an electron of mass m and speed v, we can write:

$$\lambda = \frac{h}{mv}$$

De Broglie's assumption that electrons have wave properties was confirmed experimentally already in 1927, when C. J. Davisson and L. H. Germer in the USA, G. P. Thomson in Great Britain, and P. S. Tartakovsky in the USSR established independently of one another that when a beam of electrons interacts with a diffraction grating (whose capacity was filled by metal crystals), the same diffraction pattern is observed as when a beam of X-rays acts on the crystal lattice of a metal. In these experiments, an electron behaved like a wave whose length exactly coincided with the value computed by the de Broglie equation. At present, the wave properties of electrons have been confirmed by a large number of experiments and are widely used in **electron diffraction** to study the structure of substances.

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* **Louis Victor de Broglie** (born in 1892), a French physicist, is the author of the hypothesis on the wave properties of matter, on which quantum mechanics was founded. He also worked in the field of the theory of electrons, the structure of the atomic nucleus, and the theory of propagation of electromagnetic waves. In 1929, he was awarded the Nobel Prize, and since 1958 is a foreign member of the USSR Academy of Sciences.

The de Broglie equation was also found to hold not only for electrons and photons, but also for any other microparticles. For instance, the phenomenon of neutron diffraction (for these elementary particles see Sec. 35) is used to determine the structure of substances.

It follows from the last statement that macrobodies must also have wave properties in addition to corpuscular ones because they are all built up of microparticles. In this connection, the question may arise: why do the wave properties of the bodies surrounding us manifest themselves in no way? This is associated with the fact that an exceedingly small wavelength corresponds to moving bodies having a great mass because the mass of a body is in the denominator of the equation $\lambda = h/mv$. Even for a dust particle with a mass of 0.01 mg travelling with a speed of 1 mm/s, the wavelength is about 10^{-21} cm. Consequently, the wave properties of such a particle could manifest themselves, for instance, upon interaction with a diffraction grating having a slit width of the order of 10^{-21} cm. But such a distance is considerably smaller than the size of an atom (10^{-8} cm) and even of that of an atomic nucleus (10^{-13} to 10^{-12} cm) so that upon interacting with real objects, the wave properties of a dust particle cannot manifest themselves in any way. Incidentally, a wavelength of 7.3×10^{-8} cm corresponds to an electron with a mass of 9×10^{-28} g travelling with a speed of 1000 km/s; the diffraction of such a wave can be observed when electrons interact with the atoms in crystals.

Thus, *wave-particle duality is a property of electrons as well as of photons.* The particle properties of an electron are expressed in its ability to act only as a single whole. The wave properties of an electron manifest themselves in the features of its motion, and in the diffraction and interference of electrons.

Thus, an electron is a quite intricate material formation. Back in 1907, developing the proposition of the infinite nature of the process of cognizing nature, V. I. Lenin wrote: "An electron, like an atom, is inexhaustible." Time has confirmed the correctness of this statement. Human intelligence has penetrated deeply into the internal structure of the atom. Our concepts of the nature of an electron have also broadened very extensively. There is no doubt that the further development of science will reveal still deeper and more intricate properties of microworld objects.

26. Wave Function

Proceeding from the concept of an electron having wave properties, Erwin Schrödinger* in 1925 assumed that the state of an elec-

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* **Erwin Schrödinger** (1887-1961), an Austrian physicist, was one of the founders of quantum mechanics. In 1933, he was awarded the Nobel Prize, since 1934 he was a foreign member of the USSR Academy of Sciences.

tron moving in an atom must be described by the equation of a standing electromagnetic wave well known in physics. Substituting for the wavelength in this equation its value from the de Broglie equation ($\lambda = h/mv$), he obtained a new equation relating the energy of an electron to space coordinates and the **wave function** ψ corresponding to the amplitude of a three-dimensional wave process in this equation*.

The wave function ψ is of special significance for characterizing the state of an electron. Like the amplitude of any wave process, it can take on both positive and negative values. The quantity ψ^2, however, is always positive. It has a remarkable property: the higher the value of ψ^2 in a given region of space, the greater is the probability of an electron displaying its action here, i.e. of its existence being detected in a physical process.

The following statement will be more accurate: *the probability of detecting an electron in a certain small volume* ΔV *is expressed by the product* $\psi^2 \Delta V$. Thus, the quantity ψ^2 itself expresses the **density of the probability** of finding an electron in the corresponding region of space**.

To understand the physical meaning of the square of the wave function, let us consider Fig. 5 showing a certain part of space near the nucleus of a hydrogen atom. The density of the points in Fig. 5 is proportional to the value of ψ^2 at the corresponding spot: a greater value of ψ^2 is attended by a denser arrangement of the points. If an electron had the properties of a point particle, then Fig. 5 could be obtained by repeatedly observing a hydrogen atom and registering the location of its electron each time: the density of the points in the figure would be the greater, the more frequently the electron is detected in the corresponding region of space or, in other words, the greater is the probability of finding it in this region.

We know, however, that our concept of an electron as of a point particle does not correspond to its true physical nature. Therefore, it is more correct to consider Fig. 5 as a schematic image of an electron "spread" all over the volume of an atom in the form of a so-called **electron cloud**: a greater density of the points in a given part of the volume indicates that the density of the electron cloud is greater here. In other words, *the density of an electron cloud is proportional to the square of the wave function.*

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* We have not given the Schrödinger equation owing to its complicated mathematical nature. This equation and the ways of solving it are treated in courses of physics and physical chemistry.

** The following analogue may help us understand the concept of "density of probability": the probability is related to the density of the probability ψ^2 in the same way as the mass of a body m occupying the volume ΔV is related to the density of the body ρ (by the formula $m = \rho \Delta V$).

The concept of the state of an electron as of a certain cloud of an electric charge is very convenient, it shows very well the main features of the behaviour of an electron in atoms and molecules, and will often be used on the following pages. It must be borne in mind, however, that an electron cloud does not have definite, sharply marked boundaries: even at a great distance from the nucleus there is a certain, though very small, probability of detecting an electron. We shall therefore conventionally define an electron cloud to be the region of space near the nucleus of an atom in which the predominating part (for example, 90 per cent) of the electron's charge and mass is concentrated. A more accurate definition of this region of space is given on p. 82.

27. Energy State of an Electron in an Atom

The Schrödinger equation has solutions only at definite values of the energy, and not at any values, for an electron experiencing forces of attraction to the nucleus. Thus, the quantization of the energy states of an electron in an atom (i.e. Bohr's first postulate) is a consequence of the wave properties inherent in an electron and does not require the introduction of special postulates.

For better understanding of the last statement, let us consider a simplified model of an atom, a "one-dimensional" atom in which an electron can perform only oscillating motion between the extreme points. We shall also consider that the boundaries of the atom cannot be penetrated by the electron so that it can only be inside the atom. We know that the state of an electron in an atom is characterized by a certain wave (a "de Broglie wave"). But it would be improper to imagine the propagation of this wave as something similar to the motion of a wave formed on the surface of water into which a stone

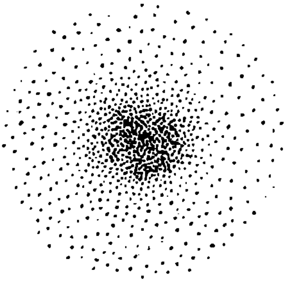

Fig. 5. Electron cloud of a hydrogen atom

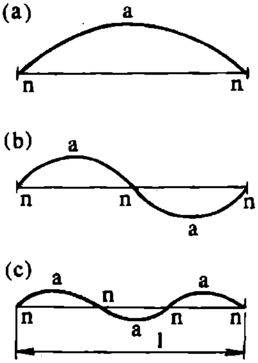

Fig. 6. Standing waves on a string

has been thrown: the water wave unlimitedly moves away from the place of its formation and gradually becomes indistinct. It has no stability in time, whereas an electron in an atom is stable. It will therefore be more correct to draw an analogy between the state of an electron in an atom and the state of a vibrating string on which so-called **standing waves** are formed.

Figure 6 schematically shows standing waves produced on a vibrating string whose extreme points are fixed. **Antinodes** appear at the points designated by the letter *a*—here the amplitude of the oscillations is maximum. At the points *n*, the string does not oscillate—these are the **nodes** at which the amplitude of the oscillations vanishes. The amplitude has intermediate values at points between the antinodes and nodes. Since the end points of the string are fixed, only nodes can appear here. Unlike an ordinary "running" wave, a standing wave does not move in space and does not transfer energy, which is only transmitted from one set of points on the string to another. It is not difficult to see (Fig. 6) that a standing wave on a string with fixed ends cannot have any length, but only one that will ensure an integral number of half-waves: one (Fig. 6*a*), two (Fig. 6*b*), three (Fig. 6*c*), etc. being accommodated on the entire string.

In the one-dimensional model of an atom being considered, the de Broglie wave must also be a standing one: this follows from the fact that an electron cannot leave the confines of the atom and, consequently, the wave function ψ (i.e. the amplitude of the wave) must vanish at the atom's boundaries. Hence, Fig. 6 can be considered as a model of a one-dimensional atom with the de Broglie standing waves that can form in this atom.

If the length of a one-dimensional atom is l, then for cases *a*, *b*, and *c* in Fig. 6, the de Broglie wavelength will be expressed as follows:

$$\lambda_1 = 2l = \frac{2l}{1}$$

$$\lambda_2 = l = \frac{2l}{2}$$

$$\lambda_3 = \frac{2l}{3}$$

Consequently, a standing wave can be formed only provided that

$$\lambda = \frac{2l}{n}$$

where $n = 1, 2, 3, \ldots$, i.e. an integer.

On the other hand, according to the de Broglie equation,

$$\lambda = \frac{h}{mv}$$

Equating the right-hand sides of the last two equations, we get the following expression for the speed v of an electron:

$$v = \frac{h}{2ml} n$$

Now, knowing the speed of an electron v, we can find its kinetic energy E:

$$E = \frac{mv^2}{2} = \frac{h^2}{8\,ml^2} n^2$$

Since n is an integer, the last expression shows that the energy of an electron in a one-dimensional atom cannot have arbitrary values: when $n = 1$, it equals the value of the fraction $h^2/8ml^2$, when $n = 2$, it is four times greater, when $n = 3$, it is nine times greater, etc. Thus, for a one-dimensional atom, the wave properties of an electron expressed by the de Broglie equation do indeed have as a consequence the quantization of the energy states of the electron. The allowable levels of the electron's energy are determined by the values of the integer n, called the **quantum number.**

Naturally, the found expression for the energy of an electron relates to a simplified model of an atom. But for a real atom too, the solution of the Schrödinger equation also leads to the conclusion on the quantization of the energy states of an electron in an atom.

The model of a one-dimensional atom makes it possible to understand why an electron that is in an atom in the stationary state does not emit electromagnetic energy (the second postulate of Bohr's theory). According to the Bohr-Rutherford model, an electron in an atom is in continuous motion with acceleration, i.e. constantly changes its state; in accordance with the requirements of electrodynamics, it must continuously emit energy. In the one-dimensional model of an atom, the stationary state is characterized by the formation of a standing de Broglie wave. As long as the length of this wave remains constant, the state of the electron also remains constant, so that no radiation of energy should occur.

The question of the state of an electron when it transfers from one stationary state to another (in Bohr's terminology—from one stationary orbit to another) also becomes clear. If, for example, an electron performs a transition from the state corresponding to Fig. 6*a* to the state corresponding to Fig. 6*b*, then during this transition the de Broglie wavelength will have a variable value not corresponding to the condition of formation of a standing wave. It is exactly for this reason that the state of the electron during this interval of time will be unstable; it will change until the de Broglie wavelength again corresponds to the condition of formation of a standing wave, i.e. until the electron is in a new stationary state.

In the simplified one-dimensional model of the atom, the position of an electron relative to the nucleus is determined by a single coordinate, and its state by the value of a single quantum number. In a two-dimensional (plane) model of an atom, the position of an electron is determined by two coordinates. Accordingly, its state is characterized by the values of two quantum numbers. Similarly, in a three-dimensional (volume) model of an atom, the state of an electron is determined by the values of three quantum numbers. Finally, studying of the properties of electrons belonging to real atoms has shown that an electron has still another quantized physical characteristic (the **spin**, see Sec. 30) not associated with the position of the electron in space. Thus, the values of four quantum numbers must be indicated to completely describe the state of an electron in a real atom.

28. Principal Quantum Number

In a one-dimensional model of an atom, the energy of an electron can take on only definite values, in other words it is **quantized.** The energy of an electron in a real atom is also a quantized quantity. The possible energy states of an electron in an atom are determined by the value of the **principal quantum number** n that can take on positive integral values: 1, 2, 3, . . ., etc. An electron has the smallest energy at $n = 1$. The energy of an electron grows with increasing n. Therefore, the state of an electron characterized by a definite value of the principal quantum number is customarily known as the **energy level** of the electron in its atom: at $n = 1$, the electron is in the first or ground energy level, at $n = 2$, it is in the second level, and so on.

The principal quantum number also determines the *dimensions of the electron cloud.* To increase these dimensions, part of the cloud must be removed to a greater distance from the nucleus. This is hindered by the forces of electrostatic attraction of the electron to the nucleus whose overcoming requires the expenditure of energy. Consequently, a higher energy of the electron in the atom and, therefore, a greater value of the principal quantum number n correspond to greater dimensions of the electron cloud. The electrons characterized by the same value of the principal quantum number form electron clouds of approximately the same dimensions in an atom. We can thus speak of the existence of **electron layers** or **electron shells** in an atom that correspond to definite values of the principal quantum number.

The following symbols are used to designate the energy levels in an atom (i.e. the electron layers or shells) corresponding to different values of n:

Principal quantum number n	1	2	3	4	5	6	7
Designation of energy level	K	L	M	N	O	P	Q

29. Orbital Quantum Number. Shapes of Electron Clouds

It is not only the energy of an electron in an atom (and the dimensions of the electron cloud associated with it) that can take on only definite values. The shape of the electron cloud also cannot be arbitrary. It is determined by the **orbital quantum number** l (it is also known as the **second** or **azimuthal quantum number**) that can take on integral values from 0 to $(n - 1)$, where n is the principal quantum number. A different number of possible values of l corresponds to different values of n. Thus, when $n = 1$, only one value of the orbital quantum number is possible—zero ($l = 0$), when $n = 2$, the number l may be 0 or 1, when $n = 3$, the number l may be 0, 1, or 2. In general, n different possible values of the orbital quantum number correspond to the given value of the principal quantum number n.

The conclusion that the shapes of atomic electron clouds cannot be arbitrary follows from the physical meaning of the quantum number l. It is exactly this number that determines the value of the **orbital angular momentum of an electron**; this quantity, like the energy, is a quantized physical characteristic of the state of an electron in an atom.

We remind our reader that the orbital angular momentum **L** of a particle travelling in an orbit about a centre of revolution is the product $m\mathbf{vr}$, where m is the mass of the particle, **v** is its velocity, and **r** is a position vector connecting the centre of revolution to the particle (Fig. 7). It is important to note that **L** is a vector quantity; the direction of this vector is at right angles to the plane containing the vectors **v** and **r**.

A quite definite value of the orbital angular momentum of an electron **L** corresponds to a definite shape of the electron cloud. But since **L** can take on only discrete values set by the orbital quantum number l, then the shape of electron clouds cannot be arbitrary: a definite shape of the electron cloud corresponds to each possible value of l.

We know that the energy of an electron in an atom depends on the principal quantum number n. In the hydrogen atom, the energy of the electron is completely determined by the value of n. In atoms with more than one electron, however, the energy of an electron depends on the value of the orbital quantum number l too; the reasons for this relationship will be considered in Sec. 31. Therefore, the states of an electron characterized by different values of l are customarily

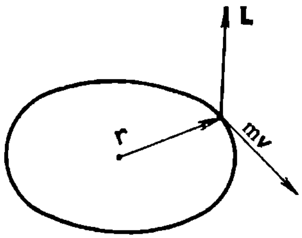

Fig. 7. Illustrating concept of orbital angular momentum

called the **energy sublevels** of an electron in an atom. They are designated by the following symbols:

Orbital quantum number	0	1	2	3	4	5	6	7
Designation of energy sublevel	*s*	*p*	*d*	*f*	*g*	*h*	*i*	*j*

In accordance with these designations, we speak of the *s* sublevel, the *p* sublevel, and so on. The electrons characterized by the values of the orbital quantum number of 0, 1, 2, and 3 are called *s* electrons, *p* electrons, *d* electrons, and *f* electrons, respectively. At a given value of the principal quantum number *n*, the *s* electrons have the lowest energy, next come the *p*, *d*, and *f* electrons.

The state of an electron in an atom corresponding to definite values of *n* and *l* is written as follows: first is the number indicating the value of the principal quantum number, next is the letter designating the orbital quantum number. Thus, the notation 2*p* relates to an electron for which $n = 2$ and $l = 1$, and the notation 3*d* to an electron for which $n = 3$ and $l = 2$.

An electron cloud does not have sharp boundaries in space. Hence, the concept of its dimensions and shape requires clarification. Let us consider as an example the electron cloud of the 1*s* electron in the hydrogen atom (Fig. 8). At point *a* at a certain distance from the nucleus, the density of the electron cloud is determined by the square of the wave function ψ_a^2. Let us draw through point *a* a **surface of**

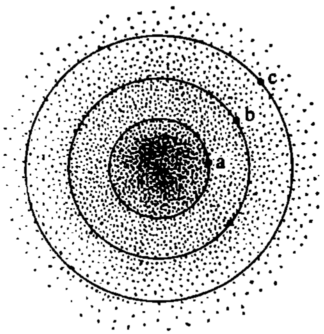

Fig. 8. Illustrating concept of dimensions and shape of an electron cloud

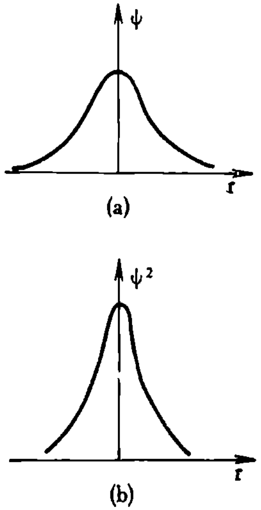

Fig. 9. Graphs of functions ψ and ψ^2 for 1*s* electron

equal electron density connecting the points at which the density of the electron cloud is characterized by the same value of ψ_a^2. For our 1*s* electron, this surface will be a sphere confining a certain part of the electron cloud (in Fig. 8 the section of this sphere by the plane of the drawing is depicted by a circle passing through point *a*). Let us now choose point *b* at a greater distance from the nucleus and also draw through it a surface of equal electron density. This surface will also have a spherical shape, but it will confine a greater part of the electron cloud than is contained inside sphere *a*. Assume, finally, that a surface of equal electron density drawn through point *c* encloses the predominating part of the electron cloud. This surface is usually conducted so that it will enclose 90% of the charge and mass of the electron. Such a surface is called a **boundary surface**, and it is exactly its shape and dimensions that are considered to be the shape and dimensions of the electron cloud. The boundary surface of a 1*s* electron is a sphere, but the relevant surfaces of *p* and *d* electrons have a more intricate shape (see below).

Figure 9 shows the values of the wave function ψ (Fig. 9*a*) and its square (Fig. 9*b*) for a 1*s* electron depending on the distance *r* from the nucleus. The depicted curves do not depend on the direction in which the measured distance *r* is laid off. This signifies that *the electron cloud of a 1s electron has spherical symmetry*, i.e. has the shape of a sphere. The curve in Fig. 9*a* is at one side of the axis of distances, i.e. of the axis of abscissas. It thus follows that the wave function of a 1*s* electron has a constant sign; we shall consider it positive.

Figure 9*b* also shows that the value of ψ^2 diminishes monotonously with an increasing distance from the nucleus. This signifies that the density of the electron cloud of a 1*s* electron decreases as the distance from the nucleus grows. Figure 5 is an illustration of this conclusion.

This does not signify, however, that the probability of detecting a 1*s* electron also diminishes monotonously. Figure 10 shows a separated thin layer confined between spheres of radii *r* and $(r + \Delta r)$, where Δr is a small quantity. With an increase in *r*, the density of the electron cloud in the spherical layer being considered diminishes. At the same time, however, the volume of this layer equal to $4\pi r^2 \Delta r$ grows. As we indicated in Sec. 26, the probability of finding an electron in the small volume ΔV is expressed by the product $\psi^2 \Delta V$. In the given case, $\Delta V = 4\pi r^2 \Delta r$. Consequently, the probability of detecting an electron in the spherical layer confined between *r* and $(r + \Delta r)$ is proportional to the quantity $4\pi r^2 \psi^2$. An increase in *r* in this product is attended by an increase in the multiplier $4\pi r^2$ and by diminishing of the multiplier ψ^2. At low values of *r*, the quantity $4\pi r^2$ grows at a faster rate than ψ^2 diminishes, while at high values of *r*, the opposite occurs. This is why the product $4\pi r^2 \psi^2$

characterizing the probability of detecting an electron at the distance r from the nucleus passes through a maximum with a growth in r.

How the quantity $4\pi r^2\psi^2$ depends on r for a 1*s* electron is shown in Fig. 11 (such graphs are called **graphs of the radial distribution of the probability** of finding an electron). As shown by Fig. 11, the probability of detecting a 1*s* electron at small distances from the nucleus is close to zero because r is small. The probability of detecting the electron at a very great distance from the nucleus is also negligible: here the multiplier ψ^2 is close to zero (see Fig. 9*b*). At a certain distance r_0 from the nucleus, the probability of detecting the electron is maximum. For the hydrogen atom, this distance is 0.053 nm, which coincides with the value of the radius calculated by Bohr for the electron's orbit the closest to the nucleus. The interpretation of this quantity in Bohr's theory and from the viewpoint of quantum mechanics is different, however. According to Bohr, the electron in the hydrogen atom *is* at a distance of 0.053 nm from the nucleus, whereas according to quantum mechanics, only the *maximum probability* of detecting the electron corresponds to this distance.

The electron clouds of *s* electrons of the second, third, and following layers, like the 1*s* electrons, have spherical symmetry, i.e.

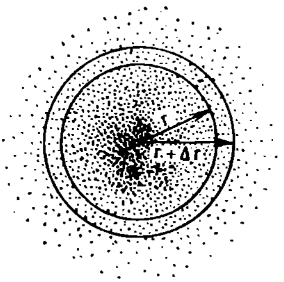

Fig. 10. Electron cloud of 1*s* electron

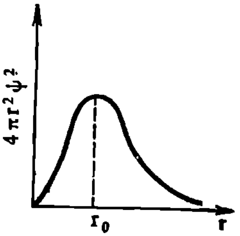

Fig. 11. Graph of radial distribution of probability for 1*s* electron

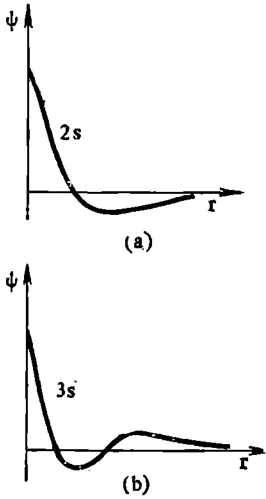

Fig. 12. Graphs of wave function for 2*s* (a) and 3*s* (b) electrons

are characterized by a spherical shape. But here the wave function changes in a more intricate way with an increasing distance from the nucleus. As shown by Fig. 12, the dependence of ψ on r for 2*s* and 3*s* electrons is not monotonous. The wave function has different signs at different distances from the nucleus, and the relevant curves have **nodal points** (or nodes) at which the value of the wave function is zero. There is one node for a 2*s* electron, two nodes for a 3*s* electron, and so on. Accordingly, the structure of the electron cloud here is also more complicated than in a 1*s* electron. Figure 13 shows schematically the electron cloud of a 2*s* electron.

The graphs of the radial distribution of the probability are also more intricate for 2*s* and 3*s* electrons (Fig. 14). Here two or three maxima appear, respectively, instead of the single one for a 1*s* electron. The principal maximum is farther from the nucleus when the principal quantum number *n* is greater.

Let us now consider the structure of the electron cloud of a 2*p* electron. With an increase in the distance from the nucleus in a certain direction, the wave function of a 2*p* electron changes in accordance with the curve shown in Fig. 15*a*. At one side of the nucleus (the right-hand one in the figure), the wave function is positive, and there is a maximum here on the curve. At the other (left-hand) side of the nucleus, the wave function is negative, and there is a minimum on the curve. At the origin of coordinates, the value of ψ becomes zero. Unlike *s* electrons, the wave function of a 2*p* electron has no spherical symmetry. This is expressed in that the height of the

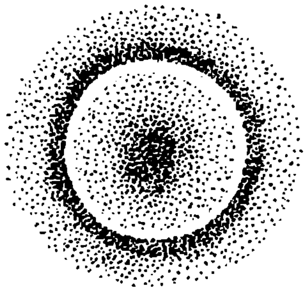

Fig. 13. Electron cloud of 2*s* electron

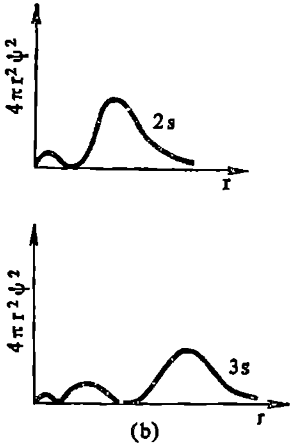

Fig. 14. Graphs of radial distribution of probability for 2*s* (a) and 3*s* (b) electrons

maximum (and, accordingly, the depth of the minimum) in Fig. 15 depends on the selected direction of the position vector *r*. In a certain direction (for unambiguity we shall consider it to be the direction of the *x*-axis), the height of the maximum is the greatest (Fig. 15*a*). In the directions making an angle with the *x*-axis, the height of the maximum is smaller when this angle is greater (Fig. 15*b*, *c*); if it is 90 degrees, the value of ψ in the relevant direction is zero at any distance from the nucleus.

The graph of the radial distribution of the probability for a 2*p* electron (Fig. 16) has a form similar to that shown in Fig. 15, the difference being that the probability of detecting an electron at a certain distance from the nucleus is always positive. The position of the maximum on the probability distribution curve does not depend on the choice of the direction. The height of this maximum, however, does depend on the direction: it is the greatest when the position vector coincides with the direction of the *x*-axis, and diminishes as the position vector deviates from this direction.

A dumbbell shape of the electron cloud corresponds to such a distribution of the probability of detecting a 2*p* electron (Fig. 17). It can be seen that the electron cloud is concentrated near the *x*-axis, and there is no electron cloud in the plane *yz* perpendicular to this axis: the probability of detecting a 2*p* electron here is zero. The plus

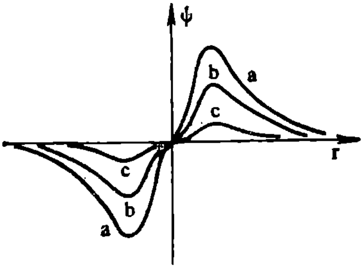

Fig. 15. Graph of wave function for 2*p* electron

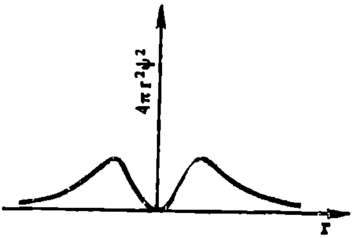

Fig. 16. Graph of radial distribution of probability for 2*p* electron

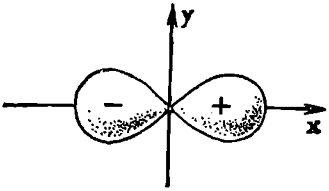

Fig. 17. Electron cloud diagram of 2*p* electron

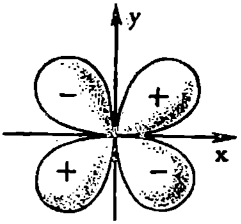

Fig. 18. Electron cloud diagram of 3*d* electron

and minus signs in Fig. 17 relate not to the probability of detecting an electron (it is always positive!), but to the wave function ψ which has a different sign in different parts of the electron cloud.

Figure 17 approximately depicts the shape of the electron cloud not only of $2p$ electrons, but also of p electrons of the third and following layers. But the graphs of the radial distribution of the probability are more intricate here: instead of the single maximum shown in the right-hand part of Fig. 16, on the relevant curves there appear two maxima ($3p$ electron), three maxima ($4p$ electron), etc. The largest maximum is farther and farther from the nucleus.

The electron clouds of d electrons ($l = 2$) have a still more intricate shape. Each of them is of a four-lobe configuration (resembling a four-leaf clover) with alternating signs of the wave function in the lobes (Fig. 18).

30. Magnetic and Spin Quantum Numbers

We learned in the preceding sections that the electron clouds in an atom cannot have any dimensions and shapes, but only ones corresponding to the possible values of the quantum numbers n and l. It follows from the Schrödinger equation that the orientation of an electron cloud in space also cannot be arbitrary: it is determined by the value of a third, **magnetic quantum number** m.

The magnetic quantum number can have any integral values, both positive and negative, within the limits from $+l$ to $-l$. The number of possible values of m thus differs for different l's. For instance, only one value of m ($m = 0$) is possible for s electrons ($l = 0$), three different values of m (-1, 0, $+1$) are possible for p electrons ($l = 1$), and five different values of m (-2, -1, 0, $+1$, $+2$) are possible for d electrons ($l = 2$). In general, $(2l + 1)$ possible values of the magnetic quantum number, i.e. $(2l + 1)$ possible arrangements of the electron cloud in space, correspond to a definite value of l.

We know that the orbital angular momentum of an electron is the vector **L** whose magnitude is quantized and determined by the value of the orbital quantum number l. It follows from the Schrödinger equation that not only the magnitude, but also the direction of this vector characterizing the orientation of the electron cloud in

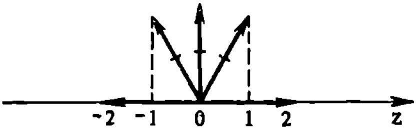

Fig. 19. Determining possible set of magnetic quantum number values. The arrows show the allowed directions of the orbital angular momentum

space cannot be arbitrary, i.e. they are quantized. It is exactly the values of the magnetic quantum number m that determine the allowable directions of the vector **L**.

The set of possible values of m can be explained as follows. Let us select a direction in space, for instance the z-axis (Fig. 19). For every direction of a vector of a given length (in our case of the orbital quantum number l*) there is a definite value of its projection onto the z-axis. It follows from the Schrödinger equation that these directions can only be ones for which the projection of the vector l onto the z-axis equals an integer (positive or negative) or zero. It is exactly the value of this projection that is the magnetic quantum number m. Figure 19 shows the case when $l = 2$. Here $m = 2$ if the directions of the z-axis and the vector l coincide; $m = -2$ if these directions are opposite; $m = 0$ if the vector l is perpendicular to the z-axis. Directions of the vector l are also possibble when m takes on values of ± 1. The magnetic quantum number can thus take on $2l + 1$ values.

The quantum number m has been called magnetic because the interaction of the magnetic field set up by an electron with the external magnetic field depends on its value. In the absence of an external magnetic field, the energy of an electron in an atom does not depend on the value of m. In this case, electrons with identical values of n and l, but with different values of m, have the same energy.

When an external magnetic field acts on an electron, however, the energy of the electron in the atom changes so that the states of the electron differing in the value of m also differ in their energy. This occurs because the energy of interaction of the electron's magnetic field with the external magnetic field depends on the value of the magnetic quantum number. It is exactly for this reason that certain atomic spectral lines split in a magnetic field: several lines appear in the spectrum of an atom instead of one line (the Zeeman effect).

The state of an electron in an atom characterized by definite values of the quantum numbers n, l, and m, i.e. by definite dimensions, shape, and orientation in space of the electron cloud, is called an **atomic electron orbital.**

Figure 20 shows the shapes and the arrangement in space of the electron clouds corresponding to $1s$, $2p$, and $3d$ orbitals. Since a single value of the magnetic quantum number ($m = 0$) corresponds to the s state ($l = 0$), then any possible arrangements of an s electron cloud in space are identical. Electron clouds corresponding to p orbitals ($l = 1$) can be characterized by three different values of m; accordingly, they can be arranged in space in three ways (Fig. 20). The three p electron clouds are oriented along mutually perpen-

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* More strictly, we ought to consider the projection onto the z-axis not of the orbital quantum number l, but of the orbital angular momentum **L** determined by it.

dicular directions, which are conventionally taken as the directions of the coordinate axes (x, y, or z); the corresponding states of the electrons are designated p_x, p_y, and p_z. For d orbitals ($l = 2$), five values of the magnetic quantum number are possible and, accordingly, five different orientations of the d electron clouds in space.

Investigations of atomic spectra showed that in addition to the quantum numbers n, l, and m, an electron is characterized by another quantized quantity not associated with the motion of the electron about the nucleus, but determining its intrinsic state. This quantity was named the **spin quantum number** or simply the spin and is usually designated by the symbol s. The spin of an electron can have only two values: $+1/2$ or $-1/2$. Thus, like the other quantum numbers, the possible values of the spin quantum number differ by unity.

In addition to its orbital angular momentum determined by the

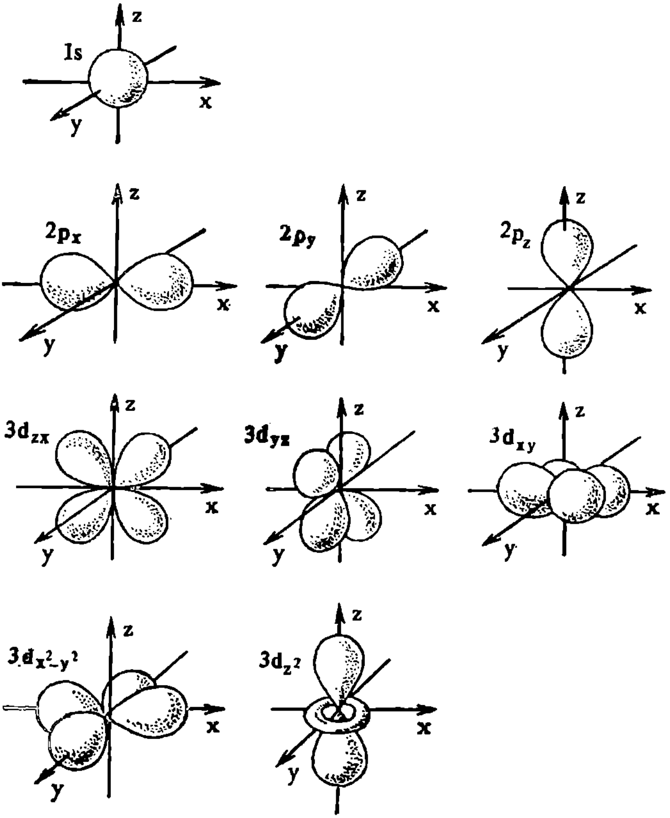


Fig. 20. Shapes and orientation in space of electron clouds of $1s$, $2p$, and $3d$ electrons

value of l, an electron also has its intrinsic angular momentum that can be considered in a simplified way as the result of spinning of the electron about its axis. It is exactly the projection of the intrinsic angular momentum of an electron onto a selected direction (for instance onto the z-axis) that is called the spin.

The four quantum numbers—n, l, m, s—completely determine the state of an electron in an atom.

31. Many-Electron Atoms

The electron in a hydrogen atom is in a force field that is set up only by the nucleus. In atoms with several electrons, not only the nucleus, but also all the remaining electrons act on each electron. The electron clouds of the individual electrons, as it were, merge into a single multiple-electron cloud. The exact solution of the Schrödinger equation for such intricate systems is associated with great difficulties and is impossible, as a rule. This is why the state of an electron in many-electron atoms and in molecules is determined by an approximate solution of the Schrödinger equation.

A common feature of all the approximate methods of solving this equation is the so-called single-electron approximation, i.e. the assumption that the wave function of a many-electron system can be represented in the form of the sum of the wave functions of the individual electrons. Hence, the Schrödinger equation can be solved separately for each electron in an atom whose state, as in a hydrogen atom, will be determined by the values of the quantum numbers n, l, m, and s. Even with this simplification, however, the solution of the Schrödinger equation for many-electron atoms and molecules is a very intricate task and requires a great volume of time-consuming calculations. During recent years, such calculations are being performed, as a rule, with the aid of quick-action electronic computers. This made the required calculations possible for the atoms of all the elements and for many molecules.

Investigation of the spectra of many-electron atoms has shown that here the energy state of the electrons depends not only on the principal quantum number n, but also on the orbital quantum number l. This is associated with the circumstance that an electron in an atom is not only attracted by the nucleus, but is also repelled by the electrons between the given electron and the nucleus. The internal electron layers form, as it were, a peculiar screen that weakens the attraction of the electron to the nucleus or, as is customarily said, screen the outer electron from the nuclear charge. This screening is not the same for electrons differing in the value of the orbital quantum number l.

Thus, in the sodium atom (its atomic number $Z = 11$), the K and L layers, the closest to the nucleus, are occupied by the ten electrons; the eleventh electron belongs to the M layer ($n = 3$). Curve *1* in Fig. 21 shows the radial distribution of the probability for the total electron cloud of the ten "inner" electrons of the sodium atom: the maximum of the electron density the closest to the nucleus corresponds to the K layer, the second maximum—to the L layer. The predominating part of the outer electron cloud of the sodium atom is outside the region occupied by the inner electrons and is therefore greatly screened. A part of this electron cloud, however, penetrates into the space occupied by the inner electrons, and is therefore screened more weakly.

Which of the possible states of the outer electron in the sodium atom—$3s$, $3p$, or $3d$—corresponds to weaker screening and, consequently, to stronger attraction to the nucleus and a lower energy of the electron? As shown in Fig. 21, the electron cloud of the $3s$ electron penetrates to a greater extent into the region occupied by the electrons of the K and L layers and is therefore screened more weakly than the electron cloud of the $3p$ electron. Hence, an electron in the state $3s$ will experience a greater attraction to the nucleus and have a smaller energy than an electron in the state $3p$. The electron cloud of the $3d$ orbital is virtually completely outside the region occupied by the inner electrons, is screened to the greatest extent, and experiences the weakest attraction to the nucleus. It is exactly for this reason that the stable state of the sodium atom corresponds to the outer electron being in the $3s$ orbital.

Thus, in many-electron atoms, the energy of the electron depends not only on the principal, but also on the orbital quantum number. The principal quantum number determines here only a certain energy zone within whose limits the exact value of the energy of an elec-

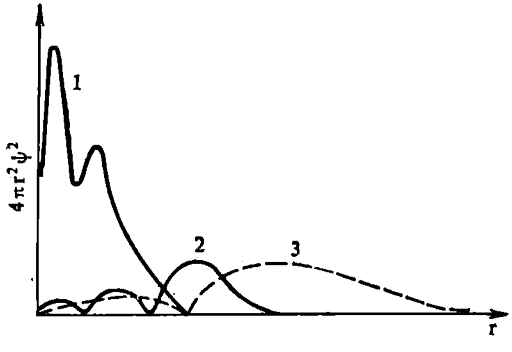


Fig. 21. Graph of radial distribution of probability in a sodium atom:
1—for the ten electrons of the K and L layers; *2*—for the $3s$ electron; *3*—for the $3p$ electron

tron is determined by the quantity l. As a result, the increase in the energy by energy sublevels occurs approximately in the following sequence (see also Fig. 22 on p. 98):

$$1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f \approx$$
$$\approx 5d<6p<7s<5f \approx 6d<7p$$

32. The Pauli Exclusion Principle. Electron Configuration of Atoms and the Periodic Table

Of great importance for determining the state of an electron in a many-electron atom is the principle formulated by Wolfgang Pauli (the **Pauli exclusion principle**) according to which *no two electrons in any given atom can have exactly the same set of four quantum numbers*. It follows that each atomic orbital characterized by definite values of n, l, and m can be occupied by not more than two electrons whose spins have opposite signs. Two such electrons in the same orbital and having opposite (antiparallel) spins are called **paired**, in contrast to a single (i.e. **unpaired**) electron occupying an orbital.

Using the Pauli exclusion principle, let us count the maximum number of electrons that can be in different energy levels and sublevels in an atom.

When $l = 0$, i.e. in the s sublevel, the magnetic quantum number is also zero. Consequently, in the s sublevel there is altogether one orbital that is conventionally represented by a box (a "quantum unit"): $\square$. As indicated above, each atomic orbital accommodates not more than two electrons with opposite spins. This can be represented symbolically as follows:

$$\boxed{\uparrow\downarrow}$$

Thus, the maximum number of electrons in the s sublevel of each electron layer is two. When $l = 1$ (the p sublevel), already three different values of the magnetic quantum number are possible (—1, 0, +1). Consequently, there are three orbitals in the p sublevel each of which can be occupied by not more than two electrons. Altogether, the p sublevel can accommodate six electrons:

$$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$$

The sublevel d ($l = 2$) consists of five orbitals corresponding to five different values of m; here the maximum number of electrons is ten:

Finally, 14 electrons can be accommodated in the f sublevel ($l = 3$); in general, the maximum number of electrons in a sublevel with the orbital quantum number l is $2(2l + 1)$.

The first energy level (the K layer, $n = 1$) contains only the s sublevel, the second energy level (the L layer, $n = 2$) consists of the s and p sublevels, etc. Taking this into consideration, let us compile a table of the maximum number of electrons in different electron layers (Table 2).

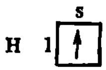
Table 2

Maximum Number of Electrons in Atom Energy Levels and Sublevels

Energy level	Energy sublevel	Possible values of magnetic quantum number m	Number of orbitals		Maximum number of electrons	
			in sublevel	in level	in sublevel	in level
$K\ (n=1)$	$s\ (l=0)$	0	1	1	2	2
$L\ (n=2)$	$s\ (l=0)$	0	1	4	2	8
	$p\ (l=1)$	−1, 0, +1	3		6	
$M\ (n=3)$	$s\ (l=0)$	0	1	9	2	18
	$p\ (l=1)$	−1, 0, +1	3		6	
	$d\ (l=2)$	−2, −1, 0, +1, +2	5		10	
$N\ (n=4)$	$s\ (l=0)$	0	1	16	2	32
	$p\ (l=1)$	−1, 0, +1	3		6	
	$d\ (l=2)$	−2, −1, 0, +1, +2	5		10	
	$f\ (l=3)$	−3, −2, −1, 0, +1, +2, +3	7		14	

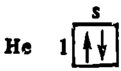
Inspection of the data contained in Table 2 reveals that the maximum number of electrons in each energy level is $2n^2$, where n is the relevant value of the principal quantum number. Thus, the K layer has a maximum of 2 electrons ($2 \times 1^2 = 2$), the L layer has a maximum of 8 electrons ($2 \times 2^2 = 8$), the M layer—18 electrons ($2 \times 3^2 = 18$), and so on. We must note that the numbers obtained coincide with the numbers of elements in the periods of the periodic table.

The most stable state of an electron in an atom corresponds to the minimum possible value of its energy. Any other state is an **excited**, unstable one: the electron passes spontaneously from it to a state with a lower energy. Therefore in an unexcited hydrogen atom (the charge of the nucleus $Z = 1$), the only electron is in the lowest of the possible energy states, i.e. in the 1*s* sublevel. The electron structure of the hydrogen atom can be represented by the diagram



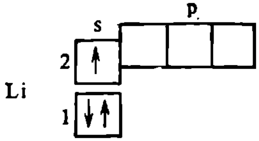
or written in the form $1s^1$ (this is read "one *s* one").

In the helium atom ($Z = 2$), the second electron is also in the state 1*s*. Its electron configuration [$1s^2$ ("one *s* two")] is depicted by the diagram:



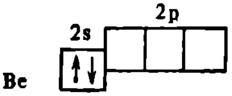
The filling of the *K* layer, which is the closest to the nucleus, is terminated in this element, and this completes the building up of the first period of the system of elements.

In lithium ($Z = 3$), the element following helium, the third electron cannot be accommodated in an orbital of the *K* layer because this would contradict Pauli's principle. It therefore occupies the *s* state of the second energy level (*L* layer, $n = 2$). Its electron configuration is written as $1s^22s^1$, which corresponds to the diagram



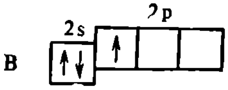
The number and the mutual arrangement of the quantum boxes in the last diagram show that (1) the electrons in the lithium atom are in two energy levels, the first of them consisting of one sublevel (1*s*) and being completely filled; (2) the second—outer—energy level corresponds to a higher energy and consists of two sublevels (2*s* and 2*p*); (3) the 2*s* sublevel includes one orbital in which there is one electron in the lithium atom; and (4) the 2*p* sublevel includes three orbitals that are equivalent from the energy standpoint; a higher energy corresponds to these three orbitals than to the $2s$ orbital; in an unexcited lithium atom, the $2p$ orbitals remain vacant.

In the following, to simplify the electron diagrams, we shall indicate in them only the incompletely occupied energy levels. Accordingly, the structure of the electron shell in an atom of the next element of the second period—beryllium ($Z = 4$)—is shown by the diagram



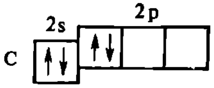
or by the formula $1s^22s^2$. Thus, the building up of the second period, as of the first one, begins with elements in which s electrons of a new electron layer appear for the first time. Owing to the similarity in the structure of the outer electron layer, such elements also have much in common in their chemical properties. This is why they are customarily related to the general family of **s elements.**

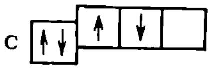
The electron structure of the atom of the element boron ($Z = 5$) following beryllium is shown by the diagram

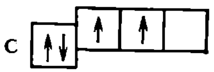


and can be expressed by the configuration $1s^22s^22p^1$.

When the charge of the nucleus again grows by unity, i.e. when we pass over to carbon ($Z = 6$), the number of electrons in the $2p$ sublevel grows to two: the configuration of the carbon atom is $1s^22s^22p^2$. Any of the following three diagrams, however, could correspond to this configuration:







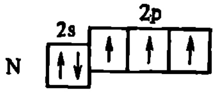
According to the first diagram, both $2p$ electrons in the carbon atom occupy the same orbital, i.e. their magnetic quantum numbers are the same, while their spins are antiparallel; the second diagram signifies that the $2p$ electrons occupy different orbitals (i.e. have different values of m) and their spins are opposite; finally, the third diagram shows that different orbitals correspond to the two $2p$ electrons, while their spins are parallel.

An analysis of the atomic spectrum of carbon shows that for an unexcited carbon atom it is exactly the last diagram that is correct—it corresponds to the greatest possible value of the **total spin of an atom** (this signifies the sum of the spins of all the electrons in an atom; for the first two diagrams of the carbon atom this sum is zero, while for the third diagram it is unity).

Such a sequence of electron arrangement in the carbon atom is a particular case of the general law expressed by **Hund's rule**: *the distribution of the electrons within the limits of an energy sublevel at which the absolute value of the total spin of the atom is maximum corresponds to the stable state of an atom.*

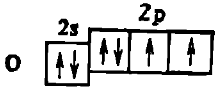
We must note that Hund's rule does not prohibit a different distribution of the electrons within the limits of a sublevel. It only states that the maximum value of the total spin of an atom corresponds to the stable, i.e. *unexcited* state in which the atom has the smallest possible energy; at any other distribution of the electrons, the energy of the atom will be higher, so that it will be in an *excited*, unstable state.

Using Hund's rule, it is a simple matter to compile a diagram of the electron structure for the atom of the element following carbon—nitrogen ($Z = 7$):

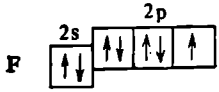


The configuration $1s^2 2s^2 2p^3$ corresponds to this diagram.

Now, when each of the $2p$ orbitals is occupied by one electron, pairing of the electrons in the $2p$ orbitals begins. The oxygen atom ($Z = 8$) has the configuration $1s^2 2s^2 2p^4$ corresponding to the following energy level diagram:



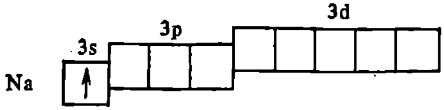
Another $2p$ electron appears in the fluorine atom ($Z = 9$). Consequently, its electron configuration is $1s^2 2s^2 2p^5$ and the diagram is

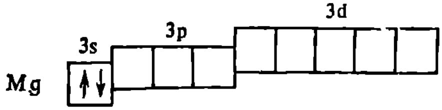


Finally, filling of the $2p$ sublevel terminates with the neon atom ($Z = 10$). This also terminates the filling of the second energy level (the L layer) and the building up of the second period of the system of elements.

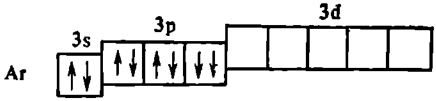
Thus, beginning with boron ($Z = 5$) and ending with neon ($Z = 10$), filling of the p sublevel of the outer electron layer occurs. The elements of this part of the second period relate, therefore, to the family of p elements.

The sodium ($Z = 11$) and magnesium ($Z = 12$) atoms, like the first elements of the second period—lithium and beryllium—contain one or two s electrons in their outer layer, respectively. Their configurations are $1s^22s^22p^63s^1$ (sodium) and $1s^22s^22p^63s^2$ (magnesium), and the energy level diagrams are:





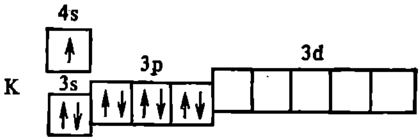
Next, beginning with aluminium ($Z = 13$), the sublevel $3p$ is filled. It terminates at the noble gas argon ($Z = 18$) whose energy level diagram is

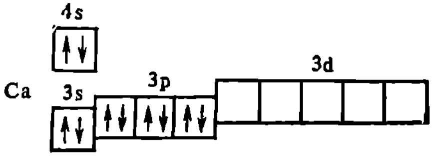


and configuration is $1s^22s^22p^63s^23p^6$.

Thus, the third period, like the second one, begins with two s elements that are followed by six p elements. The structure of the outer electron layer of the corresponding elements of the second and third periods is, consequently, similar. Thus, the lithium and sodium atoms each have one s electron in their outer electron layer, the nitrogen and phosphorus atoms each have two s and three p electrons, and so on. In other words, an increase in the charge of the nucleus is attended by periodic repetition of the electron structure of the outer electron layers in atoms. We shall see below that this also holds for the elements of the following periods. It thus follows that *the arrangement of the elements in the periodic table corresponds to the electron structure of their atoms.* But the electron structure of the atoms is determined by the charge of their nuclei and, in turn, determines the properties of the elements and their compounds. This is exactly the essence of the periodic dependence of the properties of the elements on the charge of the nucleus of their atoms expressed by the periodic law.

Let us continue our consideration of the electron configuration of atoms. We stopped at the argon atom in which the $3s$ and $3p$ sublevels are completely filled, but all the orbitals of the $3d$ sublevel are vacant. In the elements following argon, however—potassium ($Z = 19$) and calcium ($Z = 20$)—filling of the third electron layer stops temporarily and the s sublevel of the fourth layer begins to be formed: the electron configuration of the potassium atom is written as $1s^22s^22p^63s^23p^64s^1$, and of the calcium atom, $1s^22s^22p^63s^23p^64s^2$. The diagrams of these atoms are





The reason for such a sequence of filling the electron energy sublevels is as follows. We have already indicated in Sec. 31 that the energy of an electron in a many-electron atom is determined by the values of not only the principal, but also the orbital quantum number. We have also indicated there the sequence of arrangement of the energy sublevels corresponding to a growth in the energy of an electron. The same sequence is shown in Fig. 22.

It can be seen from Fig. 22 that the sublevel $4s$ is characterized by a lower energy than the sublevel $3d$. This is associated with the stronger screening of the d electrons in comparison with the s electrons. Accordingly, the arrangement of the outer electrons in the potassium and calcium atoms in the $4s$ sublevel corresponds to the most stable state of these atoms.

The sequence of filling of the atomic electron orbitals depending on the values of the principal and orbital quantum numbers was investigated by the Soviet scientist V. Klechkovsky who found that the energy of an electron grows as the sum of these two quantum numbers increases, i.e. with increasing $n + l$. Accordingly, he formulated the following rule (**Klechkovsky's first rule**): *with an* *increase in the charge of the nucleus of an atom, the electron orbitals are filled consecutively from orbitals with a smaller value of the sum of the principal and orbital quantum numbers* ($n + l$) *to orbitals with a greater value of this sum.*

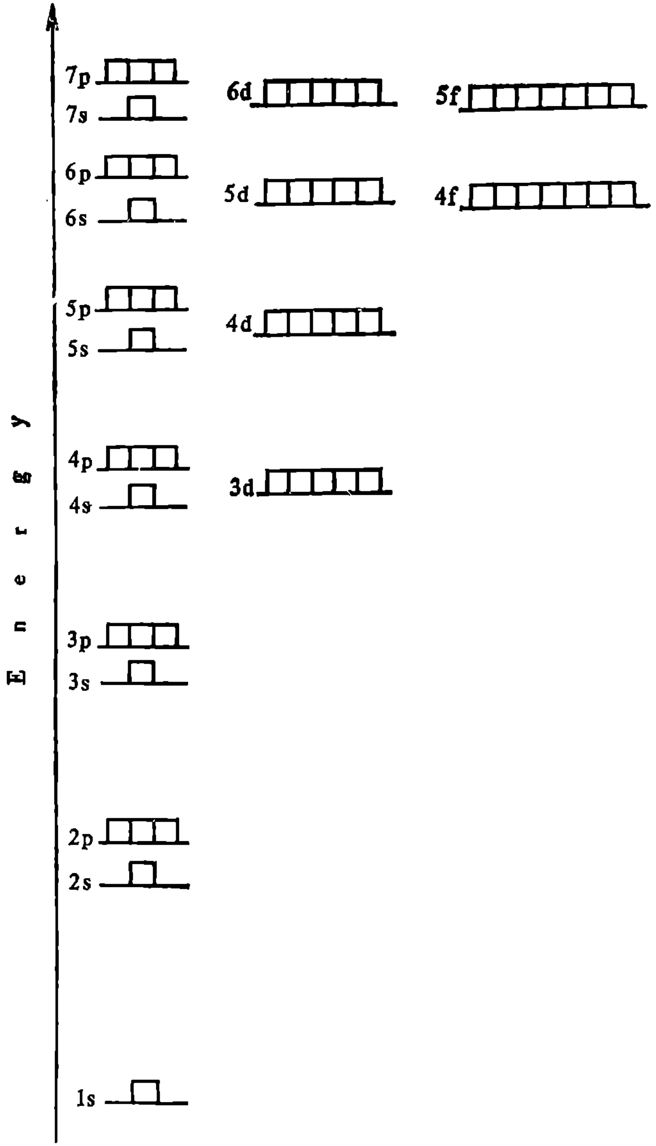
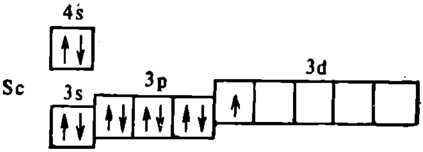


Fig. 22. Sequence of filling of the electron energy sublevels in an atom

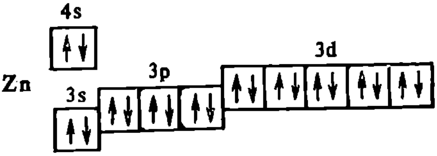
The electron structure of the potassium and calcium atoms obeys this rule. Indeed, for the 3*d* orbitals ($n = 3$, $l = 2$), the sum $n + l$ is 5; for the 4*s* orbitals ($n=4$, $l=0$) it is 4. Hence, the 4*s* sublevel should be filled before the 3*d* sublevel, and this does occur.

Thus, the building up of the 4*s* sublevel is completed in the calcium atom. When passing over to the next element—scandium ($Z = 21$), however, we have to answer the following question: which of the sublevels having the same sum $n + l$, i.e. 3*d* ($n = 3$, $l = 2$), 4*p* ($n = 4$, $l = 1$), or 5*s* ($n = 5$, $l = 0$), should be filled earlier? It was found that at identical values of the sum $n + l$ the energy of an electron is higher when the value of the principal quantum number n is greater. Here, the sequence of filling of the energy sublevels by electrons is determined by **Klechkovsky's second rule**: *at identical values of the sum $n+l$ the orbitals are filled consecutively in the direction of the growth in the value of the principal quantum number n.*

It follows from this rule that when $n + l = 5$, the sublevel 3*d* (for which $n = 3$) must be filled first, next the sublevel 4*p* (for which $n = 4$), and, finally, the sublevel 5*s* ($n = 5$). In the scandium atom, consequently, the 3*d* orbitals should begin to be filled, so that its electron configuration is $1s^22s^22p^63s^23p^63d^14s^2$* and the diagram is



Filling of the 3*d* sublevel continues in the elements following scandium—titanium, vanadium, etc.—and terminates completely in zinc ($Z = 30$), the structure of whose atom is expressed by the diagram



which corresponds to the configuration $1s^22s^22p^63s^23p^63d^{10}4s^2$.

The ten *d* elements beginning with scandium and ending with zinc belong to the **transition elements**. A feature of the structure of the electron shells of these elements in comparison with the preceding ones (the *s* and *p* elements) is that upon transition to each

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* It is customary practice in the electron configurations to first write consecutively all the states with a given value of n, and only then to pass over to states with a higher value of n. For this reason, the sequence of writing does not always coincide with the sequence of filling of the energy sublevels. Thus, when writing the electron formula of the scandium atom, the sublevel 3*d* is before the sublevel 4*s*, although these sublevels are filled in the reverse sequence.

following *d* element, a new electron appears not in the outer ($n = 4$) electron layer, but in the second one ($n = 3$) inward from it. In this connection, it is important to note that the chemical properties of the elements are determined first of all by the structure of the outer electron layer of their atoms and depend only to a smaller extent on the structure of the preceding (inner) electron layers. In the atoms of all the transition elements, the outer electron layer is formed by two *s* electrons*; this is why the chemical properties of the *d* elements do not vary as sharply as those of the *s* and *p* elements with an increase in the atomic number. All the *d* elements are metals, whereas the filling of the outer *p* sublevel results in a transition from a metal to a typical non-metal and, finally, to a noble gas.

After filling the 3*d* sublevel ($n = 3$, $l = 2$), the electrons, in accordance with Klechkovsky's second rule, occupy the sublevel 4*p* ($n = 4$, $l = 1$), thus renewing the building up of the *N* layer. This process begins in the gallium atom ($Z = 31$) and terminates in the krypton atom ($Z = 36$) whose electron configuration is $1s^22s^22p^63s^23d^{10}4s^24p^6$. Like the atoms of the preceding noble gases—neon and argon—the krypton atom is characterized by its outer electron layer having the structure ns^2np^6, where *n* is the principal quantum number (neon—$2s^22p^6$, argon—$3s^23p^6$, krypton—$4s^24p^6$).

Beginning with rubidium, the 5*s* sublevel starts to be filled; this also corresponds to Klechkovsky's second rule. The rubidium atom ($Z = 37$) has a structure with one *s* electron in its outer electron layer that is characteristic of the alkali metals. This begins the building up of a new—the fifth—period of the system of elements. As when building up the fourth period, here the *d* sublevel of the electron layer next to the outer one remains unfilled. We remind our reader that there is an *f* sublevel in the fourth electron layer too, and its filling also does not occur in the fifth period.

In the strontium atom ($Z = 38$), the sublevel 5*s* is occupied by two electrons, after which filling of the 4*d* sublevel occurs, so that the next ten elements—from yttrium ($Z = 39$) to cadmium ($Z = 48$)—belong to the transition *d* elements. The fifth period is completed by the following six *p* elements from indium to the noble gas xenon. Thus, the fourth and fifth periods are similar in structure.

The sixth period, like the preceding ones, begins with two *s* elements (cesium and barium) that complete the filling of the orbitals with the sum $n + l$ equal to 6. Now, according to Klechkovsky's rules, the sublevel 4*f* ($n = 4$, $l = 3$) with the sum $n + l$ equal to 7 and with the smallest possible value of the principal quantum

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* There are *d* elements (for instance, chromium, molybdenum, the elements of the copper subgroup) whose atoms have only one *s* electron in the outer electron layer. The reasons for these deviations from the "normal" sequence of filling the electron energy sublevels will be treated at the end of this section.

number for this sum ought to be filled. Actually, however, in lanthanum ($Z = 57$), which directly follows barium, a $5d$ electron appears instead of a $4f$ one, so that its electron configuration is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^65d^16s^2$. The building up of the sublevel $4f$, to which the single $5d$ electron, which was present in the lanthanum atom, also transfers, actually does begin, however, in the element cerium ($Z = 58$) directly following lanthanum. The configuration of the cerium atom is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^25s^25p^66s^2$. Thus, the deviation from Klechkovsky's second rule which we encountered in lanthanum is temporary: beginning with cerium, all the orbitals of the $4f$ sublevel are consecutively filled. The 14 lanthanides in this part of the sixth period relate to f elements and are close in their properties to lanthanum. A feature of the structure of the electron shells in their atoms consists in that in the transition to the next f element the new electron occupies a site not in the outer ($n = 6$) layer, and not in the preceding one ($n = 5$), but in a layer that is still deeper—the third electron layer ($n = 4$) counting from the outer one.

Owing to the absence in the atoms of the lanthanides of appreciable differences in the structure of the two outer electron layers, they exhibit a great similarity in their chemical properties.

The filling of the $5d$ sublevel that began in lanthanum is renewed in hafnium ($Z = 72$) and terminates in mercury ($Z = 80$). Next, as in the preceding periods, come six p elements. Here the $6p$ sublevel is built up, starting in thallium ($Z = 81$) and terminating in the noble gas radon ($Z = 86$), which is the last element in the sixth period.

The seventh, meanwhile incomplete period of the system of elements is built up similarly to the sixth one. Two s elements (francium and radium) and one d element (actinium) are followed by 14 f elements whose properties are rather close to those of actinium. These elements, beginning with thorium ($Z = 90$) and ending with element 103 are usually combined under the general name of **actinides**. Among them is **mendelevium** ($Z = 101$), artificially obtained by American physicists in 1955 and named in honour of Dmitri Mendeleev. Directly after the actinides come

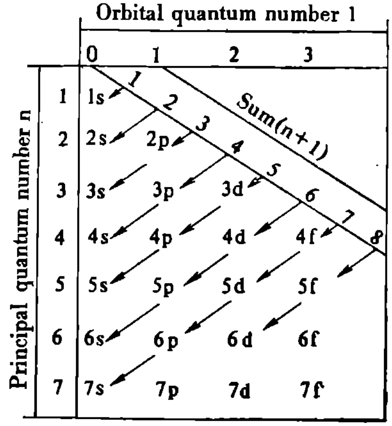


Fig. 23. Diagram showing the sequence of filling the electron energy sublevels in an atom

kurchatovium ($Z = 104$) and element 105. Both these elements were obtained artificially by a group of scientists headed by academician Georgi Flerov. They belong to the *d* elements and complete the part of the periodic table of elements we know at present.

The distribution of electrons by energy levels (layers) in the atoms of all the known chemical elements is given in the periodic table of elements at the beginning of the book. The sequence of filling of the energy levels and sublevels by electrons in atoms is shown schematically in Fig. 23, which graphically expresses Klechkovsky's rules. Filling takes place from smaller values of the sum $n + l$ to greater ones in the sequence indicated by the arrows. It is not difficult to see that this sequence coincides with that of filling the atomic orbitals shown in Fig. 22.

It must be borne in mind that the diagram in Fig. 22 (like Klechkovsky's rules themselves) does not reflect the particular features of the electron structure of the atoms of certain elements. For example, when passing from the nickel atom ($Z = 28$) to the copper atom ($Z = 29$), the number of $3d$ electrons increases not by unity, but directly by two as a result of one of the $4s$ electrons "jumping" to the $3d$ sublevel. Thus, the electron configuration of the copper atom is $1s^22s^22p^63s^23p^63d^{10}4s^1$. Similar jumping of an electron from the outer *s* sublevel to the *d* sublevel of the preceding layer occurs in copper's analogues—the atoms of silver and gold. This phenomenon is associated with the increased energy stability of the electron configurations corresponding to completely occupied energy sublevels (see Sec. 34). The transition of an electron in the copper atom from the sublevel $4s$ to the sublevel $3d$ (and similar transitions in the silver and gold atoms) leads to the formation of a completely filled *d* sublevel and is therefore advantageous from the energy viewpoint.

As will be shown in Sec. 34, an increased energy stability is also a property of electron configurations with exactly a half-filled sublevel (for example, structures containing three *p* electrons in the outer layer, five *d* electrons in the layer preceding the outer one, or seven *f* electrons in a still deeper layer). This explains the "jump" of one $4s$ electron in the chromium atom ($Z = 24$) to the $3d$ sublevel as a result of which the atom acquires a stable electron configuration ($1s^22s^22p^63s^23p^63d^54s^1$) with an exactly half-filled $3d$ sublevel. A similar jump of a $5s$ electron to the $4d$ sublevel also occurs in the molybdenum atom ($Z = 42$).

The violations of the "normal" sequence of filling the energy

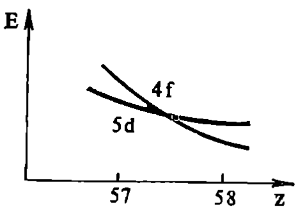


Fig. 24. Dependence of the energy of the $4f$ and $5d$ electrons on the nuclear charge.

states in lanthanum (the appearance of a 5*d* instead of a 4*f* electron) and cerium (the simultaneous appearance of two 4*f* electrons) mentioned above and similar features in the building up of the electron configurations of the atoms of the seventh period elements are explained by the following. Upon an increase in the charge of the nucleus, the electrostatic attraction to it of an electron in a given energy sublevel becomes stronger, and the energy of the electron diminishes. The energy of the electrons in different sublevels changes differently because the charge of the nucleus is screened to a different extent with respect to these electrons. In particular, the energy of 4*f* electrons diminishes with a growth in the charge of the nucleus more sharply than the energy of the 5*d* electrons (see Fig. 24). Consequently, in lanthanum ($Z = 57$), the energy of the 5*d* electrons is found to be lower, and in cerium ($Z = 58$) higher than that of the 4*f* electrons. Accordingly, the electron that in lanthanum is in the sublevel 5*d* in cerium passes over to the sublevel 4*f*.

33. The Dimensions of Atoms and Ions

Let us consider how some properties of atoms depend on the structure of their electron shells. We shall dwell first of all on the regularity in the change of the atomic and ionic radii.

Electron clouds do not have sharp boundaries. For this reason, the concept of the dimensions of an atom is not strict. But if we imagine the atoms in crystals of a simple substance in the form of spheres in contact with one another, then the distance between the centres of adjacent spheres (i.e. between the nuclei of adjacent atoms) can be assumed to equal the double radius of an atom. For instance, the smallest internuclear distance in copper crystals is 0.256 nm; this permits us to consider that the radius of a copper atom is half this value, i.e. 0.128 nm.

The dependence of the atomic radii on the charge of the nucleus of an atom *Z* is of a periodic nature. In one period, an increasing *Z* is accompanied by a tendency of a reduction in the dimensions of an atom, which is observed especially clearly in the short periods (the radii of the atoms are given in nm):

Li	**Be**	**B**	**C**	**N**	**O**	**F**
0.155	0.113	0.091	0.077	0.071	0.066	0.064
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
0.189	0.160	0.143	0.134	0.13	0.104	0.099

The explanation is the increasing attraction of the outer layer electrons to the nucleus as its charge grows.

When the building up of a new electron layer farther from the nucleus begins, i.e. in each new period, the atomic radii grow (compare, for instance, the radii of the fluorine and sodium atoms). The result is that the dimensions of the atoms grow in a subgroup with an increasing charge of the nucleus. We shall give as an example the values of the atomic radii (in nm) of the elements of selected main subgroups:

Group I	Group II	Group V
Li 0.155	Be 0.113	N 0.071
Na 0.189	Mg 0.160	P 0.13
K 0.236	Ca 0.197	As 0.148
Rb 0.248	Sr 0.215	Sb 0.161
Cs 0.268	Ba 0.221	Bi 0.182

The electrons of the outer layer whose bond to the nucleus is the weakest can break away from their atom and attach themselves to other atoms, becoming a member of the outer layer of the latter. Atoms deprived of one or more electrons become charged *positively* because the charge of the atom's nucleus exceeds the sum of the charges of the remaining electrons. Conversely, atoms that have attached surplus electrons are charged *negatively*. The charged particles formed are called **ions**.

Ions are designated by the same symbols as their parent atoms, with a superscript to the right of their symbol indicating their charge: for instance, a positive aluminium ion with a triple charge is designated Al^{3+}, and a negative chloride ion with a single charge is designated Cl^-.

The loss of electrons by atoms leads to their having smaller effective dimensions, and the attachment of surplus electrons to their having greater dimensions. This is why the radius of a positively charged ion (cation) is always smaller, and that of a negatively charged ion (anion) is always greater than the radius of the respective electrically neutral atom. For instance, the radius of a potassium atom is 0.236 nm, and that of the ion K^+ is 0.133 nm. The radii of the chlorine atom and the ion Cl^- equal 0.099 and 0.181 nm, respectively. The radius of an ion differs the greater from the radius of the parent atom, the larger is the ion's charge. For example, the radii of the chromium atom and the ions Cr^{2+} and Cr^{3+} are 0.127, 0.083, and 0.064 nm, respectively.

In one subgroup, the radii of identically charged ions grow with an increase in the charge of the nucleus. This is illustrated by the following examples (the radii of the ions are given in nm):

Group I	Group II	Group VI	Group VII
Li^+ 0.068	Be^{2+} 0.034	O^{2-} 0.136	F^- 0.133
Na^+ 0.098	Mg^{2+} 0.074	S^{2-} 0.186	Cl^- 0.181
K^+ 0.133	Ca^{2+} 0.104	Se^{2-} 0.198	Br^- 0.196
Rb^+ 0.149	Sr^{2+} 0.120	Te^{2-} 0.222	I^- 0.220

This regularity is explained by the increase in the number of electron layers and the growing distance of the outer electrons from the nucleus.

34. Ionization Energy and Affinity to Electron

The most characteristic chemical property of metals is the ability of their atoms to readily give up their outer electrons and transform into positively charged ions. Non-metals, on the contrary, are characterized by their ability to attach electrons with the formation of negative ions. To detach an electron from an atom with conversion of the latter into a positive ion, a certain energy must be spent that is called the **ionization energy.**

The ionization energy can be determined by bombarding atoms with electrons accelerated in an electric field. The smallest voltage of the field at which the speed of the electrons becomes sufficient for ionization of the atoms is called the **ionization potential** of the atoms of the given element and is expressed in volts.

The energy of an electron is often expressed in **electron-volts** (eV). One electron-volt is the energy acquired by an electron in an accelerating electric field with a potential difference of one volt ($1\ \text{eV} = 1.6 \times 10^{-19}$ J; this corresponds to an energy of 96.5 kJ/mol). The ionization energy expressed in electron-volts numerically equals the ionization potential expressed in volts.

When sufficient energy is used, two, three, and more electrons can be detached from an atom. We therefore speak of the **first ionization potential** (the energy needed to detach the first electron from an atom), the **second ionization potential** (the energy needed to detach the second electron), and so on. As electrons are consecutively detached from an atom, the positive charge of the ion formed grows. Therefore, more energy is needed to detach each following electron—in other words, the consecutive ionization potentials of an atom grow (Table 3).

Table 3

Consecutive Ionization Potentials for Atoms of Selected Second Period Elements

Element	Ionization potential, V				
	First	Second	Third	Fourth	Fifth
Lithium	5.39	75.6	122.4	—	—
Beryllium	9.32	18.2	153.8	217.7	—
Boron	8.30	25.1	37.9	259.3	340.1
Carbon	11.26	24.4	47.9	64.5	392.0

The data of Table 3 show that one electron is comparatively easily detached from a lithium atom, two from a beryllium atom, three from a boron atom, and four from a carbon atom. Detachment of the following electrons requires a much greater expenditure of energy. This corresponds to our notions on the structure of the atoms being considered. Indeed, the lithium atom has one electron in its outer electron layer, the beryllium atom has two, the boron atom three, and the carbon atom has four electrons. These electrons have a higher energy than those in the preceding layer, and therefore their detachment from the atom requires a comparatively low expenditure of energy. Upon transition to the next electron layer, the ionization energy sharply grows.

The magnitude of the ionization potential can be a measure of the greater or smaller "metallicity" of an element: the smaller the ionization potential, the easier it is to detach an electron from an atom and the stronger should the metallic properties of the element be expressed.

Let us consider from this standpoint how the first ionization potentials vary with an increase in the atomic number in atoms of the same subgroup of the periodic table (Table 4). It can be seen that an increase in the atomic number of an element is attended by diminishing of the ionization potential. This points to an increase in the metallic properties and, accordingly, a decrease in the non-metallic properties of the relevant element.

Table 4

First Ionization Potentials (in V) of Atoms of Elements of Selected Main Subgroups

Group I		Group II		Group VI		Group VII	
Li	5.39	**Be**	9.32	**O**	13.61	**F**	17.42
Na	5.14	**Mg**	7.64	**S**	10.36	**Cl**	13.01
K	4.34	**Ca**	6.11	**Se**	9.75	**Br**	11.84
Rb	4.18	**Sr**	5.69	**Te**	9.01	**I**	10.45
Cs	3.89	**Ba**	5.21				

This regularity is associated with the growth in the atomic radii mentioned in Sec. 33. In addition, an increase in the number of intermediate electron layers between the nucleus of an atom and the outer electrons leads to greater screening of the nucleus, i.e. to diminishing of its effective charge. Both these factors (the growing distance of the outer electrons from the nucleus and the diminishing of its effective charge) lead to weakening of the bond of the outer electrons with the nucleus and, consequently, to lowering of the ionization potential.

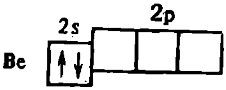
The charge of the nucleus in elements of the same period gradually grows in passing from the alkali metal to the noble gas, while the radius of the atom diminishes. Consequently, the ionization potential gradually increases, while the metallic properties weaken. This law is illustrated by the first ionization potentials of the elements of the second and third periods (Table 5).

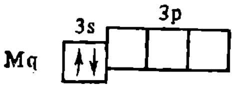
Table 5

First Ionization Potentials (in V) of Atoms of Second and Third Period Elements

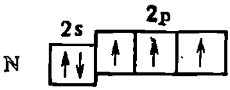
Second period	Element	Li	Be	B	C	N	O	F	Ne
	Ionization potential, V	5.39	9.32	8.30	11.26	14.53	13.61	17.42	21.56
Third period	Element	Na	Mg	Al	Si	P	S	Cl	Ar
	Ionization potential, V	5.14	7.64	5.98	8.15	10.48	10.36	13.01	15.75

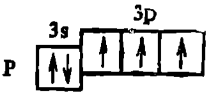
Inspection of Table 5 reveals that the general trend of a growth in the ionization energy within the limits of a period is violated in some cases. For instance, the ionization potentials of the beryllium and nitrogen atoms are higher than of the atoms of the elements boron and oxygen following them. A similar phenomenon is also observed in the third period when passing from magnesium to aluminium and from phosphorus to sulphur. Increased values of the ionization potentials are observed only in atoms with a completely filled outer energy sublevel (beryllium and magnesium)





or in atoms whose outer energy sublevel is exactly half-filled, so that each orbital of this sublevel is occupied by one electron (nitrogen and phosphorus):





These and similar facts are an experimental substantiation of the proposition mentioned in Sec. 32 according to which electron configurations corresponding to completely or exactly half-filled sublevels have an increased energy stability.

As we have noted above, atoms can not only give up, but also attach electrons. The energy liberated when an electron is attached to a free atom is called the **affinity of the atom to an electron.** The affinity to an electron, like the ionization energy, is usually expressed in electron-volts. For instance, the affinity of a hydrogen atom to an electron is 0.75 eV, of an oxygen atom—1.47 eV, and of fluorine—3.52 eV.

The affinity to an electron of atoms of metals, as a rule, is close to zero or negative. Hence, for the atoms of most metals, it is not profitable from the energy viewpoint to attach electrons. The affinity to an electron of non-metal atoms, on the other hand, is always positive, and it is the greater, the closer the non-metal is to a noble gas in the periodic table. This signifies an increase in the non-metallic properties towards the end of a period.

35. Structure of Atomic Nuclei. Isotopes

According to modern notions, atomic nuclei consist of protons and neutrons. A **proton** (from the Greek "protos" — first) is an elementary particle having a mass of 1.007 28 amu and a positive charge equal in magnitude to the charge of an electron. A **neutron** is also an elementary particle, but has no electric charge. The mass of a neutron is 1.008 67 amu. A proton is customarily denoted by the symbol p, and a neutron by n.

The sum of the number of protons and that of neutrons in the nucleus of an atom is called the **mass number of the atom** (nucleus). Since both a proton and a neutron have a mass very close to the atomic mass unit, the mass number of an atom approximately expresses its atomic mass. But the number of protons equals the number of positive charges, i.e. the atomic number of the element. Hence, the number of neutrons equals the difference between the mass number and the atomic number of an element.

Two kinds of forces act between the particles forming a nucleus: electrostatic forces of mutual repulsion of the positively charged protons and forces of attraction between all the particles forming the nucleus, called **nuclear forces.** With an increase in the distance between the interacting particles, the nuclear forces diminish much more sharply than the forces of electrostatic interaction. This is why their action is noticeable only between very close particles. But with the negligible distances between the particles forming an atomic nucleus, the nuclear forces of attraction exceed the forces of repulsion due to the presence of like charges and ensure the stability of the nuclei.

Not any combination of protons and neutrons is stable. The nuclei of atoms of the lighter elements are stable when the number of neutrons is approximately equal to the number of protons. As the charge of a nucleus grows, the relative number of neutrons needed for stability increases, and in the last rows of the periodic table it considerably predominates over the number of protons. For instance, in bismuth (atomic mass 209), there are already 126 neutrons to 83 protons. The nuclei of the heavier elements are in general unstable.

The mass of the atomic nucleus only approximately equals the sum of the masses of the protons and neutrons forming the nucleus. If, taking into account the accurate values of the masses of a proton and a neutron, we calculate the masses of various nuclei, we get a certain discrepancy with the values found experimentally.

Let us compute, for example, the mass of the helium nucleus consisting of two protons and two neutrons. The sum of the masses of the protons and neutrons forming a helium nucleus is

$$2 \times 1.007\,28 + 2 \times 1.008\,67 = 4.031\,90$$

whereas actually the mass of a helium nucleus is 4.0026, i.e. it is smaller by about 0.03 amu.

Similar results are obtained when calculating the masses of other nuclei. The mass of a nucleus is always found to be lower than the sum of the masses of all the particles making up the nucleus, i.e. of all the protons and neutrons when considered to be separated from one another. This phenomenon was named the **mass defect.**

How can we explain the decrease in the mass when atomic nuclei are formed? We have already mentioned in Sec. 4 that a relationship between the mass and the energy expressed by Einstein's equation $E = mc^2$ follows from the theory of relativity. This equation shows that a corresponding change in the energy must follow every change in the mass. If the formation of atomic nuclei is attended by an appreciable decrease in the mass, this signifies that an enormous amount of energy is liberated at the same time.

The mass defect in the formation of a helium atom nucleus is 0.03 amu, and in the formation of one mole of helium atoms it is 0.03 g $= 3 \times 10^{-5}$ kg. According to Einstein's equation, this corresponds to the liberation of energy amounting to $3 \times 10^{-5} \times \times (3 \times 10^8)^2 = 2.7 \times 10^{12}$ J. To form an idea of the colossal value of this energy, it is enough to indicate that it is approximately equal to the energy that can be produced during one hour by a power plant equal in its capacity to the Dnieper Hydroelectric Power Station.

The amount of energy liberated in the formation of a nucleus from protons and neutrons is called the **binding energy of the nucleus** and characterizes its stability: the greater the magnitude of the liberated energy, the more stable is the nucleus.

The nuclei of all the atoms of an element have the same charge, i.e. contain the same number of protons. But the number of neutrons in the nuclei of these atoms may be different. Atoms having an identical charge of their nucleus (and, consequently, identical chemical properties), but a different number of neutrons (and, therefore, a different mass number), are known as **isotopes***. For instance, natural chlorine consists of two isotopes with the mass numbers 35 and 37, magnesium of three isotopes with the mass numbers 24, 25, and 26.

Isotopes are designated using the conventional symbols of the relevant elements with the addition at the left of a superscript indicating the mass number of the isotope. For example, the isotopes of chlorine are designated ^{35}Cl and ^{37}Cl, and those of magnesium—^{24}Mg, ^{25}Mg, and ^{26}Mg. When needed, a subscript is written at the left indicating the atomic number (nucleus charge) of the isotope, for instance $^{35}_{17}Cl$ and $^{24}_{12}Mg$.

At present, the composition of all the isotopes of the chemical elements encountered in nature has been studied. It has been found that every element, as a rule, is a collection of several isotopes. This is why the atomic masses of many elements deviate considerably from integral values. For example, natural chlorine consists of 75.53% of the isotope ^{35}Cl and 24.47% of the isotope ^{37}Cl; as a result, the average atomic mass of chlorine is 35.453.

We mentioned above that the chemical properties of isotopes are identical. This means that if there does exist a certain difference between isotopes with respect to their chemical properties, it is so small that it is virtually not detected. An exception are the hydrogen isotopes ^{1}H and ^{2}H. Owing to the enormous relative difference in their atomic masses (the mass of an atom of one isotope is double that of an atom of the other isotope), the properties of these isotopes differ quite appreciably. The hydrogen isotope with the mass number 2 is called **deuterium** and is designated by the symbol D. The deuterium content in ordinary hydrogen is about 0.017%. Also known is the radioactive hydrogen isotope ^{3}H—**tritium** (with a half-life of about 12 years) prepared only artificially; its symbol is T.

The discovery of isotopes made it necessary to revise the concept of a chemical element. For this reason, the International Committee on Atomic Weights in 1923 decided to consider that a chemical element is defined by its atomic number and may consist of atoms of the same or different masses.

Thus, *a chemical element is a species of atoms characterized by a definite magnitude of the positive charge of the nucleus.*

Isotopic Indicators (Tracers). Isotopic indicators or "labelled atoms" ("tracer atoms") are widely used in studying the mechanism

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* From the Greek words "isos"—the same and "topos"—place.

of chemical and biological processes. Their use is based on the possibility of tracing the ways of transition of an element in chemical transformations by measuring the concentration of one of its isotopes in one of the substances taken for a reaction. Since all the isotopes of the same element behave virtually identically in chemical reactions, by determining the change in the composition of the isotopes of a given element in the various products, we can trace its path.

For example, the use of the heavy oxygen isotope ^{18}O in studying how carbon dioxide is assimilated by plants (carbon dioxide and water enriched with ^{18}O were used for the experiments) showed that the process occurs according to the following reactions, in which the isotope ^{18}O is marked with an asterisk:

$$6CO_2 + 12H_2\overset{*}{O} \rightarrow C_6H_{12}O_6 + 6H_2O + 6\overset{*}{O}_2$$

$$6C\overset{*}{O}_2 + 12H_2O \rightarrow C_6H_{12}\overset{*}{O}_6 + 6H_2\overset{*}{O} + 6O_2$$

It was thus established that the oxygen returned by plants to the atmosphere is taken completely from water, and not from carbon dioxide.

36. Radioactive Elements and Their Decay

The phenomenon of radioactivity has already been discussed briefly in Sec. 20. Using the concept of isotopes, we can give a stricter definition to this phenomenon: *by radioactivity is meant the spontaneous transformation of an unstable isotope of one chemical element into an isotope of another element attended by the emission of elementary particles or nuclei* (for instance, alpha particles). Radioactivity displayed by natural isotopes of elements is known as **natural radioactivity**.

The processes of radioactive transformations occur in different isotopes at a different rate. The latter is characterized by the **radioactive decay constant** showing what part of the total number of atoms of a radioactive isotope decays in one second. The greater the radioactive decay constant, the more rapidly does an isotope decay.

The investigation of radioactive decay showed that *the number of atoms of a radioactive isotope decaying in unit time is proportional to the total number of atoms of this isotope present at the given moment.* In other words, the same fraction of the available number of atoms always decays. Thus, if during a certain time one-half of a radioactive isotope at hand decayed, then in the following identical interval of time one-half of the remaining amount decays, during the next interval—one-half of this amount, and so on.

When the change in the amount of radon was observed, it was established that in 3.85 days one-half of the original amount remains, in the following 3.85 days only one-fourth remains, then one-eighth, and so on. The time dependence of the amount of undecayed radon is shown in Fig. 25.

The time needed for half of the original amount of a radioactive element to decay is called the **half-life.** This quantity characterizes the lifetime of an element.

For various radioactive elements, it ranges from fractions of a second to hundreds of millions of years. For instance, the half-life of radon is 3.85 days, of radium is 1620 years, of uranium 4500 million years.

The main kinds of radioactive decay include alpha decay, beta decay, electron capture, and spontaneous fission. These kinds of radioactive decay are often attended by the emission of gamma rays, i.e. hard (with a small wavelength) electromagnetic radiation.

In **alpha decay,** the nucleus of an atom emits two protons and two neutrons bound in a nucleus of the helium atom ${}^4_2\mathrm{He}$. The result is lowering of the charge of the initial radioactive nucleus by two, and of its mass number by four. Thus, *alpha decay results in the formation of an atom of an element having an atomic number two less than the original isotope.*

Beta decay is possible because, according to modern notions, the proton and neutron are two states of the same elementary particle—a **nucleon.** In certain conditions (for instance, when an excess of neutrons in a nucleus results in its being unstable), a neutron can transform into a proton, simultaneously "giving birth" to an electron. This process can be written as follows:

$$neutron \rightarrow proton + electron^{*} \quad \text{or} \quad n \rightarrow p + e^-$$

Thus, in beta decay, one of the neutrons in the nucleus transforms into a proton. The electron appearing in this transformation flies out of the nucleus, and the positive charge of the latter grows by unity.

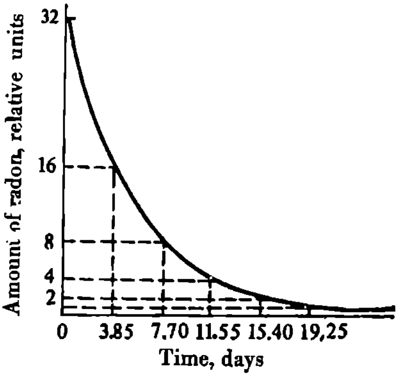

Fig. 25. Time dependence of amount of undecayed radon

A proton may also transform into a neutron as follows:

$$proton \rightarrow neutron + positron$$
$$\text{or } p \rightarrow n + e^+$$

A **positron,** whose symbol is e^+, is an elementary particle with a

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* Other elementary particles (**neutrino** and **antineutrino**) are also formed in the mutual transformations of a proton and a neutron. Since the rest mass and the electric charge of these particles are zero, their participation in radioactive transformations is not reflected in the particle reactions described here.

mass equal to that of an electron, but carrying a positive electric charge. The charges of an electron and a positron are identical in absolute value.

A proton may transform into a neutron with the formation of a positron when the instability of the nucleus is due to an excess content of protons in it. One of the protons in the nucleus transforms into a neutron, the positron that appears flies out of the nucleus, and the charge of the nucleus diminishes by unity. This kind of radioactive decay is called **positron** beta decay (or β^+ decay) in contrast to the previously considered **electron** beta decay (β^- decay). Such radioactive transformations are observed in certain artificially prepared radioactive isotopes.

The change in the charge of a nucleus in beta decay leads to the fact that *as a result of beta decay the atom is transformed into a new element whose atomic number is one greater (with β^- decay) or one less (with β^+ decay) than that of the original isotope.*

The charge of the nucleus diminishes by one with no change in the mass number of the atom not only in β^+ decay, but also in **electron capture,** when one of the electrons of an atom's electron shell is captured by the nucleus; the interaction of this electron with one of the protons in the nucleus leads to the formation of a neutron:

$$e^- + p \rightarrow n$$

An electron is captured most frequently from the K layer which is the closest to the nucleus (**K capture**), and less frequently from the L or M layers.

By **spontaneous fission** is meant the spontaneous disintegration of nuclei of heavy elements into two (sometimes into three or four) nuclei of elements in the middle of the periodic table. The variants of such fission are very diverse, so that there are no general rules of displacement in the periodic table. Most often, the initial nucleus disintegrates into a heavy and light fragments carrying about 60 and 40% of the charge and mass of the original nucleus, respectively. The relative content of neutrons in the nuclei of heavy element isotopes is higher than in the nuclei of the stable isotopes belonging to the middle of the periodic table. This is why in spontaneous fission, the disintegrating nucleus emits from two to four neutrons. The newly formed nuclei still contain excess neutrons, are unstable, and therefore undergo a consecutive series of β^- decays.

The elements at the end of the periodic table (after bismuth) have no stable isotopes. Undergoing radioactive decay, they transform into other elements. If the newly formed element is radioactive, it also decays, transforming into a third element, and so on until atoms of a stable isotope are obtained. A series of elements formed from one another in this way is called a **radioactive series.** An example is the **uranium series** given below—the sequence of the products of transformation of the isotope ^{238}U constituting the predominating part of natural uranium; for each transformation, the kind of radioactive decay (above the arrow) and the half-life (below the arrow) are indicated:

$${}^{238}_{92}\text{U} \xrightarrow[4.5\times10^{9}\text{ years}]{\alpha} {}^{234}_{90}\text{Th} \xrightarrow[24\text{ days}]{\beta^-} {}^{234}_{91}\text{Pa} \xrightarrow[1.2\text{ min}]{\beta^-}$$

$${}^{234}_{92}\text{U} \xrightarrow[2.5\times10^{5}\text{ years}]{\alpha} {}^{230}_{90}\text{Th} \xrightarrow[8\times10^{4}\text{ years}]{\alpha} {}^{226}_{88}\text{Ra} \xrightarrow[1620\text{ years}]{\alpha}$$

$${}^{222}_{86}\text{Rn} \xrightarrow[3.85\text{ days}]{\alpha} {}^{218}_{84}\text{Po} \xrightarrow[3.05\text{ min}]{\alpha} {}^{214}_{82}\text{Pb} \xrightarrow[27\text{ min}]{\beta^-}$$

$${}^{214}_{83}\text{Bi} \xrightarrow[20\text{ min}]{\beta^-} {}^{214}_{84}\text{Po} \xrightarrow[1.6\times10^{-4}\text{ s}]{\alpha} {}^{210}_{82}\text{Pb} \xrightarrow[19\text{ years}]{\beta^-}$$

$${}^{210}_{83}\text{Bi} \xrightarrow[5\text{ days}]{\beta^-} {}^{210}_{84}\text{Po} \xrightarrow[138\text{ days}]{\alpha} {}^{206}_{82}\text{Pb}\ \text{(stable)}$$

Thus, the decay product is a stable lead isotope.

In beta decay, the mass number of an isotope does not change, while in alpha decay it diminishes by four. Therefore, the existence of four radioactive series is possible: one of them includes isotopes whose mass numbers are expressed by the general formula $4n$ (here n is an integer), the second one includes isotopes with the mass numbers $4n + 1$, the third one—$4n + 2$ (this is exactly the uranium radioactive series), and the fourth one includes isotopes with the mass numbers $4n + 3$. Indeed, apart from the uranium series, we know two other natural radioactive series: the thorium series beginning with the isotope ^{232}Th and corresponding to the general formula of the mass number $4n$, and the actinium series beginning with the isotope ^{235}U ("actinouranium") and corresponding to the general formula of the mass number $4n + 3$. The stable products of the transformations in these series are also lead isotopes (^{208}Pb and ^{207}Pb). The parent of the fourth radioactive series (the neptunium series) with the general formula of the mass number $4n + 1$ is the isotope of the artificially obtained element neptunium ${}^{237}_{93}$Np; here the terminal product of decay is the stable bismuth isotope ^{209}Bi.

The accumulation of lead as a result of the decay of the radioactive elements contained in minerals makes it possible to determine their age. Knowing the rate of decay of ^{238}U, ^{232}Th, and ^{235}U and determining their content, and also the content and isotopic composition of the lead in the mineral, we can calculate the age of the mineral, i.e. the time that has elapsed from the moment of its formation (the **lead method** of determining the age). For minerals with a close crystal packing that well retains the gases contained in the crystals, the age of a radioactive mineral can be established according to the amount of helium accumulated in it as a result of the radioactive transformations (the **helium method**). To determine the age of comparatively young formations (up to 70 thousand years old), the radiocarbon method is used that is based on the radioactive decay of the carbon isotope ^{14}C (its half-life is about 5600 years). This isotope is formed in the atmosphere under the action of cosmic radiation and is assimilated by organisms, after whose death its content diminishes according to the law of radioactive decay. The age of organic matter (fossil organisms, peat, sedimentary carbonate rock) can be found by comparing the radioactivity of the carbon contained in it with that of the carbon in the atmosphere.

37. Artificial Radioactivity. Nuclear Reactions

In 1934, Irene Curie and Frederic Joliot-Curie discovered that when light elements such as boron, magnesium, and aluminium are bombarded with alpha particles, they emit positrons. They also found that if the source of the alpha particles is removed, the emission of positrons does not stop immediately, but continues for some time. This signifies that the bombardment by the alpha particles results in the formation of radioactive atoms having a definite lifetime, but emitting positrons instead of alpha particles and electrons. In this way, **artificial radioactivity** was discovered.

Irene Curie and Frederic Joliot-Curie explained the phenomena they observed by the fact that under the influence of bombardment of the nuclei by alpha particles new unstable nuclei are first formed that next decay with the emission of positrons. For instance, the process for aluminium occurs in two stages:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{30}_{15}\mathrm{P} + n$$

where $^{30}_{15}P$ is an artificially prepared isotope of phosphorus—radiophosphorus. The latter is unstable (its half-life is 3 min 15 s) and decays with the formation of a stable nucleus:

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + e^{+}$$

Similar processes occur when nuclei of boron and magnesium are bombarded with alpha particles. In the first case, radionitrogen $^{13}_{7}N$ is produced with a half-life of 14 min, and in the second radiosilicon $^{27}_{14}Si$ with a half-life of 3 min 30 s.

The results obtained by Irene Curie and Frederic Joliot-Curie opened up a new broad region for research.

To date, hundreds of radioactive isotopes have been produced artificially. The branch of chemistry studying radioactive elements and their behaviour is known as **radiochemistry***.

The obtaining of the isotope $^{30}_{15}P$ by bombarding aluminium atoms with alpha particles is an example of **nuclear reactions**, by which is

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* Radiochemistry must not be confused with **radiation chemistry** that studies the chemical processes occurring under the action of high energy ionizing radiation.

meant the interaction of nuclei with elementary particles (neutrons n, protons p, gamma photons) or with other nuclei (for example with alpha particles or deuterons ^2_1H). The first artificial nuclear reaction was conducted in 1919 by Rutherford. By treating nitrogen atoms with a stream of alpha particles, he succeeded in carrying out the following process:

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + p$$

Thus, the possibility of the artificial mutual transformation of elements was proved experimentally for the first time.

A bombarding particle must have a high energy to penetrate into the target nucleus and initiate a nuclear reaction. Special installations (cyclotrons, synchrophasotrons, and other accelerators) have been designed and constructed that make it possible to impart an enormous energy to charged particles. The streams of neutrons formed in the operation of nuclear reactors are also used to conduct nuclear reactions. The use of these powerful means allowed scientists to achieve a great number of nuclear transformations.

For example, in 1937, the element with the atomic number 43, hitherto unknown, was obtained for the first time artificially. It filled the relevant vacancy in the periodic table and was named *technetium* (Tc). It was produced by bombarding molybdenum with deuterons:

$$^{98}_{42}Mo + ^{2}_{1}H \rightarrow ^{99}_{43}Tc + n$$

Of special interest was the synthesis of a number of **transuranium elements** which, as their name implies, are after uranium in the periodic table. The first of them was produced in 1940 by treating the uranium isotope ^{238}U with neutrons. When the nuclei of this isotope absorb neutrons, a beta-radioactive uranium isotope ^{239}U is formed with a half-life of 23 min. Emitting beta particles, the ^{239}U transforms into a new element with the atomic number 93. This element, by analogy with the planet Neptune following Uranium in the solar system, was named **neptunium** (Np).

The formation of neptunium can be illustrated by the reactions

$$^{238}_{92}U + n \rightarrow ^{239}_{92}U$$

$$^{239}_{92}U \rightarrow ^{239}_{93}Np + e^-$$

It was found that ^{239}Np is also radioactive. It undergoes beta decay and transforms into an element with the atomic number 94, which has been named **plutonium** (Pu):

$$^{239}_{93}Np \rightarrow ^{239}_{94}Pu + e^-$$

Thus, the treatment of uranium with neutrons produced two transuranium elements—neptunium and plutonium.

In the following years, isotopes of transuranium elements having atomic numbers from 95 to 103 were obtained, mainly by a group of scientists working under the supervision of the American physicist Glenn Seaborg. Particularly, the element **mendelevium** (Md) with the atomic number 101 was synthesized in 1955 by bombarding **einsteinium** (Es) with alpha particles:

$$^{253}_{99}\mathrm{Es} + ^{4}_{2}\mathrm{He} \rightarrow ^{256}_{101}\mathrm{Md} + n$$

In 1964, a group of scientists headed by academician G. Flerov bombarded the plutonium isotope $^{242}_{94}\mathrm{Pu}$ with nuclei of neon $^{22}_{10}\mathrm{Ne}$ and obtained an isotope of the element 104 named **kurchatovium** (Ku)*:

$$^{242}_{49}\mathrm{Pu} + ^{22}_{10}\mathrm{Ne} \rightarrow ^{260}_{104}\mathrm{Ku} + 4n$$

In 1970, the element with the atomic number 105 was synthesized in Flerov's laboratory. Work is in hand on synthesizing still heavier elements.

The studying of nuclear reactions opened the way to the practical use of intranuclear energy. It was found that the maximum binding energy of the nucleons in a nucleus (when calculated per nucleon) corresponds to the elements in the middle of the periodic table. This signifies that both when nuclei of the heavy elements disintegrate into lighter ones (**fission reactions**) and when the nuclei of light elements combine into heavier nuclei (reactions of **thermonuclear synthesis** or **fusion**), a great amount of energy must be liberated.

The first nuclear reaction used to produce energy is the reaction of fission of the $^{235}\mathrm{U}$ nucleus initiated by a neutron penetrating into the nucleus. Two new fragment nuclei having a close mass are formed, several neutrons are emitted (the so-called **secondary neutrons**), and a tremendous energy is liberated: in the decay of one gram of $^{235}\mathrm{U}$, the amount of energy liberated is 7.5×10^7 kJ, i.e. more than in the combustion of two tonnes of coal. The secondary neutrons may be captured by other nuclei of $^{235}\mathrm{U}$ and, in turn, cause their fission. Thus, the number of separate decay events progressively grows, and a **chain reaction** of uranium nuclei fission sets in.

Not all the secondary neutrons participate in the development of this chain process: some of them manage to fly outside the confines of the piece of uranium without colliding with a nucleus of the fissionable isotope. This is why a chain reaction that has started in

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* The element 104 was named in honour of the outstanding Soviet physicist’ academician **Igor Vasilyevich Kurchatov** (1903-1960). The most important works of Kurchatov are devoted to the absorption of neutrons by nuclei and the fission of heavy nuclei. Igor Kurchatov was a prominent organizer in the field of the investigation of the atomic nucleus and made a great contribution to the setting up and development of the technical base needed for these investigations in the USSR.

a small piece of uranium may terminate: for its continuous occurrence, the mass of the piece of uranium must be sufficiently great, not smaller than the critical mass. In the fission of uranium, the chain process may become an explosion: this is exactly what occurs in the explosion of an atomic bomb. To obtain a controllable reaction of fission, it is necessary to regulate the rate of the process by changing the number of neutrons capable of continuing the reaction. This is achieved by introducing into the reaction space rods containing elements whose nuclei intensively absorb neutrons (an example of these elements is cadmium).

In addition to ^{235}U, plutonium ^{239}Pu synthesized from ^{238}U (see p. 116) and the uranium isotope ^{233}U obtained from the natural thorium isotope ^{232}Th:

$$^{232}_{90}Th + n \rightarrow {}^{233}_{90}Th \xrightarrow{\beta^-} {}^{233}_{91}Pa \xrightarrow{\beta^-} {}^{233}_{92}U$$

are used to produce nuclear energy.

The isotopes ^{239}Pu and ^{233}U, like the isotope ^{235}U, undergo fission when they capture a neutron.

The reaction of nuclear fusion can also be a source of energy. For instance, in the formation of a helium atom nucleus from nuclei of deuterium and tritium:

$$^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + n$$

the amount of energy liberated per gram of reaction mixture is 35×10^7 kJ, i.e. almost five times more than is liberated in the decay of one gram of ^{235}U. The transformation of the stock of deuterium existing on the Earth (about 4×10^{13} tonnes) into helium could therefore be a virtually inexhaustible source of energy for mankind. To conduct such reactions of nuclear synthesis, however, a very high temperature is needed (above one million degrees). Meanwhile, only an uncontrolled thermonuclear reaction has been carried out that resulted in an explosion of an enormous power. This process underlies the operation of a hydrogen bomb. At present intensive research is being conducted in a number of countries aimed at mastering a controllable process of thermonuclear fusion.

4

THE CHEMICAL BOND AND THE STRUCTURE OF MOLECULES

When atoms interact, a **chemical bond** may appear between them that leads to the formation of a stable polyatomic system—a molecule, molecular ion, or crystal. The stronger a chemical bond, the more energy has to be spent to break it. Therefore, the **bond dissociation energy**, also called simply the **bond energy**, is a measure of its strength. The bond dissociation energy is always positive because otherwise the chemical bond would spontaneously break with the liberation of energy. Hence, it follows that in the formation of a chemical bond energy is always evolved as a result of the decrease in the potential energy of the system of interacting electrons and nuclei*. This is why the potential energy of a particle formed (a molecule or crystal) is always less than the total potential energy of the initial free atoms. Thus, *a decrease in the potential energy of a system of interacting atoms is a condition for the formation of a chemical bond.*

A chemical bond is produced owing to the interaction of the electric fields set up by the electrons and nuclei of the atoms participating in the formation of the molecule or crystal. The nature of this interaction can be cognized on the basis of concepts of the atomic structure and of the wave-particle properties of an electron.

The idea of the electrical nature of a chemical bond was suggested in 1807 by the outstanding British scientist Humphry Davy. He assumed that molecules are formed owing to the electrostatic attraction of oppositely charged atoms. This idea was further developed by the prominent Swedish chemist Jöns Berzelius, who in 1812-1818 presented the **electrochemical theory** of the chemical bond. According to this theory, all atoms have positive and negative poles; in some atoms a positive pole predominates ("electropositive" atoms), and in others negative ones ("electronegative" atoms). Atoms in which opposite poles predominate attract each other. For instance, electro-

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* Here and below by a system we shall mean a collection of interacting particles (atoms, atomic nuclei, electrons).

positive atoms of calcium are attracted to electronegative atoms of oxygen, forming a molecule of calcium oxide CaO. In the molecule CaO, the electric charges of the atoms compensate each other incompletely. The molecule has an excess positive charge, and when it interacts with another molecule having an uncompensated negative charge (for example, with a molecule of CO_2), it will be attracted to the latter. The result is the formation of the more complicated molecule $CaO \cdot CO_2$ (i.e. $CaCO_3$).

While it successfully explained some chemical phenomena, the electrochemical theory contradicted, however, a number of facts. For instance, from the viewpoint of this theory, it was impossible to explain the existence of molecules formed by identical atoms (H_2, O_2, Cl_2, etc.) that according to Berzelius had like charges. The number of such contradictions grew with the development of chemistry. For this reason, Berzelius's theory soon went out of favour.

Notwithstanding its appreciable immaturity, the theory of Davy and Berzelius contained the rational idea of the electrical origin of the forces giving rise to the formation of a chemical bond.

A major step in the development of the concepts on the structure of molecules was the **theory of chemical structure** presented in 1861 by the outstanding Russian chemist Aleksandr Butlerov.

38. The Theory of Chemical Structure

Butlerov's theory is founded on the following propositions:

1. The atoms in molecules are combined with one another in a definite sequence. A change in this sequence leads to the formation of a new substance with new properties.
2. Atoms combine in accordance with their valence.
3. The properties of substances depend not only on their composition, but also on their "chemical structure", i.e. on the order in which atoms combine into molecules and on the nature of their mutual influence. Atoms directly bound to each other have the greatest mutual influence.

Thus, according to Butlerov's theory, the properties of substances are determined not only by their qualitative and quantitative composition, as was previously considered, but also by the internal structure of the molecules, and by a definite order in the combination of the atoms forming a molecule. Butlerov called this internal structure the "chemical structure".

Of special significance was Butlerov's idea that atoms, combining in a definite sequence in accordance with their valence, mutually affect one another so that their own nature, i.e. their "chemical content", partly changes. For example, the properties of a hydrogen atom change appreciably depending on whether it is combined with a chlorine atom (in the molecule HCl), an oxygen atom (in the mole-

Aleksandr Mikhailovich Butlerov (1828-1886)

Aleksandr Mikhailovich Butlerov was born on August 25, 1828, in the town of Chistopol, Kazan Province. In 1849, he graduated from the Kazan University, where his instructors were the eminent Russian chemists K. Klaus and N. Zinin.

After graduating from the university, Butlerov was allowed to remain at it to prepare for the rank of a professor. In 1851, Butlerov submitted the thesis "On the Oxidation of Organic Compounds", for which he received his master's degree, and in 1854, upon submitting the dissertation "On Ethereal Oils", he received his doctor's degree and was elected a professor of the Kazan University.

In 1868, the Council of the Petersburg University, on Mendeleev's suggestion, elected Butlerov a professor of the department of organic chemistry, after which all his scientific and pedagogical activities proceeded in Petersburg.

From the very beginning of his scientific activities, Butlerov proved himself to be a brilliant experimenter and conducted a number of remarkable syntheses. His talent as an experimenter was combined with broad theoretical generalizations and scientific prediction. Butlerov was convinced that the structure of molecules of chemical compounds can be expressed by formulas, when studying their chemical transformations.

In 1861, Butlerov presented a report on "The Chemical Structure of Substances" to a congress of German naturalists and physicians. The report ushered in a new epoch in chemistry. After returning to Kazan, he developed the new theory in detail.

In 1862-1868, Butlerov wrote his work "An Introduction to a Complete Study of Organic Chemistry", in which he arranged all the known facts of organic chemistry on the basis of a strict scientific classification following from the theory of chemical structure. The classification of organic compounds adopted in this book has remained unchanged in its main features up to the present time.

Butlerov brought up a brilliant group of pupils who continued to develop his ideas. His school gave the world such prominent scientists as V. Markovnikov and A. Favorsky.

cule H_2O), or a nitrogen atom (in the molecule NH_3). In the first case in aqueous solutions, the hydrogen atom comparatively easily detaches itself from the molecule HCl in the form of the ion H^+, and this is exactly what produces the acid properties of hydrogen chloride; a hydrogen ion detaches itself with much greater difficulty from a water molecule, so that the acid properties of water are expressed very slightly; finally, for an ammonia molecule, the detachment of a hydrogen ion is even less probable—ammonia behaves like a base. The mutual influence of atoms in the molecules of organic compounds manifests itself especially diversely (see Vol. 2, the paragraph numbered 5 in Sec. 48).

Butlerov's teaching made it possible to orient oneself in the tremendous diversity of substances, to determine the structure of molecules by studying their chemical properties, to foresee the properties of substances from the structure of their molecules, and to plan the ways of synthesizing various compounds.

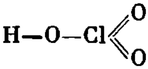
The possibility of depicting how molecules are built up by means of **structural formulas** follows from Butlerov's theory. These formulas indicate the sequence in which atoms combine with one another, while each line joining the atoms signifies a unit of valence. For example, the structure of the molecules of hydrochloric acid (HCl), hypochlorous acid (HOCl), and chloric acid ($HClO_3$) is expressed by the following structural formulas:

H—Cl

Hydrochloric acid

H—O—Cl

Hypochlorous acid

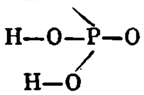


$$H{-}O{-}Cl\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$$

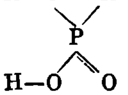
Chloric acid

These formulas show first of all that only in a molecule of HCl is the hydrogen atom bound directly to a chlorine atom, whereas in the molecules of HOCl and $HClO_3$ it is bound not to chlorine, but to an oxygen atom. In addition, the structural formula of chloric acid points to the lack of equivalence of the oxygen atoms; each of two oxygen atoms is bound to the chlorine atom by means of two valence bonds, while the third atom is bound simultaneously to the chlorine and hydrogen atoms.

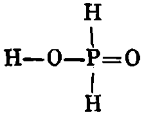
Structural formulas make it possible, for example, to understand the reason of the differences between certain properties of orthophosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), and hypophosphorous acid (H_3PO_2). A molecule of each of these acids contains three hydrogen atoms. Their structural formulas are:



orthophosphoric acid



phosphorous acid



hypophosphorous acid

It can be seen that in a molecule of orthophosphoric acid each hydrogen atom is bound to an oxygen atom. All these hydrogen atoms can be replaced by atoms of metals: hence, H_3PO_4 is tribasic. In a molecule of phosphorous acid, only two hydrogen atoms are bound directly to oxygen atoms and can be replaced with atoms of metals: this acid is dibasic. In a molecule of hypophosphorous acid, only one hydrogen atom is bound to an oxygen atom, which is why the acid is monobasic.

The use of structural formulas to depict the chemical structure of molecules is especially important when studying organic substances (see Vol. 2, Sec. 49).

Structural formulas reflect only the sequence of combination of atoms with one another, and not their mutual arrangement in space. Structural formulas may be used for depicting the chemical structure only for substances consisting of molecules. Many substances, however, consist not of molecules, but of atoms (for example, silicon carbide SiC), or have an ionic structure (for example, sodium chloride NaCl). The structure of such substances is determined by the kind of their **crystal lattice** and will be considered in greater detail in Chap. 5.

The theory of chemical structure explained the phenomenon of **isomerism**, which consists in the existence of compounds having the same qualitative and quantitative composition, but different properties. Such compounds were named **isomers.**

The phenomenon of isomerism will be treated in detail when studying organic compounds (see Vol. 2, Sec. 48), among which it is very widespread. It must be borne in mind, however, that isomerism is also encountered in inorganic substances. For instance, back in 1824, Justus Liebig found that the silver salts of fulminic acid AgONC and of cyanic acid AgNCO have the same composition, whereas the properties of these substances greatly differ. We shall also encounter examples of isomerism when studying complex compounds (see Vol. 2, Sec. 91).

In working out the theory of chemical structure, Butlerov did not pose the problem of elucidating the nature of the chemical bond, believing quite correctly that chemistry at that time was not yet ready to solve this problem. Indeed, an essential prerequisite for creating the theory of the chemical bond was the elucidation of the structure of an atom. Only after the main features of the electron structure of atoms became known did the possibility appear for developing such a theory. In 1916, the American physicochemist G. Lewis advanced the assumption that a chemical bond appears as a result of the formation of an electron pair simultaneously belonging to two atoms. This idea was the starting point for the development of the modern theory of the **covalent bond.** In the same year 1916, the German scientist W. Kossel assumed that when two atoms interact, one of them gives up and the other accepts electrons. The first atom transforms into a positively charged ion, and the second into a negatively charged one. It is exactly the mutual electrostatic attraction of the ions produced that results in the formation of a stable compound. The further development of Kossel's ideas resulted in the creation of today's notions of the ionic **bond.**

39. Covalent Bond. The Method of Valence Bonds

We know that a stable molecule can form only provided that the potential energy of the system of interacting atoms diminishes. To describe the state of the electrons in a molecule, we ought to compile the Schrödinger equation for the relevant system of electrons and atomic nuclei and find its solution corresponding to the minimum energy of the system. But, as indicated in Sec. 31, no success was achieved in obtaining an exact solution of the Schrödinger equation for many-electron systems. Therefore, a quantum-mechanical description of the structure of molecules is obtained, as for many-electron atoms, only on the basis of approximate solutions of the Schrödinger equation.

Such an approximate calculation was performed for the first time for a hydrogen molecule by W. Heitler and F. London in 1927. They first considered a system of two hydrogen atoms at a great distance from each other. For this condition, it is possible to take into account only the interaction of each electron with its "own" nucleus, and to disregard all other interactions (the mutual repulsion of the nuclei, the attraction of each electron to the "foreign" nucleus, the interaction between the electrons). It is therefore possible to express the dependence of the wave function of the system being considered on the coordinates and thus determine the density of the common electron cloud at any point of space. (We remind our reader that the density of an electron cloud is proportional to the square of the wave function—see Sec. 26.)

Heitler and London assumed further that the dependence of the wave function on the coordinates which they had found is also retained when the hydrogen atoms approach each other. Here, however, it is already necessary to take into consideration also the interactions (between the nuclei, between the electrons, etc.) that could be disregarded when the atoms are far apart. These additional interactions are treated as corrections ("disturbances") to the initial state of the electrons in the free hydrogen atoms.

As a result, Heitler and London obtained equations allowing them to find the dependence of the potential energy E of a system consisting of two hydrogen atoms on the distance r between the nuclei of these atoms. It was found that the results of the calculations depend on whether the spins of the interacting electrons are identical (parallel) or opposite (antiparallel). When the spins are identical

(Fig. 26, curve *a*), approaching of the atoms leads to a continuous growth in the energy of the system. Energy must be spent in this case to bring the atoms closer together. Hence, such a process is not profitable from the energy viewpoint, and no chemical bond appears between the atoms. When the spins are opposite (Fig. 26, curve *b*), approaching of the atoms to a certain distance r_0 is attended by diminishing of the system's energy. When $r = r_0$, the system has the lowest potential energy, i.e. is in the most stable state; further approaching of the atoms again leads to a growth in the energy. But this is exactly what signifies that with opposite spins of the atom electrons a molecule of H_2 is formed, i.e. a stable system of two hydrogen atoms at a definite distance from each other.

The formation of a chemical bond between the hydrogen atoms is the result of mutual penetration ("overlapping") of the electron clouds when the interacting atoms approach each other (Fig. 27). This overlapping causes the density of the negative electric charge in the internuclear space to grow. The positively charged atomic nuclei are attracted to the region of electron cloud overlapping. This attraction predominates over the mutual repulsion of the electrons with a like charge, and the result is the formation of a stable molecule.

The calculated values of the internuclear distance and the binding energy in a hydrogen molecule obtained by Heitler and London (and later determined more exactly by other investigators) were found to be close to the experimentally established values. This signified that the approximations used by Heitler and London in solving the Schrödinger equation do not introduce noticeable errors and can be considered as justified. Thus, the investigation conducted by Heitler and London made possible the conclusion that the chemical bond in a hydrogen molecule is achieved by the formation of a pair of electrons with opposite spins belonging to both atoms. The process of "pairing" of the electrons in the formation of a

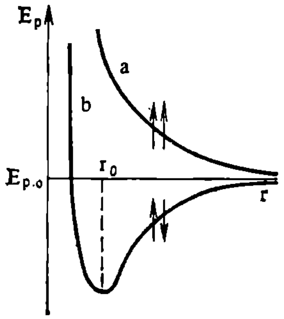


Fig. 26. Energy of a system consisting of two hydrogen atoms:
a—with parallel electron spins; *b*—with antiparallel electron spins; E_0—energy of system consisting of two uninteracting hydrogen atoms; r_0—internuclear distance in a hydrogen molecule

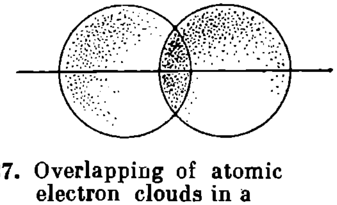
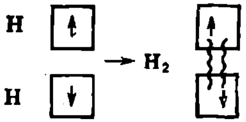


Fig. 27. Overlapping of atomic electron clouds in a hydrogen molecule

hydrogen molecule can be depicted by the following diagram:



The wavy lines in the diagram show that each electron in a hydrogen molecule occupies a place in the quantum boxes of both atoms, i.e. travels in the force field produced by two force centres—the nuclei of the hydrogen atoms.

Such a two-electron bond between two centres is called a **covalent bond** (or, sometimes, an **electron pair bond**).

The concepts of the mechanism of chemical bond formation developed by Heitler and London using the example of the hydrogen molecule were extended to more intricate molecules. The theory of the chemical bond developed on this basis was named the **method of valence bonds** (the **VB method**). This method gave a theoretical substantiation of the most important properties of the covalent bond and made it possible to understand the structure of a great number of molecules. Although, as we shall see on a later page, this method is not universal and sometimes cannot describe correctly the structure and properties of molecules (see Sec. 45), it played a great role in the development of the quantum-mechanical theory of the chemical bond and has not lost its significance to date.

The VB method is based on the following propositions:

1. A covalent chemical bond is formed by two electrons with antiparallel spins, this electron pair belonging to two atoms.

Combinations of such two-electron bonds between two centres reflecting the electron structure of a molecule are known as **electron dot formulas** (or **Lewis electron formulas**).

2. The strength of a covalent bond grows with an increasing degree of overlapping of the interacting electron clouds.

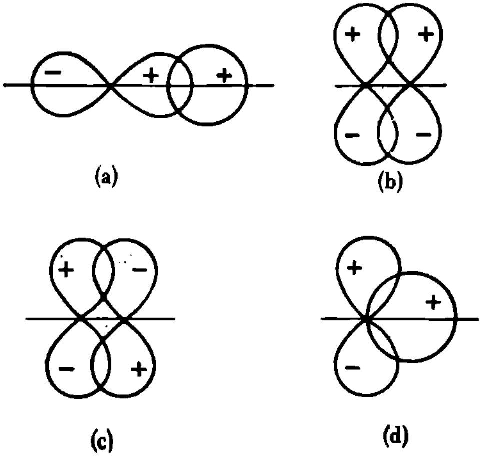
When assessing the degree of overlapping of the electron clouds, the signs of the electron wave functions must be taken into account. Since electrons possess wave properties, then upon the interaction of two electrons, a common "electron wave" is formed. Where the amplitudes of the initial waves have the same signs, their summation yields a net wave with an amplitude having a greater absolute value than the initial amplitudes. Conversely, where the amplitudes of the initial waves have different signs, their summation yields a net wave with an amplitude having a smaller absolute value—the waves will "damp" each other. But, as we have already indicated, the part of the amplitude of an electron wave is played by the wave function ψ (see Sec. 26). Consequently, in the regions of space where the wave functions of the interacting electrons have identical signs, the absolute value of the wave function for the net electron cloud formed will be greater than the values of ψ for the isolated atoms. The quantity ψ^2, i.e. the density of the electron cloud, will also grow. Here **positive overlapping** of the electron clouds occurs that results in mutual attraction of the nuclei. In the regions of space where the signs of the wave functions of the interacting electrons are opposite, the absolute value of the net wave function will be smaller than in the isolated atoms. Here the quantity ψ^2 and, accordingly, the density of the electron cloud, will diminish. In this case, we have to do with **negative overlapping** resulting in the mutual repulsion of the nuclei.

Some possible variants of electron cloud overlapping with indication of the signs of the relevant wave functions are depicted in Fig. 28.

The electron dot formulas are usually depicted as follows. The electrons in the outer electron layer are designated by dots around the chemical symbol of the atom. The electrons shared by two atoms are depicted by dots placed between their chemical symbols. A double or a triple bond is designated respectively by two or three pairs of shared dots. Using these symbols, we can represent the formation of a hydrogen molecule as follows:

$$H\cdot + \cdot H \rightarrow H:H$$

This formula shows that when two hydrogen atoms combine into a molecule, each of the atoms acquires a stable two-electron shell like the electron shell of the helium atom.



(a) (b)

(c) (d)

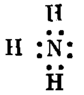
Fig. 28. Different variants of electron cloud overlapping:
a and *b*—positive overlapping; *c*—negative overlapping; *d*—net overlapping equal to zero

Similar formulas can be used to show the formation of a nitrogen molecule:

$$:\underset{\cdot}{\dot{N}}\cdot + \cdot\underset{\cdot}{\dot{N}}: \rightarrow :N:::N:$$

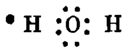
When two nitrogen atoms combine into a molecule, three pairs of electrons are shared (a **triple bond**). As a result, the outer shell of each atom is built up to the stable eight-electron configuration of the neon atom.

The structure of the molecules of some compounds such as ammonia, water, carbon dioxide, and methane can be depicted by the formulas:



$$\begin{matrix} & H & \\ H & :\ddot{\underset{\cdot\cdot}{N}}: & \\ & H & \end{matrix}$$

ammonia

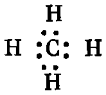


$$\bullet H :\ddot{\underset{\cdot\cdot}{O}}: H$$

water

$$\ddot{\underset{\cdot\cdot}{O}}: \; :C: \; :\ddot{\underset{\cdot\cdot}{O}}$$

carbon dioxide

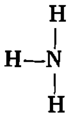


$$\begin{matrix} & H & \\ H & :\ddot{\underset{\cdot\cdot}{C}}: & H \\ & H & \end{matrix}$$

methane

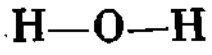
In the ammonia molecule, each of the three hydrogen atoms is bound to the nitrogen atom by a pair of shared electrons (one electron from the hydrogen atom and the other from the nitrogen atom). Thus, the nitrogen has an eight-electron outer shell, while the nucleus of each hydrogen atom is surrounded by two electrons forming a stable "helium" shell. The hydrogen atoms in the water and methane molecules have identical shells. In the carbon dioxide molecule, where the carbon atom is bound to each of the oxygen atoms by two pairs of electrons (a **double bond**), all three atoms have eight-electron outer shells.

Inspection of the above electron dot formulas shows that each pair of electrons binding two atoms corresponds to one line depicting a valence bond in structural formulas:



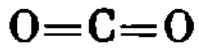
$$\begin{matrix} & H \\ & | \\ H - & N \\ & | \\ & H \end{matrix}$$

ammonia



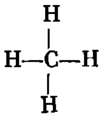
$$H-O-H$$

water



$$O=C=O$$

carbon dioxide



$$\begin{matrix} & H & \\ & | & \\ H - & C & - H \\ & | & \\ & H & \end{matrix}$$

methane

The number of such shared electron pairs binding an atom of a given element to other atoms or, in other words, the number of covalent bonds formed by an atom is called the **covalence** of the element in the relevant compound. Thus, the covalence of nitrogen in the molecules N_2 and NH_3 is three, that of oxygen in the molecules H_2O and CO_2 is two, and that of carbon in the molecules CH_4 and CO_2 is four.

40. Non-Polar and Polar Covalent Bond

If a diatomic molecule consists of atoms of a single element as, for instance, the molecules H_2, N_2, and Cl_2, then each electron cloud formed by a shared pair of electrons and responsible for a covalent bond is distributed symmetrically in space relative to the nuclei of both atoms. In such cases, a covalent bond is called **non-polar** or **homopolar.** If a diatomic molecule consists of atoms of different elements, the common electron cloud is displaced towards one of the atoms so that asymmetry appears in the distribution of the charge. In such cases, a covalent bond is called **polar** or **heteropolar.**

To assess the ability of an atom of a given element to attract a shared electron pair, the quantity known as the **relative electronegativity** is used. The greater the electronegativity of an atom, the stronger does it attract a shared electron pair. In other words, when a covalent bond is formed between two atoms of different elements, the common electron cloud is displaced to the atom having a higher electronegativity. This displacement grows with an increasing difference between the electronegativities of the interacting atoms. The values of the electronegativities of the atoms of selected elements with respect to the electronegativity of fluorine, which is taken equal to four, are given in Table 6*.

Table 6

Relative Electronegativity of Atoms

H						
2.1						
Li	Be	B	C	N	O	F
0.98	1.5	2.0	2.5	3.07	3.50	4.0
Na	Mg	Al	Si	P	S	Cl
0.93	1.2	1.6	1.8	2.2	2.6	3.0
K	Ca	Ga	Ge	As	Se	Br
0.91	1.04	1.8	1.8	2.1	2.5	2.8
Rb	Sr	In	Sn	Sb	Te	I
0.89	0.99	1.5	1.8	1.8	2.1	2.6

A glance at Table 6 shows that the electronegativity changes regularly depending on the position of an element in the periodic table. Each period begins with elements having the lowest electronegativ-

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* The relative electronegativity of an atom is not a strictly constant quantity: it depends both on the valence displayed by the atom in the relevant compound and on the atoms of what other elements the given atom combines with. Therefore, the data contained in Table 6 can serve only for an assessment of the direction of displacement of the electrons in the formation of molecules.

ity—typical metals, and terminates (before the noble gases) in elements having the highest electronegativity, i.e. typical non-metals. The electronegativity of elements belonging to the same subgroup tends to diminish with a growth in the nucleus charge. Thus, with a growth in the metallic properties of an element, its electronegativity lowers; with a growth in the non-metallic properties of an element, its electronegativity increases.

In the formation of a polar covalent bond, the common electron cloud is displaced and the average density of the negative electric charge is higher near an atom with a greater electronegativity and lower near one with a smaller electronegativity. As a result, the first atom acquires an excess negative charge, and the second atom an excess positive one. These charges are called the **effective charges** of the atoms in a molecule.

For example, in a hydrogen chloride molecule, the shared electron pair is displaced towards the more electronegative chlorine atom, which acquires an effective negative charge equal to 0.17 of the charge of an electron. The hydrogen atom acquires an effective positive charge of the same magnitude. Hence, the molecule HCl is a polar molecule. It can be considered as a system of two charges equal in magnitude, but opposite in sign, at a definite distance from each other. Such systems are known as electric **dipoles**. Although the net charge of a dipole is zero, an electric field is formed in the space surrounding it as shown in Fig. 29. The strength of this field is proportional to the **dipole moment** μ of the molecule, which is the product of the absolute value of the charge q of an electron and the distance l between the centres of the positive and negative charges in the

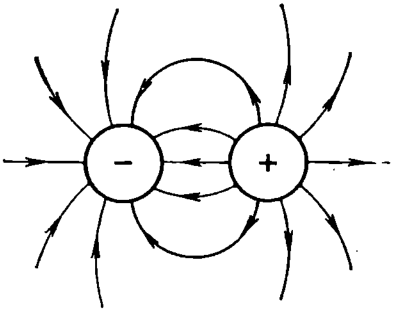

Fig. 29. Electric field of a dipole.
The arrows show the directions of the field lines

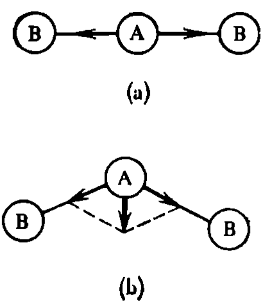

Fig. 30. Dipole moments of individual bonds in type AB_2 molecules of different structure:
a—linear structure; *b*—V-shaped structure; the thick middle arrow shows the vector of the molecule's net dipole moment

molecule (the separation distance):

$$\mu = ql$$

The dipole moment of a molecule is a quantitative measure of its polarity. The dipole moments of molecules are usually measured in **debyes** (D)*: 1 D = 3.33×10^{-30} C·m.

A molecule is more polar, the more the shared electron pair is displaced towards one of the atoms, i.e. the higher are the effective charges of the atoms and the greater is the length of the dipole. Consequently, in a series of similarly constructed molecules, the dipole moment grows with an increase in the difference between the electronegativities of the atoms forming a molecule. For instance, the dipole moments of HCl, HBr, and HI are respectively 1.04, 0.79, and 0.38 D, which is associated with the reduction in the difference between the electronegativities of the atoms when transferring from HCl to HBr and HI (see Table 6).

Polyatomic molecules may also be non-polar—with a symmetrical distribution of the charges, or polar—with an asymmetrical distribution of the charges. In the latter case, the dipole moment of a molecule will differ from zero. A definite dipole moment can be ascribed to each bond in a polyatomic molecule that characterizes the polarity of this bond. Here account must be taken not only of the magnitude of the dipole moment, but also of its direction, i.e. the dipole moment of each bond should be treated as a vector. Hence, the net dipole moment of the molecule as a whole may be considered equal to the vector sum of the dipole moments of the individual bonds. A dipole moment is usually considered to be directed from the positive end of the dipole to its negative one.

The dipole moments of molecules can be found experimentally by measuring certain macroscopic properties of the relevant substance, for example, its permittivity**. The values of the dipole moments found in this way contain important information on the geometrical structure of the relevant molecules.

Figure 30 shows as an example possible shapes of a type AB_2 molecule; the vectors of the dipole moments of the individual bonds A—B are depicted by arrows directed from A to B. With a linear structure (Fig. 30*a*), the dipole moments of the two bonds A—B equal in magnitude are opposite in direction. Consequently, the dipole moment of such a molecule will be zero. With a V-shaped structure (Fig. 30*b*), the vector sum of the dipole moments of the two bonds

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* This unit was named in honour of the Dutch physicist Peter Debye known for his works in the field of solid state physics, X-ray structural analysis, and the theory of polar liquids.

** The **permittivity** of a substance is defined as the number showing how many times the interaction between charges in a medium of the given substance is weaker than in a vacuum.

A—B differs from zero. Such a molecule has a dipole moment and is polar. This is why the presence or absence of a dipole moment in a type AB_2 molecule permits us to draw a conclusion on its geometrical structure. For example, the fact that the molecule CO_2 is non-polar, while the molecule SO_2 has a dipole moment ($\mu = 1.61$ D) indicates the linear structure of the first molecule and the V-shaped structure of the second one.

Figure 31 shows possible shapes of a type AB_3 molecule. If the molecule is constructed in the form of a plane triangle (Fig. 31*a*), the vector sum of the dipole moments of the individual bonds is zero—the molecule is non-polar. If the molecule has a pyramidal structure (Fig. 31*b*), its net dipole moment differs from zero—the molecule is polar. This allows us to arrive at the conclusion that the molecule BF_3 whose dipole moment is zero has a plane structure, whereas the polar molecule NH_3 ($\mu = 1.46$ D) is constructed in the form of a pyramid*.

The polarity of molecules appreciably affects the properties of the substances they form. Polar molecules tend to orient themselves relative to one another with oppositely charged ends. A consequence of such dipole-dipole interaction is the mutual attraction of polar molecules and strengthening of the bonds between them. This is why substances formed of polar molecules have, as a rule, higher melting and boiling points than substances whose molecules are non-polar.

When a substance consisting of polar molecules or having an ionic structure is dissolved in a liquid also consisting of polar molecules, electrostatic forces of dipole-dipole or ion-dipole interaction appear between the molecular dipoles of the solvent and the molecules or crystals of the solute that facilitate disintegration of the solute into ions (see

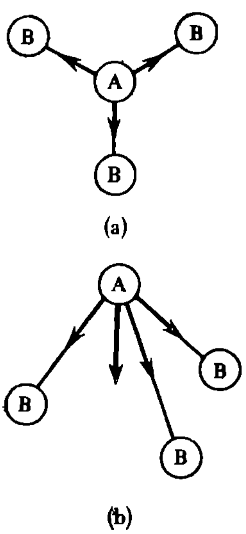

Fig. 31. Dipole moments of individual bonds in type AB_3 molecules:
a—plane triangle; *b*—pyramid; the thick arrow shows the vector of the molecule's net dipole moment

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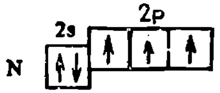
* It must be borne in mind that the magnitude of the dipole moment of a molecule is affected not only by the polarity of the individual bonds and the geometrical structure of the molecule, but also by the presence of unshared electron pairs in the hybrid orbitals (see p. 145).

Sec. 83). Hence, liquids consisting of polar molecules display properties of **ionizing solvents**, i.e. promote the electrolytic dissociation of the substances dissolved in them. For instance, hydrogen chloride dissolves both in water and in benzene, but its solutions in water are good conductors of an electric current, which points to the virtually complete dissociation of the molecules of HCl into ions, whereas solutions of HCl in benzene do not have an appreciable electrical conductance.

41. Ways of Forming a Covalent Bond

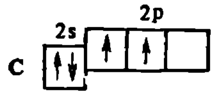
We have already mentioned that a shared electron pair producing a covalent bond can be formed at the expense of unpaired electrons present in the unexcited interacting atoms. This is what occurs, for instance, in the formation of molecules such as H_2, HCl, and Cl_2. Here each of the atoms has one unpaired electron. When two atoms interact, a shared electron pair is produced—a covalent bond is formed.

An unexcited nitrogen atom has three unpaired electrons:

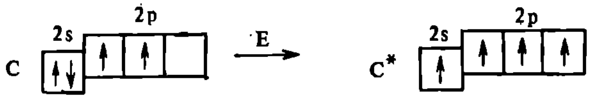


Consequently, a nitrogen atom can participate in the formation of three covalent bonds at the expense of the unpaired electrons. This is exactly what happens, for example, in the molecules N_2 or NH_3, in which the covalence of nitrogen is three.

The number of covalent bonds may also exceed the number of unpaired electrons in an unexcited atom, however. For example, in the normal (ground) state, the outer electron layer of a carbon atom has the structure:

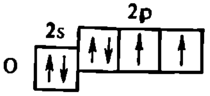


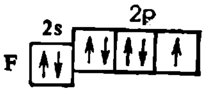
A carbon atom can form two covalent bonds at the expense of the unpaired electrons present in it. At the same time, characteristic of carbon are compounds in which each of its atoms is bound to the neighbouring ones by means of four covalent bonds (for example, CO_2 and CH_4). This is possible owing to the fact that when a certain amount of energy is spent, one of the 2*s* electrons in an atom can be transferred to the 2*p* sublevel. As a result, the atom passes over to an excited state, and the number of unpaired electrons grows. Such a process of excitation attended by "unpairing" of electrons can be depicted as follows (the excited state is indicated by an asterisk at the symbol of the element):



Now the outer electron layer of the carbon atom contains four unpaired electrons. Consequently, an excited carbon atom can participate in the formation of four covalent bonds. The increase in the number of covalent bonds produced is attended by the liberation of a greater amount of energy than is used to transfer the atom to the excited state.

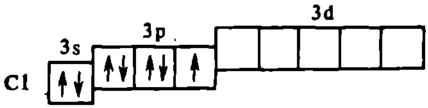
If the excitation of an atom leading to an increase in the number of unpaired electrons is associated with very great expenditures of energy, these expenditures are not compensated by the energy of formation of new bonds. Such a process as a whole is not profitable from the energy viewpoint. For example, oxygen and fluorine atoms have no free orbitals in their outer electron layer:



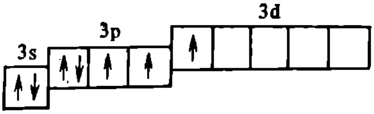


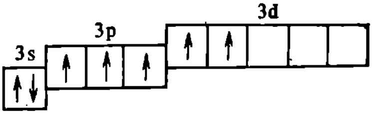
Here the number of unpaired electrons can grow only as a result of one of the electrons passing over to the next energy level, i.e. to the state 3*s*. Such a transition, however, is associated with a very great expenditure of energy that is not compensated by the energy liberated in the appearance of new bonds. Therefore, an oxygen atom can form not more than two covalent bonds at the expense of its unpaired electrons, and a fluorine atom only one. Indeed, these elements are characterized by a constant covalence equal to two for oxygen and to one for fluorine.

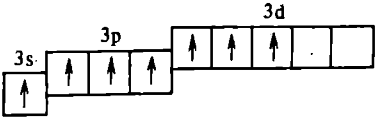
Atoms of elements of the third and following periods have in their outer electron layer a *d* sublevel to which the *s* and *p* electrons of the outer layer may pass upon excitation. Consequently, additional possibilities of increasing the number of unpaired electrons appear here. For instance, a chlorine atom having one unpaired electron in the unexcited state



may pass over, when a certain energy is spent, to the excited state (Cl*) characterized by three, five, or seven unpaired electrons:

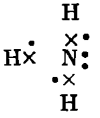




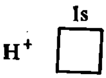


Thus, unlike the fluorine atom, a chlorine atom can participate in the formation of not only one, but also three, five, or seven covalent bonds. For example, in chlorous acid $HClO_2$, the covalence of chlorine is three, in chloric acid $HClO_3$ it is five, and in perchloric acid $HClO_4$ it is seven. Similarly, a sulphur atom also having an unoccupied 3*d* sublevel can pass to excited states with four or six unpaired electrons and participate, consequently, in the formation of not only two, as for oxygen, but also four or six covalent bonds. This is exactly the reason why compounds exist in which sulphur displays a covalence equal to four (SO_2, SCl_4) or six (SF_6).

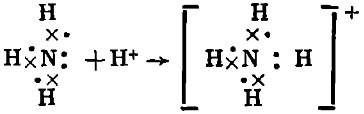
Covalent bonds often appear also at the expense of the paired electrons in the outer electron layer of an atom. Let us consider, for example, the electron structure of an ammonia molecule:



Here the dots stand for electrons originally belonging to the nitrogen atom, and the crosses stand for the electrons originally belonging to the hydrogen atoms. Of the eight outer electrons of the nitrogen atom, six form three covalent bonds and are common for the nitrogen atom and the hydrogen atoms. But two electrons belong only to the nitrogen and form an **unshared electron pair.** Such a pair of electrons can also participate in the formation of a covalent bond with another atom if the outer electron layer of this atom has a free orbital. An unfilled 1*s* orbital is present, for example, in the hydrogen ion H^+, which in general is deprived of electrons:



Therefore, when a molecule of NH_3 interacts with a hydrogen ion, a covalent bond is produced between them. The unshared pair of electrons of the nitrogen atom becomes common for the two atoms, as a result of which an *ammonium* ion NH_4^+ is formed:



$$H\overset{\bullet}{\times}\overset{\overset{H}{\times\bullet}}{\underset{\underset{H}{\bullet\times}}{N}}: + H^+ \rightarrow \left[H\overset{\bullet}{\times}\overset{\overset{H}{\times\bullet}}{\underset{\underset{H}{\bullet\times}}{N}} : H \right]^+$$

Here, the covalent bond was produced at the expense of the pair of electrons originally belonging to one atom (to the **donor** of the electron pair), and of the free orbital of another atom (the **acceptor** of the electron pair). This is the so-called **donor-acceptor** way of forming a covalent bond. In the example considered, the nitrogen atom is the donor of the electron pair, and the hydrogen atom is its acceptor.

It has been established experimentally that the four N—H bonds in the ammonium ion are equivalent in all respects. It follows that a bond formed in the donor-acceptor way does not differ in its properties from a covalent bond produced at the expense of the unpaired electrons of the interacting atoms*.

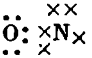
Another example of a molecule containing bonds formed in the donor-acceptor way is the dinitrogen oxide molecule N_2O.

The structural formula of this compound was previously depicted as follows:

$$O{=}N{\equiv}N$$

According to this formula, the central nitrogen atom is joined to the neighbouring atoms by five covalent bonds so that its outer electron layer contains ten electrons (five electron pairs). But such a conclusion contradicts the electron structure of the nitrogen atom because its outer *L* layer contains only four orbitals (one *s* and three *p* orbitals) and cannot accommodate more than eight electrons. Therefore, the above structural formula cannot be acknowledged as correct.

Let us consider the electron structure of dinitrogen oxide. We shall designate the electrons belonging to the separate atoms alternately with dots or crosses. The oxygen atom having two unpaired electrons forms two covalent bonds with the central nitrogen atom:



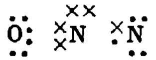
$$\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}\!:\,{}_{\times}^{\times}\overset{\times\times}{\underset{\times}{N}}{}_{\times}$$

The central nitrogen atom still has an unpaired electron which it

---

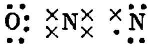
* A covalent bond formed in the donor-acceptor way is sometimes called for short a donor-acceptor bond. By this term, we should understand, however, not a special *kind* of bond, but only a definite *way* of forming a covalent bond.

uses to form a covalent bond with the second nitrogen atom:



$$\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}\!:\ {}^{\times}_{\times}\underset{\times}{\overset{\times\times}{N}}\ \ {}^{\times}_{\bullet}\underset{\bullet\bullet}{\overset{\bullet\bullet}{N}}$$

Thus, the outer electron layers of the oxygen atom and the central nitrogen atom are filled: here stable eight-electron configurations are formed. But the outer electron layer of the extreme nitrogen atom accommodates only six electrons. Hence, this atom can be the acceptor of another electron pair. The adjacent central nitrogen atom, on the other hand, has an unshared electron pair and can play the role of a donor. This results in the formation of another covalent bond between the nitrogen atoms in the donor-acceptor way:



$$\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}}\!:\ {}^{\times}_{\times}N^{\times}_{\times}\ \ {}^{\times}_{\bullet}\underset{\bullet\bullet}{\overset{\bullet\bullet}{N}}$$

Now each of the three atoms forming the molecule N_2O has a stable eight-electron structure of its outer layer. If we denote the covalent bond formed in the donor-acceptor way by an arrow directed from the donor atom to the acceptor one, as is customary practice, then the structural formula of dinitrogen oxide can be represented as follows:

$$O{=}N \rightrightarrows N$$

Thus, in dinitrogen oxide, the covalence of the central nitrogen atom is four, and of the extreme one is two.

The above examples show that atoms have a variety of possibilities for forming covalent bonds: at the expense of unpaired electrons of an unexcited atom, at the expense of unpaired electrons appearing as a result of excitation of an atom ("unpairing" of electron pairs), and, finally, in the donor-acceptor way. Nevertheless, the total number of covalent bonds which a given atom can form is restricted. It is determined by the total number of valence orbitals, i.e. of orbitals whose use for the formation of covalent bonds is advantageous from the energy viewpoint. Quantum-mechanical calculations show that such orbitals include the *s* and *p* orbitals of the outer electron layer and the *d* orbitals of the preceding layer. Sometimes, as we have seen when considering the examples of the chlorine and sulphur atoms, the valence orbitals may also include the *d* orbitals of the outer layer.

The atoms of all the second-period elements have four orbitals in their outer electron layer with *d* orbitals being absent in the preceding layer. Consequently, the valence orbitals of these atoms can accommodate not more than eight electrons. This means that the maximum covalence of the second-period elements is four.

Atoms of elements of the third and following periods can use not only the *s* and *p* orbitals, but also the *d* orbitals to form covalent bonds. Compounds of *d* elements are known in which the *s* and *p* orbitals of the outer electron layer and all five *d* orbitals of the preceding layer participate in the formation of covalent bonds. In such cases, the covalence of the relevant element reaches nine.

The ability of atoms to participate in the formation of a restricted number of covalent bonds has been called the **saturability** of covalent bonding.

42. Direction of a Covalent Bond

The properties of a molecule, its ability to enter into chemical reactions with other molecules (its **reactivity**) depend not only on the strength of the chemical bonds in the molecule, but to a considerable extent on its dimensional structure too. The branch of chemistry studying the geometrical structure of molecules, their structure in space, is called **stereochemistry.**

We have already mentioned on an earlier page (Sec. 39) that the

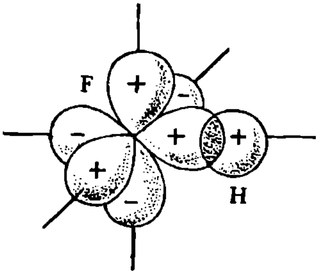


Fig. 32. Overlapping of the 2*p*-electron cloud of the fluorine atom and the 1*s*-electron cloud of the hydrogen atom in the formation of a sigma bond in the molecule HF:
+and —are the signs of the wave function

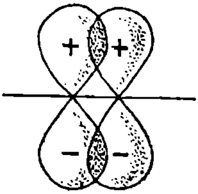


Fig. 34. Overlapping of the *p*-electron clouds in the formation of a pi bond

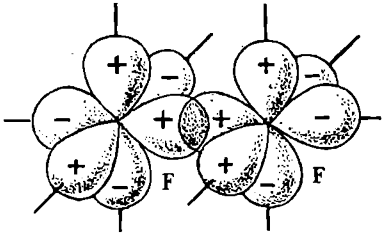


Fig. 33. Overlapping of the 2*p*-electron clouds of the fluorine atoms in the formation of a sigma bond in the molecule F_2

formation of a covalent bond is a result of overlapping of the valence electron clouds of the interacting atoms. But such overlapping is possible only with a definite mutual orientation of the electron clouds; here the overlap region is arranged in a definite direction with respect to the interacting atoms. In other words, a covalent bond is **directional.**

For instance, in a hydrogen molecule (see Fig. 27, p. 125), the atomic *s*-electron clouds overlap near the imaginary straight line joining the nuclei of the interacting atoms (i.e. near the **bond axis**). A covalent bond formed in such a way is known as a **σ (sigma) bond.**

If *p*-electron clouds are oriented along the bond axis, they can also participate in the formation of a sigma bond. Thus, in the molecule HF (Fig. 32), a covalent sigma bond is produced owing to overlapping of the 1*s*-electron cloud of the hydrogen atom and the 2*p*-electron cloud of the fluorine atom. The chemical bond in the molecule F_2 (Fig. 33) is also a sigma bond; it is formed by the 2*p*-electron clouds of the two fluorine atoms.

When *p*-electron clouds oriented perpendicularly to the bond axis (Fig. 34) interact, two overlap regions are formed at both sides of this axis instead of a single region. Such a covalent bond is called a **π (pi) bond.**

Let us consider the formation of the nitrogen molecule N_2. Each nitrogen atom has three unpaired 2*p* electrons whose electron clouds

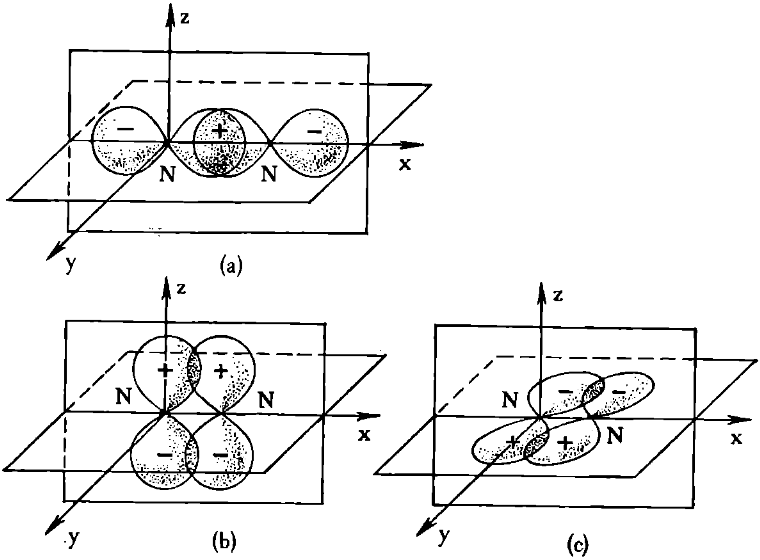


Fig. 35. Overlapping of the 2*p*-electron clouds in the molecule N_2:
a—sigma bond; *b* and *c*—pi bonds

are oriented in three mutually perpendicular directions:

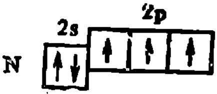


Figure 35 shows the overlapping of the p-electron clouds in the molecule N_2 (for convenience of illustration, the overlapping of the p_x, p_y, and p_z clouds is shown separately). Nitrogen atoms are bound in the molecule N_2 by three covalent bonds. But these bonds are not equivalent: one of them is a sigma bond, and the other two are pi bonds. The non-equivalence of the bonds in the nitrogen molecule is confirmed by the fact that their bond dissociation energy is different.

The concept of covalent bonds being directional makes it possible to explain the mutual arrangement of the atoms in polyatomic molecules. Thus, in the formation of a water molecule, the electron clouds of the two unpaired $2p$ electrons of the oxygen atom overlap with the $1s$-electron clouds of the two hydrogen atoms. This overlapping is shown schematically in Fig. 36. Since the p-electron clouds of the oxygen atom are oriented in mutually perpendicular directions, the molecule H_2O has, as shown in Fig. 36, a V-shaped structure, and we can expect the angle between the O—H bonds to be 90 deg.

The molecule NH_3 formed upon the interaction of the three p electrons of a nitrogen atom with the s electrons of three hydrogen atoms (Fig. 37) has the shape of a pyramid with the nitrogen atom at its apex and the hydrogen atoms at the apices of its base. In this case too, we can expect the angles between the N—H bonds to be 90 deg.

These conclusions on the mutual arrangement of the atoms in the molecules NH_3 and H_2O correspond to actual facts. The consid-

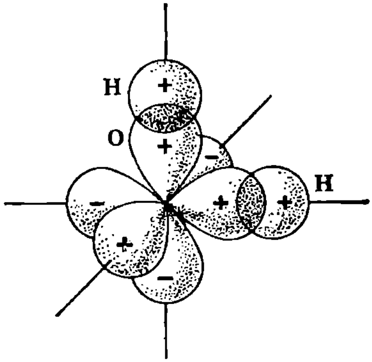


Fig. 36. Formation of chemical bonds in a water molecule

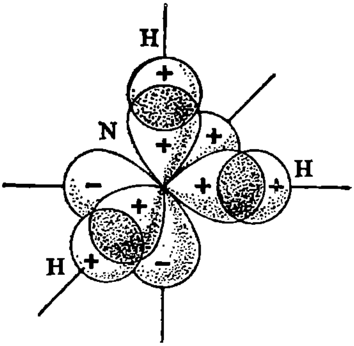


Fig. 37. Formation of chemical bonds in an ammonia molecule

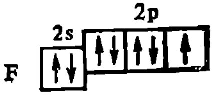
erable polarity of a water molecule ($\mu = 1.84$ D) and an ammonia molecule ($\mu = 1.48$ D) and also the data of structural investigations indicate that the molecule H_2O has a V-shaped structure, while the molecule NH_3 is constructed in the shape of a pyramid. The angles between the bonds, however (the valence angles) differ from 90 deg: in the water molecule the angle HOH is 104.3 deg, and in the ammonia molecule the angle HNH is 107.8 deg.

To explain why the valence angles in the molecules H_2O and NH_3 differ from 90 deg, we must take into account that the stable state of a molecule is the result of its geometrical structure and an arrangement of the electron clouds of the outer shells of the atoms in space such that corresponds to the minimum potential energy of the molecule. This is the reason why in the formation of a molecule, the shapes and mutual arrangement of the atomic electron clouds change in comparison with their shapes and mutual arrangement in the free atoms. The result is a more complete overlapping of the valence electron clouds and, consequently, the formation of stronger covalent bonds. Within the limits of the method of valent bonds, such an alteration in the electronic structure of an atom is considered on the basis of the notion of **atomic orbital hybridization.**

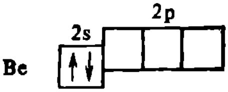
43. Hybridization of Atomic Electron Orbitals

The method of hybridization of atomic orbitals proceeds from the assumption that in the formation of a molecule, instead of the initial atomic s-, *p*-, and *d*-electron clouds, equivalent "blended" or **hybrid** electron clouds are formed that are stretched out in a direction towards the neighbouring atoms, the result being their more complete overlapping with the electron clouds of these atoms. Such deformation of the electron clouds requires the expenditure of energy. But more complete overlapping of the valence electron clouds leads to the formation of a stronger chemical bond and, consequently, to an additional gain in energy. If this gain in energy is sufficient to more than compensate the expenditure of energy for the deformation of the initial atomic electron clouds, such hybridization in the long run leads to diminishing of the potential energy of the molecule formed and, consequently, to an increase in its stability.

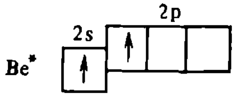
Let us consider as an example of hybridization the formation of a molecule of beryllium fluoride BeF_2. Each fluorine atom in this molecule has one unpaired electron that participates in the formation of a covalent bond:



A beryllium atom in the unexcited state ($1s^22s^2$) has no unpaired electrons:



Therefore, to participate in the formation of chemical bonds, the beryllium atom must pass over into the excited state ($1s^22s^12p^1$):



The excited atom Be* that is formed has two unpaired electrons: the electron cloud of one of them corresponds to the state 2*s*, and of the other to the state 2*p*. When these electron clouds overlap with the *p*-electron clouds of the two fluorine atoms, covalent bonds may form (Fig. 38).

As already mentioned above, however, when a certain amount of energy is spent, two equivalent hybrid orbitals (*sp* hybrids) may be formed instead of the initial *s* and *p* orbitals of the beryllium atom. The shape and arrangement of these orbitals are shown in Fig. 39,

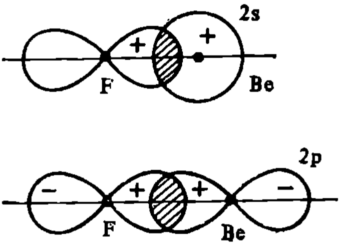


Fig. 38. Overlapping of the 2*p*-electron clouds of the fluorine atoms with the 2*s*- and 2*p*-electron clouds of the beryllium atom (each bond is shown separately).
The regions of overlapping of the electron clouds are hatched

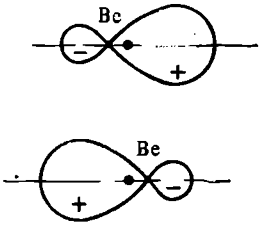


Fig. 39. Shape (schematic representation) and mutual arrangement of the hybrid *sp*-electron clouds of the beryllium atom (separately for each hybrid orbital)

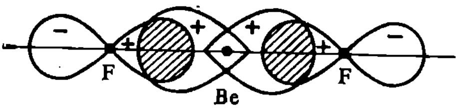


Fig. 40. Formation of chemical bonds in the molecule BeF_2.
To simplify the drawing, the hybrid *sp*-electron clouds of the beryllium atom are shown only partly, without the small lobes

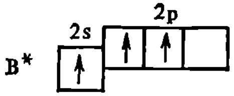
from which it can be seen that the *sp* hybrid orbitals are extended in opposite directions.

The overlapping of the hybrid *sp*-electron clouds of the beryllium atom with the *p*-electron clouds of the fluorine atoms is shown in Fig. 40. The extended shape of the hybrid orbitals results in more complete overlapping of the interacting electron clouds, and, consequently, stronger chemical bonds are formed. The energy liberated in the formation of these bonds is greater than the overall expenditures of energy for the excitation of the beryllium atom and hybridization of its atomic orbitals. This is why the process of formation of the BeF_2 molecule is favourable from the energy viewpoint.

The above example of hybridization of one *s* and one *p* orbital leading to the formation of two *sp* orbitals is called ***sp* hybridization.** A glance at Fig. 39 shows that the *sp* orbitals are oriented in opposite directions, which results in a linear structure of the molecule. Indeed, the molecule BeF_2 is linear, and both Be—F bonds in this molecule are equivalent in all respects.

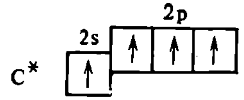
Other cases of atomic orbital hybridization are also possible, but the number of hybrid orbitals formed always equals the total number of initial atomic orbitals participating in hybridization. For example, in the hybridization of one *s* and two *p* orbitals (***sp*^{2} hybridization**—read "ess-pea-two"), three equivalent sp^2 orbitals are formed. In this case, the hybrid electron clouds are arranged in directions that are in one plane and oriented at 120 deg to one another (Fig. 41). It is evident that the formation of a planar triangular molecule corresponds to this type of hybridization.

The boron trifluoride molecule BF_3 is an example of a molecule with sp^2 hybridization. Here instead of the initial one *s* and two *p* orbitals of an excited boron atom



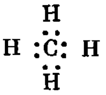
three equivalent sp^2 orbitals are formed. Therefore, the molecule BF_3 is constructed in the shape of a regular triangle with the boron atom at its centre and the fluorine atoms at its corners. All three B—F bonds in the molecule BF_3 are equivalent.

If one *s* and three *p* orbitals participate in hybridization (***sp*^{3} hybridization**), the result is the formation of four sp^3 hybrid orbitals extended towards the corners of a tetrahedron, i.e. oriented at 109 deg 28 min relative to one another (Fig. 42). Such hybridization occurs, for instance, in an excited carbon atom



when a methane molecule CH_4 is being formed. This is why the methane molecule has the shape of a tetrahedron, all four C—H bonds in this molecule being equivalent.

Let us return to the consideration of the water molecule structure. Its formation is attended by sp^3 hybridization of the oxygen atomic orbitals. It is exactly for this reason that the valence angle HOH in the H_2O molecule (104.3 deg) is close not to 90 deg, but to the tetrahedral angle (109.5 deg). The slight deviation of this angle from 109.5 deg can be understood if we take into account the non-equivalence of the state of the electron clouds encompassing the oxygen atom in the water molecule. Indeed, in a methane molecule (I)



$$\begin{array}{c} H \\ H\;:\overset{..}{\underset{..}{C}}:\;H \\ H \end{array}$$

I

$$H\;:\overset{..}{\underset{..}{O}}:\;H$$

II

all eight electrons occupying the sp^3 hybrid orbitals in the carbon atom participate in the formation of the covalent bonds C—H. This underlies the symmetrical distribution of the electron clouds with respect to the carbon atom nucleus. In a water molecule (II), only four of the eight electrons occupying the sp^3 hybrid orbitals of the oxygen atom form O—H bonds, while two electron pairs remain unshared, i.e. belong only to the oxygen atom. This leads to a certain asymmetry in the distribution of the electron clouds surrounding the oxygen atom and, consequently, to deviation of the angle between the O—H bonds from 109.5 deg.

In the formation of an ammonia molecule, sp^3 hybridization of the atomic orbitals of the central atom (nitrogen) also occurs. It is exactly for this reason that the valence angle HNH (107.8 deg) is close to a tetrahedral one. The slight deviation of this angle from 109.5 deg is explained, as for the water molecule, by asymmetry in the distribution of the electron clouds about the nucleus of the nitrogen atom: of four electron

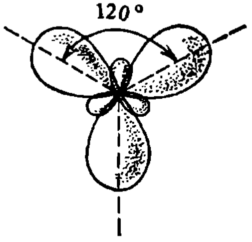


Fig. 41. Mutual arrangement of hybrid sp^2-electron clouds

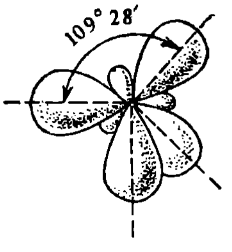


Fig. 42. Mutual arrangement of hybrid sp^3-electron clouds

pairs, three participate in the formation of the N—H bonds, and one remains unshared.

Examination of Figs. 39, 41, and 42 reveals that the hybrid electron clouds are displaced relative to the atomic nucleus. Therefore, the centre of the electric charge of an unshared electron pair on a hybrid orbital does not coincide with the position of the atomic nucleus, i.e. with the centre of the positive charge in the atom. Such a displacement of the charge of the unshared electron pair results in the appearance of a dipole moment appreciably contributing to the total dipole moment of the relevant molecule. It thus follows that the polarity of a molecule depends not only on the polarity of the individual bonds and their mutual arrangement (see Sec. 40), but also on the presence of unshared electron pairs in the hybrid orbitals and on the arrangement of these orbitals in space.

In elements of the third and following periods, *d* orbitals can also participate in the formation of hybrid electron clouds. Of special significance is sp^3d^2 hybridization, when one *s*, three *p*, and two *d* orbitals participate in the formation of the hybrid orbitals. Here, six equivalent hybrid orbitals are formed that are extended towards the apices of an octahedron. The octahedral structure of the molecule SF_6, the ions $[SiF_6]^{2-}$, $[Fe(CN_6)]^{3-}$, and many others is explained by the sp^3d^2 hybridization of the atomic orbitals in the central atom.

44. Multiple-Centre Bonds

As the method of valence bonds developed, it was found that sometimes all the electron dot formulas possible for a given molecule agree poorly with the properties of this molecule established experimentally: the true properties of the molecule are found to be intermediate between the ones ascribed to it by each individual formula. In such cases, the structure of a molecule can be expressed by a set of several electron dot formulas. This way of describing molecules has been named the **method of superposition of electron dot formulas.**

Let us consider, for example, the electron structure of a molecule of nitric acid HNO_3. The hydrogen atom in this molecule is bonded to an oxygen atom by means of a covalent bond:

$$\mathrm{H}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\cdot$$

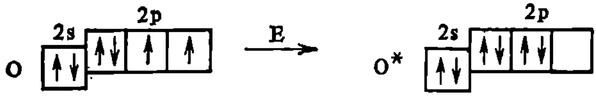
The oxygen atom forms a covalent bond with the nitrogen atom at the expense of its remaining unpaired electron:

$$\mathrm{H}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}{:}\underset{\cdot\cdot}{\overset{\cdot}{\mathrm{N}}}\cdot$$

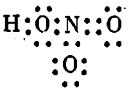
The two unpaired electrons of the nitrogen atom, in turn, participate in the formation of two covalent bonds with the second oxygen atom:

$$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\underset{\cdot\cdot}{\mathrm{N}}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}$$

We see that the nitrogen atom still has an unshared pair of electrons, so that here the nitrogen, playing the role of an electron pair donor, is capable of forming another covalent bond in the donor-acceptor way. The acceptor of the nitrogen atom electron pair in the molecule HNO_3 is the third oxygen atom that passes into the excited state in which it has one free $2p$ orbital*:

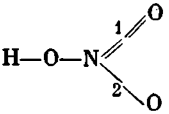


We thus get the following electron dot formula for a nitric acid molecule:



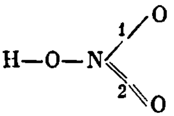
$$\begin{array}{l}\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\underset{\cdot\cdot}{\mathrm{N}}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\\ \qquad :\underset{\cdot\cdot}{\mathrm{O}}:\end{array}$$

or the valence formula



(I)

According to the last formula (in which the nitrogen-oxygen bonds are numbered), the bonds 1 and 2 in the molecule HNO_3 are not identical: the bond 1 is double, and the bond 2 is single. Actually, however, these bonds in all respects (the bond energy, the internuclear N—O distances, etc.) are equivalent. This signifies that the structure of the molecule HNO_3 can with equal right be described by the similar valence formula



(II)

Each of the formulas (I) and (II) does not accurately describe the structure and properties of the nitric acid molecule. The true struc-

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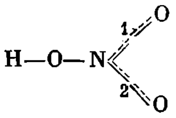
* Here the excitation of the atom is expressed not in unpairing of electrons as occurred in the cases treated earlier (see Sec. 41), but in the transition of an unpaired electron to an orbital occupied by another unpaired electron. Such a transition requires the expenditure of energy. We remind our reader that Hund's rule (see Sec. 32) does not forbid such excited states, but only indicates their lower stability in comparison with the ground (unexcited) state of an atom.

ture of this molecule is intermediate between formulas (I) and (II) and can be considered as the result of combination (or superposition) of these formulas.

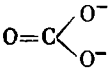
It does not follow from what has been said above that nitric acid can actually exist in the two different forms (I) and (II). A description of the molecule HNO_3 with the aid of a set of electron dot or valence formulas only means that each of these formulas taken separately does not correspond to the true electronic structure of the molecule.

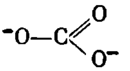
The distribution of the electrons in a nitric acid molecule can be represented more accurately by the following formula:

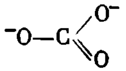


The dash lines here signify that one of the shared electron pairs belongs completely neither to bond 1 (formula I) nor to bond 2 (formula II), but is distributed to an equal extent between these bonds. In other words, this electron pair belongs not to two, but to three atoms—the nitrogen atom and two oxygen atoms. The bond it forms, consequently, is not a two-centre one, but a **three-centre bond.**

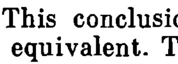
The electron structure of the ion CO_3^{2-} can be represented by three valence formulas







each of which indicates that the carbon-oxygen bonds are not equivalent. This conclusion is wrong: all three C—O bonds in the CO_3^{2-} ion are equivalent. The true structure of this ion can be considered as the result of superposition of all three formulas given above, i.e. can be represented in the following form:



Here, as previously, the dash lines indicate that one of the shared electron pairs is distributed to an equal extent between all three C—O bonds. This electron pair belongs to all four atoms in the ion CO_3^{2-}. The covalent bond it forms is a **four-centre** one.

Examples of molecules with multiple-centre bonds are also the molecules of benzene C_6H_6 (see Vol. 2, Sec. 53) and diborane B_2H_6 (see Vol. 2, Sec. 103).

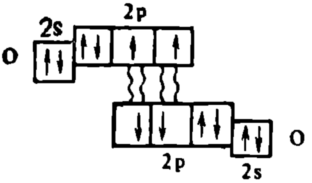
As indicated in Sec. 39, one of the propositions of the VB method consists in that all chemical bonds are between two centres. Actually, however, as shown by the examples considered above, it is sometimes more correct to treat two-electron bonds as multiple-centre ones

45. The Method of Molecular Orbitals

As indicated in the preceding sections, the VB method permits us to understand the ability of atoms to form a definite number of covalent bonds, explains the directivity of a covalent bond, and gives a satisfactory description of the structure and properties of a great number of molecules. In a number of cases, however, the VB method cannot explain the nature of chemical bonds formed or leads to improper conclusions on the properties of molecules.

Thus, according to the VB method, all covalent bonds are achieved by a shared pair of electrons. Back at the end of the 19th century, however, it was found that there exists a quite strong molecular hydrogen ion H_2^+: the bond dissociation energy here is 256 kJ/mol. No electron pair can be formed here, however, because the ion H_2^+ contains only one electron. Hence, the VB method does not explain satisfactorily the existence of the ion H_2^+.

Further, the formation of the oxygen molecule O_2 is described by the VB method to be the result of the production of two shared electron pairs:



According to this description, the molecule O_2 contains no unpaired electrons. The magnetic properties of oxygen, however, indicate that the molecule O_2 contains two unpaired electrons.

Each electron, because of its having a spin, sets up an intrinsic magnetic field. The direction of this field is determined by the direction of the spin so that the magnetic fields set up by two paired electrons mutually compensate each other. This is why molecules containing only paired electrons do not produce an intrinsic magnetic field. Substances consisting of such molecules are **diamagnetic**—they are ejected from a magnetic field. Conversely, substances whose molecules contain unpaired electrons have an intrinsic magnetic field and are **paramagnetic**; such substances are pulled into a magnetic field.

Oxygen is a paramagnetic substance, which points to the presence of unpaired electrons in its molecule.

It is also difficult to explain on the basis of the VB method why the detaching of electrons from certain molecules results in strengthening of the chemical bond. For example, the bond dissociation energy in the molecule F_2 is 155 kJ/mol, whereas in the molecular ion F_2^+

it is 320 kJ/mol. Similar quantities for the molecule O_2 and the molecular ion O_2^+ are, respectively, 494 and 642 kJ/mol.

The above and many other facts are explained more satisfactorily on the basis of the **method of molecular orbitals** (the **MO method**). We know that the state of the electrons in an atom is described by quantum mechanics as a collection of atomic electron orbitals (atomic electron clouds). Each such orbital is characterized by a definite set of atomic quantum numbers. The MO method proceeds from the assumption that the state of the electrons in a molecule can also be described as a collection of molecular electron orbitals (molecular electron clouds), a definite set of molecular quantum numbers corresponding to each molecular orbital (MO). As in any other many-electron system, the Pauli exclusion principle (p. 91) holds for a molecule, so that each molecular orbital can accommodate a maximum of two electrons, and they must have opposite spins.

A molecular electron cloud may be concentrated near one of the atomic nuclei in the molecule: such an electron virtually belongs to one atom and does not participate in the formation of chemical bonds. In other cases, the predominating part of an electron cloud is in a region of space near two atomic nuclei: this corresponds to the formation of a two-centre chemical bond. In the most general case, however, an electron cloud belongs to several atomic nuclei and participates in the formation of a **multiple-centre** chemical bond. Thus, from the viewpoint of the MO method, a two-centre bond is only a particular case of a multiple-centre chemical bond.

The main problem of the MO method is the finding of the wave functions describing the state of the electrons in the molecular orbitals. The most widespread variant of this method, whose abbreviated name is "the MO LCAO method" (molecular orbitals, linear combination of atomic orbitals), solves this problem as follows.

Suppose that the electron orbitals of interacting atoms are characterized by the wave functions $\psi_1, \psi_2, \psi_3, \ldots$, etc. The wave function ψ corresponding to a molecular orbital is then assumed to be represented in the form of the sum

$$\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \ldots$$

where $C_1, C_2, C_3, \ldots$ are numerical coefficients.

To understand the physical meaning of such an approach, let us remember that the wave function ψ corresponds to the amplitude of the wave process characterizing the state of an electron (see Sec. 26). It is general knowledge that when, for example, sound or electromagnetic waves interact, their amplitudes are summated. We can see that the above equation is equivalent to the assumption that the amplitudes of a molecular "electron wave" (i.e. the molecular wave function) are also formed by the summation of the amplitudes of the interacting atomic "electron waves" (i.e. by the summation of the atomic wave functions). Under the influence of the force fields of the nuclei and electrons of neighbouring atoms, however, the wave function of each atomic electron changes in comparison with the initial wave function of this electron in an isolated atom. In the MO LCAO method, these changes are taken into account by introducing the coefficients C_1, C_2, etc. so that when finding a molecular wave function not the initial, but the altered amplitudes, namely, $C_1\psi_1$, $C_2\psi_2$, etc. are summated.

Let us determine the appearance of the molecular wave function ψ formed as a result of the interaction of the wave functions (ψ_1 and ψ_2) of the 1*s* orbitals of two identical atoms. To do this, we shall find the sum $C_1\psi_1 + C_2\psi_2$. In the given case, both atoms being considered are identical, so that the coefficients C_1 and C_2 are equal in magnitude ($C_1 = C_2 = C$), and the problem consists in determining the sum $C(\psi_1 + \psi_2)$. Since the constant coefficient C does not affect the form of the required molecular wave function, but only changes its magnitudes, we shall limit ourselves to finding the sum $\psi_1 + \psi_2$.

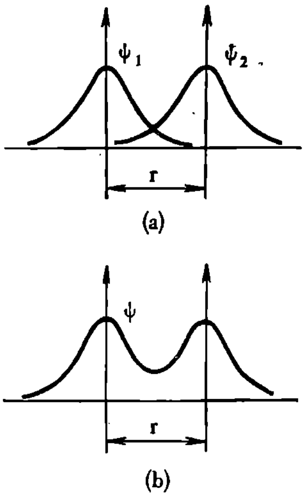
For this purpose, we shall arrange the nuclei of the interacting atoms at the distance from each other (r) at which they are in the molecule and shall depict the wave functions of the 1*s* orbitals of these atoms (Fig. 43*a*). Each of these functions has the form shown in Fig. 9*a* (p. 81). To find the molecular wave function ψ, we shall summate the quantities ψ_1 and ψ_2. The result is the curve shown in Fig. 43*b*. It can be seen that the values of the molecular wave function ψ in the space between the nuclei are greater than those of the initial atomic wave functions. But the square of a wave function characterizes the probability of finding an electron in the corresponding region of space, i.e. the density of the electron cloud (see Sec. 26). Hence the growth of ψ in comparison with ψ_1 and ψ_2 means that in the formation of an MO the density of the electron cloud grows in the internuclear space. The result is the appearance of forces of attraction of the positively charged atomic nuclei to this region—a chemical bond is formed. This is why an MO of the type considered above is called a **bonding** one.

In the given case, the region of increased electron density is near the bond axis so that the formed MO is of the sigma type. Accordingly, a bonding MO obtained as a result of interaction of two atomic 1*s* orbitals is designated $\sigma^b 1s$.

The electrons in a bonding MO are called **bonding electrons**.

As indicated on p. 82, the wave function of a 1*s* orbital has a constant sign. For an individual atom, the choice of this sign is arbitrary: up to now we considered it to be positive. But when two atoms interact, the signs of the wave functions of their 1*s* orbitals may be different. Hence, in addition to the case shown in Fig. 43*a* where the signs of both wave functions are the same, the case is also possible when the signs of the wave functions of the interacting 1*s* orbitals are different. This case is depicted in Fig. 44*a*: here the wave function of the 1*s* orbital of one atom is positive, and of the other is negative. Summation of these wave functions yields the curve shown in Fig. 44*b*. A molecular orbital formed upon such interaction is characterized by diminishing of the magnitude of the wave function in the internuclear space in comparison with its value in the initial atoms: a point appears on the bond axis at which the value of the wave function and, consequently, of its square, is even equal to zero. This signifies that in the case being considered, the density of the electron cloud in the space between the atoms also decreases. As a result, the attraction of each atomic nucleus in a direction towards the internuclear region of space is weaker than in the opposite direction, i.e. forces appear that lead to mutual repulsion of the nuclei. Here, consequently, no chemical bond appears. The MO formed in this case is called an **antibonding** molecular orbital (σ^{ab} 1*s*), and the electrons in it—**antibonding electrons.**

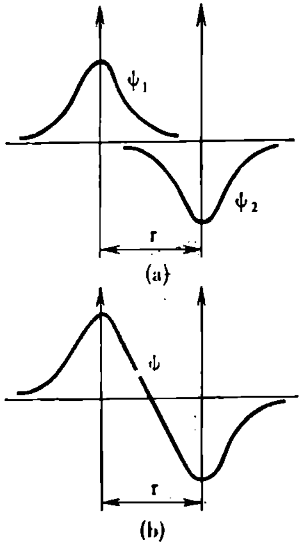
The transition of electrons from the atomic 1*s* orbitals to a bonding MO leading to the appearance of a chemical bond is attended by the liberation of energy. Conversely, the transition of electrons from atomic 1*s* orbitals to an antibonding MO requires the expenditure of energy. Thus, the energy of the electrons in the orbital σ^{b} 1*s* is lower, and in the orbital σ^{ab} 1*s* is higher than in the atomic



(a)

(b)

Fig. 43. Formation of a bonding MO from atomic 1*s* orbitals



(a)

(b)

Fig. 44. Formation of an antibonding MO from atomic 1*s* orbitals

1*s* orbitals. This relation of the energies is shown in Fig. 45, which depicts both the initial 1*s* orbitals of two hydrogen atoms and the molecular orbitals σ^b 1*s* and σ^{ab} 1*s*. It can be assumed approximately that the same amount of energy is evolved in the transition of a 1*s* electron to a bonding MO that must be spent to transfer it to an antibonding MO.

We know that in the most stable (unexcited) state of an atom, the electrons occupy atomic orbitals characterized by the lowest possible energy. In exactly the same way, the most stable state of a molecule is achieved when the electrons occupy MO's corresponding to the minimum energy. Therefore, in the formation of a hydrogen molecule, both electrons will pass over from the atomic 1*s* orbitals to the bonding molecular orbital σ^b 1*s* (Fig. 46). According to

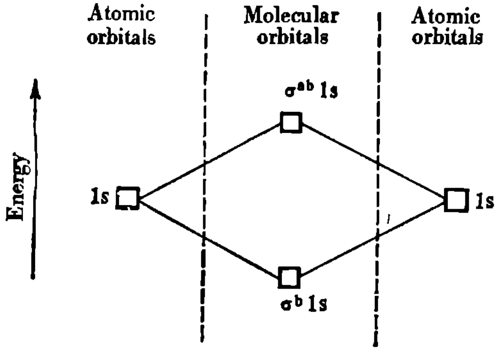


Fig. 45. Energy-level diagram showing the formation of MO's upon the interaction of the 1*s* orbitals of two identical atoms

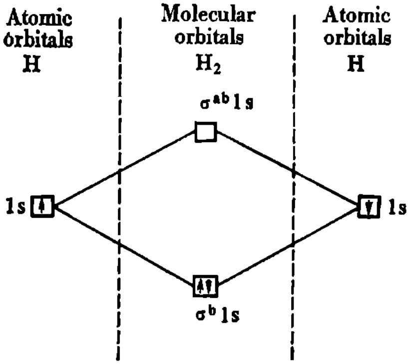


Fig. 46. Energy-level diagram showing the formation of a hydrogen molecule

the Pauli exclusion principle, the electrons in one MO must have opposite spins. Using the symbols denoting the arrangement of electrons in the atomic and molecular orbitals, the formation of a hydrogen molecule can be represented as follows:

$$2H[1s^1] \rightarrow H_2[(\sigma^b 1s)^2] \quad +435 \text{ kJ}$$

In the VB method, the multiplicity of a bond is determined by the number of shared electron pairs: a bond formed by one shared pair of electrons is considered to be a single one, a bond formed by two shared pairs—a double one, and so on. Similarly, in the MO method, the multiplicity of a bond is determined according to the number of bonding electrons participating in its formation: two bonding electrons correspond to a single bond, four bonding electrons—to a double bond, and so on. Antibonding electrons compensate the action of the corresponding number of bonding electrons. For instance, if a molecule contains six bonding and two antibonding electrons, the number of bonding electrons is greater than that of the antibonding ones by four, which corresponds to the formation of a double bond. Consequently, from the standpoint of the MO method, the chemical bond in the hydrogen molecule formed by two bonding electrons should be considered as a single bond.

Now it becomes clear why the stable molecular ion H_2^+ can exist. Upon its formation, the only electron passes over from the atomic orbital 1*s* to the bonding orbital $\sigma^b 1s$, which is attended by the liberation of energy (Fig. 47) and can be expressed as follows:

$$H[1s^1] + H^+ \rightarrow H_2^+[(\sigma^b 1s)^1] \quad +259 \text{ kJ}$$

The molecular ion He_2^+ (Fig. 48) has altogether three electrons. The bonding molecular orbital $\sigma^b 1s$ can accommodate, according to the Pauli exclusion principle, only two electrons. Therefore, the third electron occupies the antibonding orbital $\sigma^{ab} 1s$. Thus, the number of bonding electrons here is one greater than the number of antibonding ones. Consequently, the ion He_2^+ should be stable as regards its energy. Indeed, the existence of the ion He_2^+ has been confirmed experimentally, and it has been found that its formation is attended by the liberation of energy:

$$He[1s^2] + He^+[1s^1] \rightarrow He_2^+[(\sigma^b 1s)^2(\sigma^{ab} 1s)^1] \quad +293 \text{ kJ}$$

Conversely, the hypothetic molecule He_2 must be unstable from the energy viewpoint because here of the four electrons that must be accommodated in the MO's, two will occupy bonding and two antibonding MO's. Hence, the formation of the molecule He_2 will not be accompanied by the liberation of energy. Indeed, molecules of He_2 have not been discovered experimentally.

In molecules of second-period elements, the MO's are formed as a result of the interaction of the atomic 2*s* and 2*p* orbitals. The participation of the inner 1*s* electrons in the formation of a chemical bond is negligibly small here. Thus, Fig. 49 contains an energy-level diagram showing the formation of the Li_2 molecule. Here there are two bonding electrons, which corresponds to the formation of a single bond. In the molecule Be_2, however, the number of bonding and antibonding electrons is the same, so that this molecule, like the molecule He_2, is unstable as regards its energy. Indeed. the molecule Be_2 has never been discovered.

An energy-level diagram showing the formation of MO's upon the interaction of atomic 2*p* orbitals is depicted in Fig. 50. Inspection of the figure reveals that six MO's are formed from the initial six 2*p* orbitals—three bonding and three antibonding ones. One bonding ($\sigma^b 2p$) and one antibonding ($\sigma^{ab} 2p$) orbitals belong to the sigma type: they are formed by the interaction of the atomic 2*p*

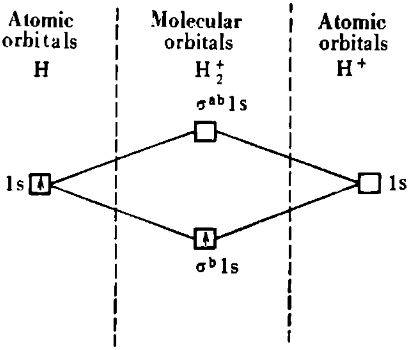


Fig. 47. Energy-level diagram showing the formation of a molecular ion of hydrogen H_2^+

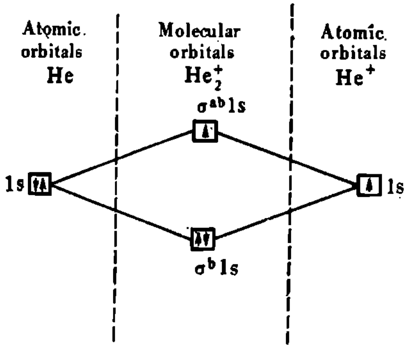


Fig. 48. Energy-level diagram showing the formation of a molecular ion of helium He_2^+

orbitals oriented along the bond axis. Two bonding ($\pi^b\,2p$) and two antibonding ($\pi^{ab}\,2p$) orbitals are formed by the interaction of the $2p$ orbitals oriented perpendicularly to the bond axis. These orbitals belong to the pi type. Figure 51 presents an energy-level diagram showing how the MO's are filled in the nitrogen molecule N_2. Here, the MO's must accommodate six $2p$ electrons of the two nitrogen atoms. They fill three bonding MO's, while all the antibonding MO's remain vacant. The total number of bonding electrons in the molecule N_2 is six, which corresponds to the formation of a triple bond.

In the oxygen molecule O_2 (Fig. 52), four $2p$ electrons of each atom participate in the formation of chemical bonds. Hence, altogether eight electrons must pass over to the MO's. Six of them occupy three bonding MO's, and two are accommodated on the antibonding molecular orbitals $\pi^{ab}\,2p$. Here, the number of bonding electrons exceeds the number of antibonding ones by four, and the bond is a

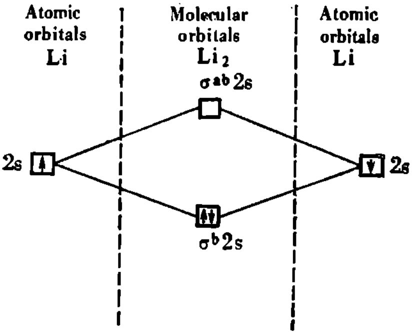


Fig. 49. Energy-level diagram showing the formation of a lithium molecule Li_2

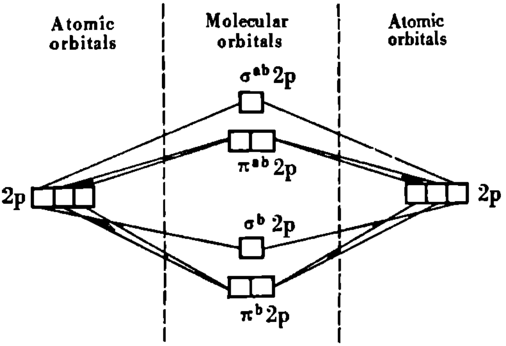


Fig. 50. Energy-level diagram showing the formation of MO's upon the interaction of the $2p$ orbitals of two identical atoms

double one. Both orbitals $\pi^{ab}\,2p$ are equivalent with respect to energy, and the electrons must be arranged here in accordance with Hund's rule (p. 95), which also remains true when applied to molecules. Therefore, each of the orbitals $\pi^{ab}\,2p$ is occupied by one electron, and in a way such that the spins of these electrons are parallel. It can be seen from the diagram in Fig. 52 that the molecule O_2 has two unpaired electrons, owing to which this molecule should be paramagnetic. As indicated on a previous page (p. 148), this is confirmed experimentally. Thus, the MO method explains the magnetic properties of molecular oxygen.

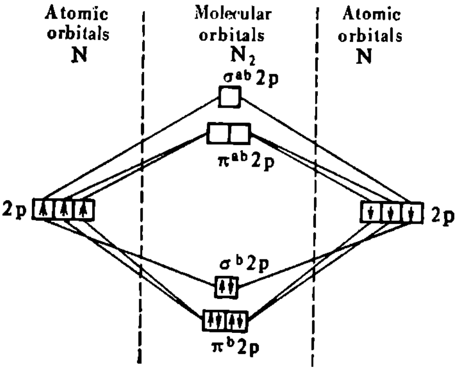


Fig. 51. Energy-level diagram showing the formation of a nitrogen molecule N_2

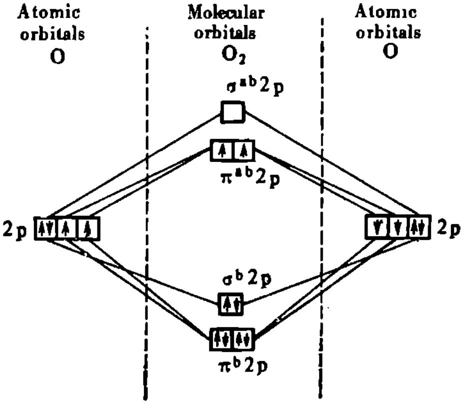


Fig. 52. Energy-level diagram showing the formation of an oxygen molecule O_2

When the ion O_2^+ is formed from the molecule O_2, the electron removed is the one having the maximum energy, i.e. it is in the antibonding molecular orbital $\pi^{ab}2p$. Diminishing of the number of antibonding electrons leads to a growth in the bond multiplicity (the number of bonding electrons becomes greater than the number of antibonding ones by five instead of four) and, consequently, to the formation of a stronger molecule. It is exactly for this reason that the dissociation energy of the molecular ion O_2^+ is higher than that of the molecule O_2 (see p. 149).

The formation of molecules consisting of different atoms is considered in a similar way by the MO method. Figure 53 contains an energy-level diagram showing the formation of a molecule of carbon monoxide CO. Here, four 2*p* electrons of the oxygen atom and two 2*p* electrons of the carbon atom pass over to MO's. The energy of the 2*p* electrons of the combining atoms is not the same: the charge of the oxygen atom nucleus is greater than that of the carbon atom nucleus so that the 2*p* electrons in the oxygen atom are attracted more strongly by the nucleus. This is why the arrangement of the oxygen atom 2*p* orbitals in Fig. 53 corresponds to a lower energy in comparison with the 2*p* orbitals of the carbon atom. The diagram shows that all six electrons participating in the formation of the bond are accommodated on three bonding MO's.

The presence in the CO molecule of six bonding electrons in the absence of antibonding electrons corresponds to the formation of a triple bond, as in the nitrogen molecule (see Fig. 51). This explains the considerable similarity in the properties of free nitrogen and carbon monoxide, for example, the close values of the dissociation

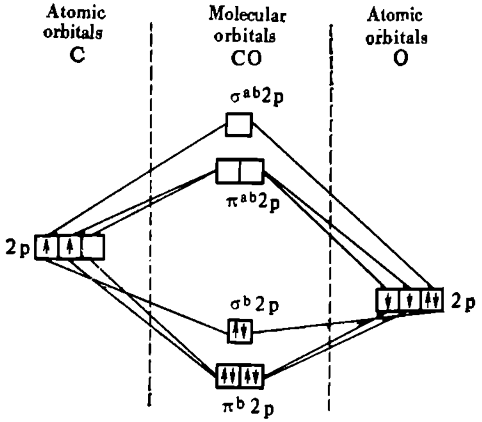


Fig. 53. Energy-level diagram showing the formation of a carbon monoxide molecule CO

energy of the molecules (N_2—945, and CO—1076 kJ/mol), of the internuclear distances in the molecules (0.110 and 0.113 nm, respectively), and of the melting points (63 and 68 K) and the boiling points (77 and 82 K).

The examples considered above show that the MO method successfully explains the structure and properties of molecules whose description with the aid of the VB method encounters appreciable difficulties.

46. Ionic Bond

A bond of this type is formed as a result of the mutual electrostatic attraction of oppositely charged ions. Ions may be simple, i.e., monatomic (for example, the cations Na^+, K^+ and the anions F^-, Cl^-), and complex, i.e. polyatomic (for example, the cation NH_4^+, the anions OH^-, NO_3^-, SO_4^{2-}). Monatomic ions having a positive charge are formed the easiest from atoms of elements having a low ionization potential; they include the metals of the main subgroups of groups I and II (see Tables 4 and 5 on pp. 106 and 107). The formation of monatomic negatively charged ions, on the contrary, is characteristic of the atoms of typical non-metals having a high affinity to an electron. Consequently, the alkali metal halides such as NaCl and CsF are typical compounds with an ionic type of bond.

Unlike the covalent bond, *the ionic bond is non-directional.* The explanation is that the electric field of an ion has spherical symmetry, i.e. diminishes with the distance according to the same law in any direction. This is why ions interact in the same way regardless of the direction. As we have already indicated on an earlier page (see Fig. 29 on p. 130), a system of two charges that are identical in magnitude but opposite in sign set up an electric field in the surrounding space. This signifies that two ions of opposite signs that have attracted each other retain their ability to interact electrostatically with other ions. This is another difference between the ionic and covalent types of bond: *an ionic bond does not have saturability.* Hence, a different number of ions of the opposite sign can be attached to a given ion. This number is determined by the relative dimensions of the interacting ions, and also by the fact that the forces of attraction of oppositely charged ions must predominate over the forces of mutual repulsion exerted between ions of the same sign.

The absence of directionality and saturability in an ionic bond is the reason why ionic molecules tend to associate, i.e. to combine with one another. At elevated temperatures, the kinetic energy of motion of the molecules predominates over the energy of their mutual attraction. This is why ionic compounds in the gaseous state exist mainly in the form of unassociated molecules. But upon lowering of the temperature, when the substance becomes a liquid and, especially, a solid, the association of ionic compounds manifests itself strongly. All ionic compounds in the solid state have not a molecular, but an ionic crystal lattice (see Chap. 5) in which each ion is surrounded by several ions of the opposite sign. All the bonds of a given ion with its neighbour ions are equivalent so that the entire crystal can be considered as a single giant "molecule".

As we have indicated in Sec. 34, atoms of non-metals are characterized by positive values of their affinity to an electron: the attachment of an electron to such an atom is attended by the liberation of energy. The attachment of a second electron to an atom of any non-metal, however, requires the expenditure of energy so that the formation of simple multiply charged anions (for instance, O^{2-}, N^{3-}) is not energetically favourable. For this reason, a "purely" ionic bond is not formed in compounds such as oxides (BaO, Al_2O_3, etc.) or sulphides (for example, ZnS and CuS). The chemical bond here is always of a partly covalent nature. At the same time, multiply charged polyatomic anions (such as SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}) may be energetically stable because the excess electrons are distributed among several atoms so that the effective charge of each of the atoms does not exceed the charge of an electron.

But even in typical ionic compounds, for example in the alkali metal halides, complete separation of the negative and positive charges (i.e. complete transition of an electron from one atom to another) does not occur. For instance, in a crystal of NaCl, the effective negative charge of the chlorine atom is only 0.94 of the charge of an electron. The sodium atom has a positive charge of the same magnitude.

The incomplete separation of the charges in ionic compounds can be explained by the mutual **polarization** of the ions, i.e. by their influence on one another that leads to deformation of the electron shells of the ions. Polarization is always caused by an electric field (see, for example, Fig. 54; the deformation of the electron shell of an ion in an electric field is depicted by the dash line) that displaces the electrons and atomic nuclei in opposite directions. Every ion, being a carrier of an electric charge, is a source of an electric field. Hence, oppositely charged ions interact and polarize each other.

The outer layer electrons experience the greatest displacement in polarization. We can consider in a first approximation that only the outer electron shell is deformed. The same electric field, however,

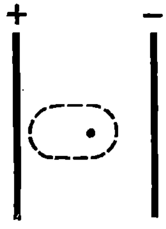


Fig. 54. Polarization of an ion in an electric field

deforms different ions to a different degree. In other words, the **polarizability** of various ions is different: the weaker the outer electrons are bound to the nucleus, the easier is an ion polarized and the stronger is it deformed in an electric field. For ions having an identical charge and a similar structure of their outer electron layer, the polarizability grows with an increase in the size of an ion because the outer electrons are farther and farther from the nucleus, are screened by a greater number of electron layers, and, as a result, are retained more weakly by the nucleus. Thus, the polarizability of alkali metal ions grows in the following order:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

In exactly the same way, the polarizability of halogen ions changes in the following order:

$$F^- < Cl^- < Br^- < I^-$$

The transformation of an atom into a positively charged ion always results in diminishing of its dimensions (see p. 104). In addition, the excess positive charge of a cation hinders the deformation of its outer electron clouds. Conversely, negatively charged ions always have greater dimensions than neutral atoms, while an excess negative charge results here in repulsion of the electrons and, consequently, in weakening of their bond to the nucleus. For these reasons, the polarizability of anions, as a rule, is considerably greater than that of cations.

The **polarizing power** of ions, i.e. their ability of exerting a deforming action on other ions, also depends on the charge and size of an ion. The greater the charge of an ion, the stronger is the electric field it produces. Hence, multiply charged ions have the greatest polarizing power. With the same charge, the strength of the electric field near an ion is the greater, the smaller are its dimensions. Consequently, the polarizing power of ions having the same charge and a similar electron structure diminishes with an increasing ionic radius. For instance, in the series of alkali metal cations, the polarizing power changes in an order which is the reverse of that in which the polarizability changes:

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

We have mentioned above that anions have a greater size than cations. As a result, anions, as a rule, have a smaller polarizing power than cations.

Thus, anions in comparison with cations are characterized by a strong polarizability and a weak polarizing power. Hence, when unlike ions interact, the negative ion is mainly subjected to polarization. The polarization of the positive ion may be disregarded in the majority of cases.

The influence of the size of an anion on its polarization, and also the influence of the size and charge of the cation, are illustrated by the diagram given in Fig. 55.

As a result of the polarizing action of a cation, the outer electron cloud of an anion is displaced (Fig. 56). What occurs is, as it were, a reverse transfer of part of the electron charge from the anion to the cation. This is exactly why the effective charges of the atoms in an ionic compound are less than a whole charge of an electron. Figure 56 also shows that owing to polarization, the electron clouds of the cation and the anion are incompletely separated and partly overlap, so that the bond between the atoms transforms from a purely ionic one into a greatly polar covalent bond. It thus follows that an ionic bond can be considered not as a special kind of bond, but as the limit case of a polar covalent bond.

The polarization of ions appreciably affects the properties of the compounds they form. Since an increase in polarization is attended by a growth in the degree of covalence of a bond, this affects the dissociation of salts in aqueous solutions. For example, barium chloride $BaCl_2$ belongs to strong electrolytes (see Sec. 84) and in aqueous solutions virtually completely decomposes into ions, while mercury chloride $HgCl_2$ does not practically dissociate into ions. The explanation is the strong polarizing action of the ion Hg^{2+} whose radius (0.112 nm) is noticeably smaller than that of the ion Ba^{2+} (0.138 nm).

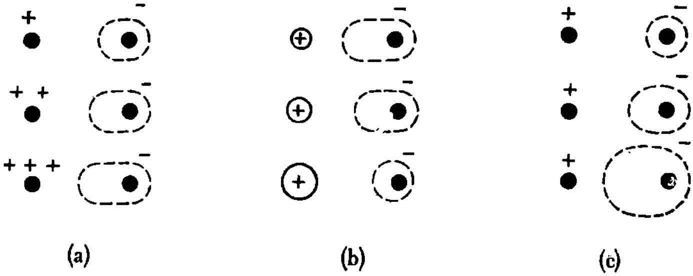


Fig. 55. Diagram showing the influence on the polarization of negative ions of:

a—the charge of the positive ion; *b*—the size of the positive ion; *c*—the size of the negative ion

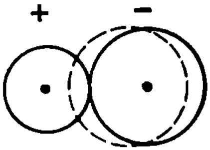


Fig. 56. Displacement of the electron cloud of an anion due to polarization: The position of the deformed electron cloud is shown by a dash line

The hydrogen ion H^+, which differs from all other ions in its much smaller size and the complete absence of electrons, has an especially high polarizing effect. For this reason, a hydrogen ion does not experience repulsion from an anion and can approach it up to a very small distance, entering its electron shell and causing its great deformation. For instance, the radius of the chloride ion Cl^- is 0.181 nm, while the distance between the nuclei of the chlorine and hydrogen atoms in the molecule HCl is only 0.127 nm. We shall see in the following that many acids in a number of their properties (stability, ability of dissociating in aqueous solutions into ions, oxidizing power) differ greatly from the salts they form. It is exactly the strong polarizing effect of the hydrogen ion that is one of the reasons of such differences.

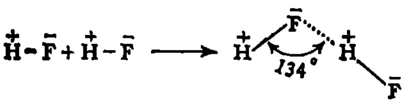
47. Hydrogen Bond

It was noted back in the 19th century that compounds in which the hydrogen atom is directly bound to atoms of fluorine, oxygen, and nitrogen, have a number of anomalous properties. This manifests itself, for instance, in the values of the melting and boiling points of such compounds. Customarily, the melting and boiling points rise with an increasing atomic mass of an element in a series of like compounds of elements of the same subgroup. This is explained by the growth in the mutual attraction of the molecules, which is associated with a growth in the size of the atoms and an increase in the dispersion interaction between them (see Sec. 48). For example, the melting points in the series HCl-HBr-HI are —114.2, —86.9, and —50.8 °C, respectively. A similar relationship is observed in the series H_2S-H_2Se-H_2Te. As shown by Figs. 57 and 58, however, hydrogen fluoride and water melt and boil at anomalously high temperatures.

It has been established at present that this and some other features of the above compounds are explained by the ability of the hydrogen atom, when bound to an atom of a highly electronegative element, to form one more chemical bond with another similar atom. This bond is known as a **hydrogen bond.**

The appearance of a hydrogen bond can be explained in a first approximation by the action of electrostatic forces. Thus, in the formation of a polar covalent bond between a hydrogen atom and a fluorine atom, which is highly electronegative, the electron cloud originally belonging to the hydrogen atom is greatly displaced towards the fluorine atom. As a result, the fluorine atom acquires a considerable effective negative charge, while the nucleus of the hydrogen atom (proton) at the "external" side relative to the fluorine atom is almost deprived of an electron cloud. Electrostatic attraction between the proton of the hydogen atom and the negatively charged fluorine atom leads to the formation of a hydrogen bond. The reason is that a hydrogen ion (proton) is capable of penetrating into the electron shells of other atoms because it has negligibly small dimensions and, unlike other cations, has no inner electron layers that are repelled by negatively charged atoms.

The formation of a hydrogen bond when two HF molecules interact can be represented as follows:



Here the dotted line designates a hyrogen bond, and the symbols "+" and "—" relate to the effective charges of the atoms.

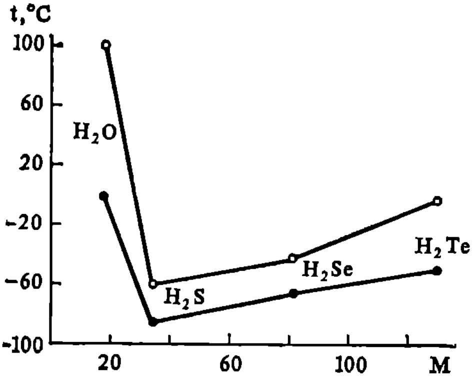


Fig. 57. Dependence of the melting (●) and boiling (○) points of hydrogen compounds of Group VI main subgroup elements on the molecular mass

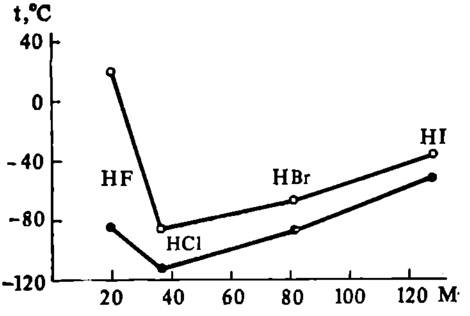


Fig. 58. Dependence of the melting (●) and boiling (○) points of hydrogen compounds of halides on the molecular mass

It is clear from what has been said above that the condition for the formation of a hydrogen bond is the high electronegativity of the atom that is directly bound to a hydrogen atom in a molecule. Only in this condition is the electron cloud of the hydrogen atom displaced to a sufficient extent towards the partner atom, and the latter acquires a high effective negative charge. It is exactly for this reason that the hydrogen bond is characteristic of compounds of the most electronegative elements: it manifests itself the greatest in compounds of fluorine and oxygen, weaker in nitrogen compounds, and still weaker in compounds of chlorine and sulphur.

The energy of a hydrogen bond is considerably lower than that of an ordinary covalent bond (150 to 400 kJ/mol). It is about 8 kJ/mol in nitrogen compounds and reaches about 40 kJ/mol in fluorine compounds. This energy, however, is sufficient to cause **association** of molecules, i.e. their combination into dimers (doubled molecules) or polymers, which sometimes exist not only in the liquid state of a substance, but are also retained when it transforms into a vapour. It is exactly the association of molecules hampering their breaking away from one another that is the reason for the anomalously high melting and boiling points of substances such as hydrogen fluoride, water, and ammonia. Other features of these substances due to the formation of hydrogen bonds and the association of molecules will be treated on following pages when studying separate compounds.

The hydrogen bond is the reason of certain important features of water—a substance playing a tremendous role in processes occurring in animate and inanimate nature. It also determines to a considerable extent the properties of such biologically important substances as proteins and nucleic acids.

5

THE STRUCTURE OF SOLIDS AND LIQUIDS

48. Intermolecular Interaction

When a substance is in the gaseous state, the particles forming it—molecules or atoms—move chaotically and are at great distances from one another (in comparison with their own dimensions) the predominating part of the time. As a result, the forces of interaction between them are negligibly small.

Matters are different when a substance is in a **condensed** state—liquid or solid. Here, the distances between the particles of the substance are small, and the forces of interaction between them are great. These forces retain the particles of a liquid or solid near one another. This is why substances in the condensed state, unlike gases, have a constant volume at a given temperature.

The forces retaining the particles of a liquid or solid near one another are of an electrical nature. But these forces differ quite appreciably depending on what the particles are—whether they are atoms of a metal or non-metal element, ions, or molecules.

If a substance is built up of atoms, but is not a metal, its atoms are usually bound to one another by a covalent bond. If the substance is a metal, then a part of the electrons of its atoms will be shared by all the atoms; these electrons travel freely between the atoms, binding them to one another. If the substance has an ionic structure, the ions forming it are retained near one another by forces of electrostatic attraction. The covalent and ionic bonds were treated in Chap. 4. The bond between particles in metals will be discussed in Vol. 2, Chap. 6. **Intermolecular** interaction occurs in substances with a molecular structure.

The forces of intermolecular interaction, also known as van-der-Waals forces, are weaker than covalent forces, but manifest themselves at greater distances. They are based on the electrostatic interaction of dipoles; the mechanism of the appearance of dipoles in various substances is different, however.

If a substance consists of polar molecules, for instance, molecules of H_2O or HCl, in the condensed state neighbouring molecular dipoles are oriented relative to each other with oppositely charged poles, and as a result their mutual attraction is observed. This kind of intermolecular interaction is called **orientational** or **dipole-dipole** interaction. The thermal motion of the molecules prevents their mutual orientation, hence the orientation effect weakens with increasing temperature.

In substances consisting of non-polar molecules, but that are capable of polarization, for instance CO_2, induced dipoles appear. The reason for their appearance usually consists in that each atom sets up near itself an electric field exerting a polarizing effect on the nearest atom of the adjacent molecule. The latter becomes polarized, and the induced dipole formed, in turn, polarizes the adjacent molecules. The result is the mutual attraction of the molecules. This **induction** interaction is also observed in substances with polar molecules, but it is usually considerably weaker than dipole-dipole interaction.

Finally, the motion of the electrons in atoms, and also the vibration of the nuclei and the associated continuous change in the mutual position of electrons and nuclei lead to the appearance of instantaneous dipoles. As shown by quantum mechanics, instantaneous dipoles appear in solids and liquids in agreement, the closest portions of neighbouring molecules next to each other are oppositely charged, which leads to their attraction. This phenomenon, called **dispersion** interaction, occurs in all substances in the condensed state. Particularly, it underlies the transition of the noble gases at low temperatures into the liquid state.

The relative magnitude of the intermolecular forces considered above depends on the polarity and the polarizability of the molecules of the substance. The greater the polarity of the molecules, the greater are the orientation forces. An increase in the deformability is attended by weaker bonds of the outer electrons of the atoms, i.e. the dispersion forces are more considerable in larger atoms. Thus, in a series of substances of the same type, the dispersion interaction grows with an increase in the dimensions of the atoms forming the molecules of these substances. For example, in HCl, 81% of all the intermolecular interaction falls to the part of the dispersion forces, in HBr this quantity is 95%, and in HI it is 99.5%. The induction forces are almost always small.

49. The Crystalline State of a Substance

Most substances have a crystalline structure in the solid state. It is a simple matter to verify this by breaking a piece of a substance and examining the fracture obtained. Usually small crystal faces arranged at various angles and glittering because they reflect light differently can be easily noticed in the fracture (for example, in sugar, sulphur, and metals). When the crystals are very small, the crystalline structure of a substance can be established with the aid of a microscope.

Every substance usually forms crystals of an absolutely definite shape. For instance, sodium chloride crystallizes in the form of cubes (Fig. 59*a*), alum in the form of octahedrons (Fig. 59*b*), and sodium nitrate in the form of prisms (Fig. 59*c*). A crystalline form is one of the characteristic properties of a substance.

The classification of crystalline forms is based on the symmetry of crystals. The different cases of symmetry of crystalline polyhedrons are treated in detail in courses of crystallography. We shall only indicate here that the great diversity of crystalline forms can be condensed into seven groups, or **crystal systems**, which, in turn, are divided into classes.

Many substances, particularly iron, copper, diamond, and sodium chloride, crystallize in the **cubic** system. The simplest forms of this system are the cube, octahedron, and tetrahedron. Magnesium, zinc, ice, and quartz crystallize in the **hexagonal** system. The basic forms of this system are hexagonal prisms and bipyramids.

Natural crystals, and also crystals produced artificially, rarely correspond exactly to the theoretical forms. Usually when a molten substance solidifies, the crystals intergrow, and therefore the shape of each of them is not completely regular. When a substance crystallizes rapidly from a solution, crystals are also obtained whose shape is distorted owing to the non-uniform growth in the conditions of crystallization.

But no matter how unevenly a crystal has developed, and no matter how its form is distorted, the angles between the faces of a crystal of a given substance remain the same. This is one of the fundamental laws of crystallography—the **law of constancy of interfacial angles**. Therefore, the value of the dihedral angles in a crystal permits us to establish the crystal system and class which a given crystal belongs to.

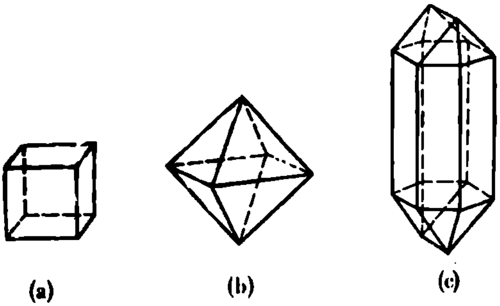

(a) (b) (c)

Fig. 59. Shapes of crystals:
a—sodium chloride; *b*—alum; *c*—sodium nitrate

The features of crystalline bodies are not restricted only to the shape of the crystals. Although a substance in a crystal is absolutely homogeneous, many of its physical properties—strength, thermal conductivity, its relation to light, etc.—are not always the same in different directions inside a crystal. This important feature of crystalline substances is known as **anisotropy**.

Let us cut out two bars of identical thickness from a cubic crystal of rock salt in different directions (Fig. 60), and determine the ultimate tensile strength of these bars. We shall find that for failure of the second bar a force is needed that is 2.5 times the force needed for failure of the first bar. It is evident that the strength of rock salt crystals in a direction at right angles to the faces of a cube is only two-fifths of the strength in the direction of the diagonals.

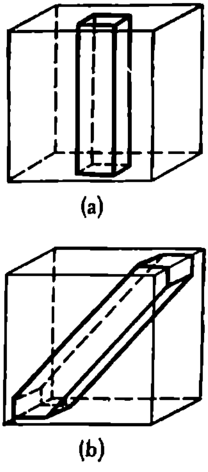
In many crystals, the difference between the strength in different directions is so great that when struck or broken they split along planes at right angles to which the strength is minimum. This property of crystals is known as **cleavage**. Mica crystals, which, as is general knowledge, split into very thin flakes, are an example of the manifestation of cleavage.

50. The Internal Structure of Crystals

It was assumed a long time ago that the external shape of a crystal reflects its internal structure and is due to the regular arrangement of the particles forming the crystal—molecules, atoms, or ions. This arrangement can be represented in the form of a **crystal lattice**—a three-dimensional lattice formed by intersecting straight lines. At the points of intersection of the lines—the **lattice points**—the centres of the particles are found.

Investigation of the internal structure of crystals became possible in the 20th century after the diffraction of X-rays, on which **X-ray structural analysis** is based, was discovered in 1912.

When a beam of monochromatic (i.e. having the same wavelength) X-rays falls onto the face of a crystal, the major part of the beam passes through the crystal, but a certain fraction of it is reflected. This


(a)

(b)

Fig. 60. Bars cut out from rock salt crystals:
a—at right angles to the cube faces; *b*—diagonally to one of the cube faces

reflection occurs from the planes formed by the particles which the crystal lattice of the given substance consists of. These planes play the role of the lines of a diffraction grating; the distances between them are close to the wavelengths of X-rays, therefore the latter interfere with one another upon reflection from the parallel planes. At definite angles of incidence of a beam of rays onto the face of a crystal, the reflected ray is amplified, which is registered on a photographic film—an **X-ray photograph** of the given crystal is obtained. When the wavelength of the radiation used is known, it is deciphered to determine the distances between adjacent planes or, which is the same, between adjacent atoms (ions) in a crystal of the given substance.

X-ray structural analysis is the main way of studying the structure of solids. Sometimes, the diffraction of electrons (electron-diffraction analysis) and also of neutrons is employed. To date, X-ray structural analysis has been used to study the structure of tens of thousands of inorganic and organic substances of practical and scientific importance. Great success has been achieved in deciphering the structures of biologically important substances (for instance, of hemoglobin). X-ray structural analysis allows scientists to establish the molecular structure of the hereditary substance of living organisms.

Molecular, atomic, ionic, and metallic lattices are distinguished depending on the nature of the particles at the points of a crystal lattice and on what forces of interaction predominate between them in a given crystal.

The points of **molecular** lattices are occupied by molecules. Intermolecular forces bind them to one another. The points of **atomic** lattices are occupied by atoms. They are joined to one another by covalent bonds. The points of **ionic** lattices are occupied by alternating positively and negatively charged ions. Forces of electrostatic attraction bind them to one another. Finally, the points of **metallic** lattices accommodate atoms of the relevant metal between which electrons shared by these atoms freely travel. Metallic lattices will be treated in Chap. 6 of Vol. 2.

Substances with a covalent bond have molecular and atomic lattices, ionic compounds have ionic lattices, and metals and their alloys have metallic lattices.

There are comparatively few substances having atomic lattices. Among them are diamond, silicon, and a few inorganic compounds. These substances are characterized by a great hardness, they are refractory, and do not dissolve in virtually any solvents. These properties are due to the strength of a covalent bond.

Very many substances have a molecular lattice. They include non-metals except for carbon and silicon, all organic compounds with a non-ionic bond, and many inorganic substances. The forces of intermolecular interaction are considerably weaker than those of a covalent bond; consequently molecular crystals have a low hardness, a low melting point, and are volatile.

Compounds with an ionic bond forming ionic lattices include most salts and a small number of oxides. Ionic lattices as regards their strength are inferior to atomic lattices, but are superior to molecular ones. Ionic compounds have a comparatively high melting point. Their volatility in the majority of cases is not great.

Substances exist in whose crystals two kinds of interaction between their particles play a considerable role. For instance, the carbon atoms in graphite are bound to one another by a covalent bond in some directions, and by a metallic bond in others. Hence, the graphite lattice can be considered as both an atomic and a metallic one. In many inorganic compounds, for example, in BeO, ZnS, and CuCl, the bond between the particles at the lattice points is partly ionic and partly covalent. The lattices of such compounds can be considered as intermediate between ionic and atomic ones.

The lattices of various substances differ from one another not only in the nature of the particles forming them, but also in the spatial arrangement of the particles—in their structure. Every lattice can be characterized by its **elementary cell**—the smallest part of a crystal having all the features of the structure of the given lattice (see Fig. 61). It can be seen that in a crystal of NaCl each ion is surrounded by six closest ions of the opposite sign, and in a crystal of CsCl by eight. This number of closest particles for a particle in a crystal is called its **coordination number**. Thus, the coordination number of the ion Na^+ and of the ion Cl^- in the NaCl crystal is 6, and of the ions Cs^+ and Cl^- in the CsCl crystal is 8. In crystals of both of these salts, and also of other ionic compounds, all the bonds of each ion with the closest ions of the opposite sign are equivalent. It thus follows that the concept of a molecule can be applied neither to crystalline substances with an ionic bond nor to crystals with an atomic or combined atomic and ionic structure. In substances

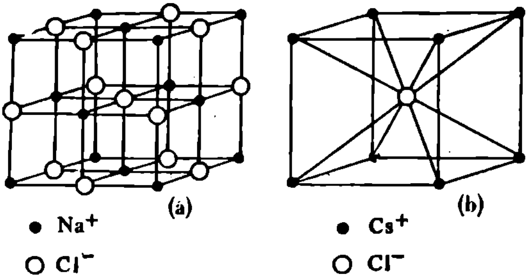


Fig. 61. Crystal lattices of sodium chloride (*a*) and cesium chloride (*b*)

such as diamond and carborundum SiC having an atomic lattice or as ZnS and Al_2O_3 having an intermediate atomic and ionic structure, all the bonds of each atom with its closest neighbours are equivalent.

51. Real Crystals

The internal structure of a crystal characterized by a strict three-dimensional periodicity described in Sec. 50 is a certain idealization. The investigation of the structure of real crystals has shown that this periodicity is always violated somewhat in any crystal. **Structural defects** are observed in real crystals. The number of these defects and their type affect some properties of crystalline substances. This influence is sometimes very great, while certain of such **structurally sensitive** properties are of a very great practical significance.

The structural defects of real crystals are quite diverse. First of all, point, linear, and surface defects are distinguished. The simplest and at the same time the most important point defects are unoccupied lattice points or **vacancies** and atoms in the interstices. The existence of such defects is associated with the fact that individual atoms or ions of a lattice have an energy exceeding its average value at a given temperature. Such atoms vibrate more intensively than others and can pass over from one site to another, for example, from a lattice point to an interstice. An atom that has left its point is called **dislocated**, and the unfilled site where it was earlier, a vacancy. At any moment, an atom neighbouring with a vacancy may occupy it, forming a new vacancy. Thus, vacancies pass from one site to another. Point defects have a very great influence on the properties of semiconductor materials.

Linear structural defects are known as **dislocations**. An edge dislocation is the simplest kind of these defects. It is the edge of one of the atomic planes terminating inside a crystal. Dislocations appear both during the growth of crystals and as a result of local mechanical, thermal, and other actions on crystals (see, for example, Fig. 38*a* and *b* in Sec. 77 of Vol. 2). Figure 62 shows an edge dislocation (line *AB*) appearing as a result of shear of part of the crystal along plane *ABCD* in the direction indicated by the arrow.

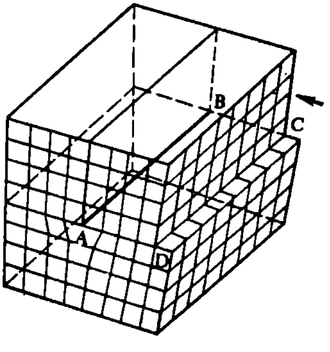


Fig. 62. Schematic view of an edge dislocation

Like point defects, dislocations are mobile. Their mobility is especially great in metallic crystals. The mechanical properties of metals depend greatly on the density of the dislocations (i.e. on their number per unit volume) and on their ability to move along a crystal (see Vol. 2, Sec. 77).

The surface defects observed on the surface of a crystalline body or on the interface of crystals are combinations of a large number of point and linear defects.

52. The Amorphous State of a Substance

Some solids are encountered in a fracture of which no indications of crystals can be detected. For instance, if we split a piece of ordinary glass, its fracture will be smooth and, unlike the fractures of crystals, it will be bounded by oval surfaces instead of plane ones. A similar picture is observed when pieces of pitch, glue, and some other substances are split. Such a state of a substance is called **amorphous.**

The difference between crystalline and amorphous bodies manifests itself especially sharply in their behaviour when heated. Whereas crystals of any substance melt at a strictly definite temperature, and solidification of the substance occurs at the same temperature, amorphous bodies have no definite melting point. When heated gradually, an amorphous substance softens, begins to flow, and, finally, becomes completely liquid. When cooled, it also gradually solidifies.

Because of the absence of a definite melting point, amorphous bodies also have another feature: many of them are fluid-like liquids, i.e. they gradually change their shape under the prolonged action of comparatively small forces. For example, a piece of pitch placed on a flat surface in a warm room during a few weeks flows and acquires the shape of a disk.

The difference between the internal structure of a substance in the crystalline and amorphous states is as follows. The ordered arrangement of the particles in a crystal reflected by its elementary cell is retained on great portions of the crystals, and throughout the entire volume of well formed crystals. In amorphous bodies, order is observed in the arrangement of the particles only on very small sections. Moreover, in a number of amorphous bodies, even this local order is only approximate. This difference can be formulated in short as follows: the structure of crystals is characterized by **long-range order**, and that of amorphous bodies by **short-range** order.

The amorphous state is characteristic, for example, of silicate glass (Vol. 2, Sec. 68). Some substances can be both in the crystalline and in the amorphous state. For example, silicon dioxide SiO_2 is encountered in nature as well formed quartz crystals, and also in the amorphous state (the mineral flint). The crystalline state is always more stable. For this reason, the spontaneous transition of a substance from the crystalline state to the amorphous one is impossible, while the reverse transformation—the simultaneous transition from the amorphous state to the crystalline one—is possible and is observed sometimes. An example of such a transformation is **devitrification**—the spontaneous crystallization of glass at elevated temperatures attended by its destruction.

53. Liquids

The liquid state is intermediate between the gaseous and the crystalline one. In some properties, liquids are close to gases, in others—to solids. Liquids resemble gases first of all in their isotropic nature and fluidity; the latter underlies the ability of a liquid to easily change its external shape. The high density and low compressibility of liquids, however, make them closer to solids.

The ability of liquids to easily change their shape points to the absence of rigid forces of intermolecular interaction in them. At the same time, the low compressibility of liquids, which explains their ability to retain a constant volume at a given temperature, points to the considerable forces of interaction between their particles, although these forces are not rigid.

Each state of aggregation is characterized by its own relationship between the potential and kinetic energies of the particles of a substance. The average potential energy of the particles of a solid is greater than their average kinetic energy. This is why the particles in solids occupy definite positions relative to one another and only vibrate about these positions. The relationship between the energies is the opposite for gases, owing to which the molecules of a gas are always in a state of chaotic motion, and binding forces between its molecules are virtually absent. For this reason, a gas always occupies the entire volume at its disposal. The potential and kinetic energies of the particles of a liquid are approximately the same, i.e. the particles are bound to one another, but not rigidly. This is why liquids are fluid, but have a constant volume at a given temperature.

As a result of employing the methods of structural analysis for liquids, their structure was found to be similar to that of amorphous bodies. In the majority of liquids, short-range order is observed—the number of closest neighbours in each molecule and their mutual arrangement are approximately the same throughout the volume of a given liquid.

The degree of order of the particles in various liquids is different. In addition, it varies with a change in the temperature. At low temperatures insignificantly exceeding the melting point of a given substance, the degree of order in the arrangement of the particles of a given liquid is high. Elevation of the temperature is attended by diminishing of the degree of order, and the properties of a liquid when heated become closer and closer to those of a gas. When the critical temperature is reached (see Sec. 71), the difference between a liquid and a gas vanishes.

Owing to the similarity in the internal structure of liquids and amorphous bodies, the latter are often considered as liquids with a very high viscosity, and only substances in the crystalline state are related to solids. When considering amorphous bodies to be similar to liquids, however, we must remember that in amorphous bodies, unlike conventional liquids, the particles have an insignificant mobility—the same as in crystals.

6

FUNDAMENTAL LAWS OF CHEMICAL REACTIONS

54. Energy Conversions in Reactions

Chemical reactions proceed with the liberation or absorption of energy. The latter is usually liberated or absorbed in the form of heat. For instance, combustion, the combining of metals with sulphur or chlorine, the neutralization of acids by alkalies are attended by the liberation of considerable amounts of heat. Conversely, such reactions as the decomposition of calcium carbonate and the formation of nitrogen monoxide from nitrogen and oxygen require a continuous supply of heat from outside for their completion and immediately stop if heating is discontinued. It is quite obvious that these reactions proceed with the absorption of heat.

The liberation of heat when different substances react makes us acknowledge the fact that these substances had a definite energy in the latent form even before the reaction. Such a form of energy concealed in substances and evolved in chemical, and also in certain physical processes (for instance, in the condensation of a vapour into a liquid or in the crystallization of a liquid) is called the **internal energy** of a substance (see also Sec. 66).

In chemical transformations, a part of the energy contained in substances is liberated. By measuring the amount of heat evolved in a reaction (the **heat effect of a reaction**), we can assess the change in this store of energy.

In some reactions, the liberation or absorption of radiant energy is observed. When light is liberated in a reaction, the internal energy usually transforms into radiation not directly, but through heat. For instance, light appears in the combustion of coal because the heat liberated in the reaction makes the coal hot and it begins to glow. But processes are also known in which the internal energy transforms directly into radiant energy. These processes are known as cold glow or **luminescence**. Of great importance are the processes of the mutual conversion of internal and electrical energy (see Sec. 98). In reactions proceeding with an explosion, the internal energy is transformed into mechanical energy, partly directly and partly first into heat.

Thus, chemical reactions are attended by the mutual conversion of the internal energy of substances, on the one hand, and of heat, radiant, electrical, or mechanical energy on the other. Reactions proceeding with the liberation of energy are called **exothermic**, and reactions in which energy is absorbed, **endothermic.**

55. Thermochemistry

The energy changes attending chemical reactions are of great practical significance. They are sometimes even more important than the formation of new substances in the given reaction. (As an example, it is sufficient to remember the reaction of fuel combustion.) This is why the heat effects of reactions have been studied very thoroughly for a long time. The branch of chemistry devoted to a quantitative study of the heat effects of reactions is called **thermochemistry**.

It was established at the end of the 18th century that *if a certain amount of heat is released (or absorbed) in the formation of a compound, upon the decomposition of this compound in the same conditions an identical amount of heat is absorbed (or released)*. This statement follows from the law of energy conservation. It shows that the greater the amount of heat evolved in the formation of a compound, the more energy has to be used to decompose it. This is why substances in whose formation a great amount of heat is evolved are very stable and are difficult to decompose.

The results of thermochemical measurements—the heat effects of reactions—are customarily related to one mole of the substance formed. The amount of heat liberated in the formation of one mole of a compound from simple substances is called the **heat of formation** of the given compound. For instance, the expression "the heat of formation of water is 285.8 kJ/mol" signifies that 285.8 kJ are liberated in the formation of 18 g of liquid water from 2 g of hydrogen and 16 g of oxygen.

If an element can exist in the form of several simple substances, then when calculating the heat of formation the element is taken in the form of the simple substance that is the most stable in the given conditions. The heats of formation of the most stable simple substances in the given conditions are taken equal to zero. The heats of formation of the less stable simple substances are thus taken equal to the heats of their formation from the stable ones. For example, in ordinary conditions, the most stable form of oxygen is molecular oxygen O_2 whose heat of formation is considered to equal zero. The heat of formation of ozone O_3, however, equals —142 kJ/mol because in the formation of one mole of ozone from molecular oxygen 142 kJ are absorbed.

Heat effects can be included in the equations of reactions. Chemical equations in which the amount of liberated or absorbed heat is indicated are known as **thermochemical equations.** The value of the heat effect is usually indicated in the right-hand side of an equation with a plus sign for an exothermic reaction and a minus sign for an endothermic one. For example, the thermochemical equation of the reaction of formation of liquid water has the form

$$2H_2+O_2=2H_2O \quad +571.6\ \text{kJ}$$

or

$$H_2+\frac{1}{2}O_2=H_2O \quad +285.8\ \text{kJ}$$

The heat of formation of nitrogen monoxide is negative and is —90.25 kJ/mol. The relevant thermochemical equation has the form

$$N_2+O_2=2NO \quad -180.5\ \text{kJ}$$

or

$$\frac{1}{2}N_2+\frac{1}{2}O_2=NO \quad -90.25\ \text{kJ}$$

A very important characteristic of substances used as fuel is their **heat of combustion.** This quantity is also customarily related to one mole of the substance. Thus, the expression "the heat of combustion of acetylene is 1300 kJ/mol" is equivalent to the thermochemical equation

$$C_2H_2+2\frac{1}{2}O_2=H_2O+2CO_2 \quad +1300\ \text{kJ}$$

The magnitude of the heat effect depends on the nature of the reactants (initial substances) and the reaction products, their state of aggregation, and temperature. For convenience in comparing various reactions according to the values of their heat effects, the latter are usually indicated for the case when the temperature of the reactants and the products is 25 °C*. It is also borne in mind that the substances participating in a reaction are in the state of aggregation that is stable at this standard temperature. If, however, what is of interest is the heat of formation of a substance that is in a different state of aggregation than the one in which it is stable at 25 °C, this state is indicated in the equation of the reaction. The crystalline state is indicated by the symbol (c) next to the formula of the relevant substance, the liquid state by the symbol (lq), and the gaseous state by (g). Thus, the heat of formation of water vapour is 241.8 kJ/mol; the corresponding thermochemical equation has the

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* All heat effects given in this book, including the heats of formation of substances, relate to 25 °C.

form

$$H_2 + \frac{1}{2} O_2 = H_2O(g) \quad +241.8 \text{ kJ}$$

It is obvious that the difference between the heat of formation of liquid water (285.8 kJ/mol) and of water vapour (241.8 kJ/mol) is the heat of vaporization of water at 25 °C related to one mole (18 g).

56. Thermochemical Calculations

The fundamental principle on which all thermochemical calculations are based was established in 1840 by the Russian chemist, academician G. Hess. This principle is known as Hess's law and is a particular case of the law of energy conservation. It can be formulated as follows:

> *The heat effect of a reaction depends only on the initial and the final state of substances and does not depend on the intermediate stages of the process.*

Let us consider an example explaining Hess's law. A solution of sodium sulphate can be prepared from solutions of sulphuric acid and sodium hydroxide in two ways:

1. By mixing a solution containing two moles of NaOH with a solution containing one mole of H_2SO_4.
2. By mixing a solution containing one mole of NaOH with a solution containing one mole of H_2SO_4 and adding another mole of NaOH to the obtained solution of the acid salt ($NaHSO_4$).

We now write the thermochemical equations of these reactions. First way:

$$2NaOH(aq) + H_2SO_4(aq) = Na_2SO_4(aq) + 2H_2O \quad +131.4 \text{ kJ}$$

Second way:

$$NaOH(aq) + H_2SO_4(aq) = NaHSO_4(aq) + H_2O \quad +61.7 \text{ kJ}$$

$$NaHSO_4(aq) + NaOH(aq) = Na_2SO_4(aq) + H_2O \quad +69.7 \text{ kJ}$$

The symbol (aq) signifies that the substance has been taken in the form of an aqueous solution.

According to Hess's law, the heat effect in both cases must be the same. Indeed, by adding the heat effects corresponding to the two stages of the second way, we get the same total heat effect that is observed in the first way of conducting the process, namely, $61.7 + 69.7 = 131.4$ kJ.

Thus, like the conventional equations of chemical reactions, thermochemical equations can be summated.

Hess's law allows us to calculate the heat effects of reactions when for some reason or other they cannot be measured directly.

Let us consider as an example of such calculations the determination of the heat of formation of carbon monoxide from graphite and oxygen. It is very difficult to measure the heat effect of the reaction

$$\text{C(graphite)} + \frac{1}{2}\text{O}_2 = \text{CO}$$

because upon the combustion of graphite in a limited amount of oxygen what is obtained is not carbon monoxide, but its mixture with carbon dioxide. But the heat of formation of CO can be computed if we know its heat of combustion (283.0 kJ/mol) and the heat of formation of carbon dioxide (393.5 kJ/mol).

The combustion of graphite is expressed by the thermochemical equation

$$\text{C(graphite)} + \text{O}_2 = \text{CO}_2 \quad +393.5\ \text{kJ}$$

To calculate the heats of formation of CO, we shall write this reaction as two stages:

$$\text{C(graphite)} + \frac{1}{2}\text{O}_2 = \text{CO} \quad +x\ \text{kJ}$$

$$\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2 \quad +283.0\ \text{kJ}$$

and summate the thermochemical equations corresponding to these stages. We get the summary equation

$$\text{C(graphite)} + \text{O}_2 = \text{CO}_2 \quad +(x+283.0)\ \text{kJ}$$

According to Hess's law, the heat effect of this summary reaction equals the heat effect of the reaction of direct combustion of graphite, i.e. $x + 283.0 = 393.5$. Hence, $x = 110.5$ kJ, or

$$\text{C(graphite)} + \frac{1}{2}\text{O}_2 = \text{CO} \quad +110.5\ \text{kJ}$$

Let us consider another example of application of Hess's law. We shall calculate the heat effect of the reaction of combustion of methane CH_4 knowing the heats of formation of methane (74.9 kJ/mol) and of the products of its combustion—carbon dioxide (393.5 kJ/mol) and water (285.8 kJ/mol). To perform our calculations, we shall write the reaction of methane combustion first directly, and then in stages. The corresponding thermochemical equations will be:

$$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} \quad +x\ \text{kJ}$$

$$\text{CH}_4 = \text{C(graphite)} + 2\text{H}_2 \quad -74.9\ \text{kJ}$$

$$\text{C(graphite)} + \text{O}_2 = \text{CO}_2 \quad +393.5\ \text{kJ}$$

$$2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \quad +2 \times 285.8\ \text{kJ}$$

Summating the last three thermochemical equations corresponding to conducting of the reaction by stages, we get the summary equation of methane combustion:

$$CH_4+2O_2=CO_2+2H_2O \quad +(-74.9+393.5+571.6) \text{ kJ}$$

According to Hess's law, $-74.9 + 393.5 + 571.6 = x$, whence the heat of methane combustion $x = 890.2$ kJ.

The example considered above illustrates a practically important corollary of Hess's law: *the heat effect of a chemical reaction equals the sum of the heats of formation of the products less the sum of the heats of formation of the reactants.* Both sums are determined with account taken of the number of moles of the substances participating in the reaction in accordance with its equation.

57. Rate of a Chemical Reaction

Chemical reactions proceed at different rates (speeds). Some of them terminate completely in small fractions of a second, others are completed in minutes, hours, or days. Reactions are known requiring several years, decades, and even longer periods of time for their completion. Moreover, the same reaction may proceed at a faster rate in one set of conditions, for instance at elevated temperatures, and more slowly in other conditions, for example when cooled; the difference in the rate of the same reaction may be very great.

The knowledge of the rates of chemical reactions is of a very great scientific and practical significance. For example, in the chemical industry, the size and capacity of the apparatus and the amount of the product depend on the rate of the reaction.

In treating the rate of a reaction, we must distinguish between reactions proceeding in a homogeneous system (**homogeneous reactions**) and reactions proceeding in a heterogeneous system (**heterogeneous reactions**).

A **system** in chemistry is defined as the substance or combination of substances being considered. The surroundings—the substances surrounding the system, are opposed to a system. A system is usually separated physically from its surroundings.

Homogeneous and **heterogeneous systems** are distinguished. A homogeneous system is one consisting of a single phase, and a heterogeneous system is one consisting of several phases. By a **phase** is meant a part of a system separated from its other parts by an interface upon passing through which the properties change in a jump.

Any gas mixture is an example of a homogeneous system (all gases at not very high pressures dissolve unlimitedly in one another), for instance a mixture of nitrogen and oxygen. Another example of a homogeneous system is a solution of several substances in a single solvent, for instance, a solution of sodium chloride, magnesium sulphate, nitrogen, and oxygen in water. In each of these two examples, the system consists of a single phase: a gaseous phase in the first one and an aqueous solution in the second.

Heterogeneous systems can be exemplified as follows: water with ice, a saturated solution with a precipitate, coal dust and sulphur in an atmosphere of air. In the latter case, the system consists of three phases: two solid and one gaseous phases.

If a reaction proceeds in a homogeneous system, it goes on throughout the entire volume of the system. For example, when solutions of sulphuric acid and sodium thiosulphate are poured together (and stirred), the turbidity due to the appearance of sulphur is observed throughout the entire volume of the solution:

$$H_2SO_4+Na_2S_2O_3=Na_2SO_4+H_2O+SO_2\uparrow+S\downarrow$$

If a reaction proceeds between substances forming a heterogeneous system, it can proceed only on the interface of the phases forming the system. For example, the dissolving of a metal in an acid

$$Fe+2HCl=FeCl_2+H_2\uparrow$$

can go on only on the surface of the metal where the two reactants come into contact. This is why the rate of a homogeneous reaction and that of a heterogeneous one are determined differently.

By the rate of a homogeneous reaction is meant the amount of substance entering into a reaction or formed in the reaction in unit time and in unit volume of the system.

By the rate of a heterogeneous reaction is meant the amount of substance entering into a reaction or formed in the reaction in unit time and on unit surface area of a phase.*

Both these definitions can be written in a mathematical form. Let us introduce the notation J_{hom} = reaction rate in a homogeneous system, J_{het} = reaction rate in a heterogeneous system, n = number of moles of one of the reaction products, V = volume of the system, t = time, A = surface area of the phase on which the reaction is going on, Δ = the symbol of an increment ($\Delta n = n_2 - n_1$, $\Delta t = t_2 - t_1$). Hence,

$$J_{\text{hom}}=\frac{\Delta n}{V\,\Delta t}$$

$$J_{\text{het}}=\frac{\Delta n}{A\,\Delta t}$$

The first of these equations can be simplified. The ratio of the number of moles (n) of a substance to the volume (V) of a system is

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* It is not always a simple matter to measure the surface of a solid. For this reason, the rate of a heterogeneous reaction is sometimes related not to a unit area, but to a unit mass or volume of the solid phase.

the molar-volume concentration (C) of the given substance:

$$\frac{n}{V}=C$$

Hence,

$$\frac{\Delta n}{V}=\Delta C$$

And, finally,

$$J_{\text{hom}}=\frac{\Delta C}{\Delta t}$$

The last equation is a mathematical expression of a different definition of the rate of a reaction in a homogeneous system: *by the rate of a reaction in a homogeneous system is meant the change in the concentration of one of the reactants or products occurring in unit time.*

We have already mentioned that in the practical use of chemical reactions it is very important to know the rate of a given reaction in definite conditions, and how these conditions have to be altered for the reaction to proceed at the required rate. The branch of chemistry studying the rates of chemical reactions is called **chemical kinetics.**

The most important factors affecting the rate of a reaction include the following: the nature of the reactants, their concentrations, temperature, the presence of catalysts in the system. The rate of some heterogeneous reactions also depends on the intensity of flow of the relevant liquid or gas near the surface on which the reaction occurs.

58. Dependence of Reaction Rate on the Reactant Concentrations

An essential condition for chemical interaction to occur between the particles (molecules, ions) of the reactants is their collision with one another. More exactly, the particles must approach one another to a close distance such that the atoms of one of them will experience the action of the electric fields produced by the atoms of the other substance. Only in these conditions are the transitions of electrons and regroupings of the atoms possible as a result of which molecules of new substances—the reaction products—are formed. Consequently, the rate of a reaction is proportional to the number of collisions experienced by the molecules of the reactants.

The number of collisions, in turn, grows with the concentration of each of the reactants, or, which is the same, with an increasing product of the reactant concentrations. Thus, the rate of the reaction

$$\mathrm{A}+\mathrm{B}=\mathrm{C}$$

is proportional to the product of the concentration of substance A and the concentration of substance B. Denoting the concentrations of A and B by [A] and [B], respectively, we can write:

$$J = k[\mathrm{A}][\mathrm{B}]$$

where k is a coefficient of proportionality known as the **rate constant** of the given reaction.

The equation obtained expresses the **law of mass action** for a chemical reaction proceeding when two particles collide:

> *At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants.*

This law was discovered experimentally by C. Guldberg and P. Waage (Norway) in 1867.

A reaction proceeds much less frequently as a result of the simultaneous collision of three reacting particles. For example, a reaction of the type $2A + B = A_2B$ can proceed as a result of a triple collision:

$$\mathrm{A} + \mathrm{A} + \mathrm{B} \rightarrow \mathrm{A_2B}$$

Hence, according to the law of mass action, we can write:

$$J = k[\mathrm{A}][\mathrm{A}][\mathrm{B}]$$

that is

$$J = k[\mathrm{A}]^2[\mathrm{B}]$$

Here the concentration of each of the reactants in the expression for the rate of a reaction has an exponent equal to the relevant coefficient in the equation of the reaction.

The probability of a simultaneous collision of more than three particles is extremely low. Consequently, complex reactions whose equations contain a great number of particles are a combination of consecutive or parallel processes each of which occurs, as a rule, owing to the collision of two particles or to the decomposition of a separate particle. In such cases, the law of mass action may be applied only to each separate step of a reaction, but not to the reaction as a whole.

The value of the rate constant k depends on the nature of the reactants, on the temperature, and on the presence of catalysts. but does not depend on the concentrations of the substances.

As an example of the application of the law of mass action, we can give the equation showing how the rate of the reaction of oxidation of nitrogen monoxide

$$2\mathrm{NO} + \mathrm{O_2} = 2\mathrm{NO_2}$$

depends on the concentrations of NO and O_2:

$$J = k\,[NO]^2\,[O_2]$$

The equations of the law of mass action for heterogeneous reactions include only the concentrations of the substances that are in the gaseous phase or in a solution. The concentration of the substances in the solid phase is usually a constant quantity and is therefore included in the rate constant. For example, for the reaction of carbon combustion

$$C + O_2 = CO_2$$

the law of mass action will be written as

$$J = k'\cdot \text{const}\cdot [O_2] = k\,[O_2]$$

where $k = k'\cdot\text{const}$.

59. Dependence of Reaction Rate on the Temperature and Nature of the Reactants

The molecular-kinetic theory of gases and liquids makes it possible to count the number of collisions between the molecules of substances in definite conditions. If we use the results of such calculations, the number of collisions between the molecules of substances in conventional conditions will be found to be so great that all reactions ought to proceed virtually instantaneously. Actually, however, far from all reactions terminate rapidly. This contradiction can be explained if we assume that not any collision between molecules of reactants leads to the formation of the reaction product. For a reaction to occur, i.e. for new molecules to form, it is first necessary to break or weaken the bonds between the atoms and molecules of the reactants. This requires a definite energy. If the colliding molecules do not have such an energy, a collision will be ineffective—it will not lead to the formation of a new molecule. But if the kinetic energy of colliding molecules is sufficient for weakening or breaking their bonds, the collision may result in reconstruction of the atoms and in the formation of a molecule of a new substance.

The excess energy that molecules must have for their collision to be effective is called the **activation energy** of the given reaction. The activation energy is expressed in kJ/mol. Molecules having such an energy are called **active molecules.**

The number of active molecules grows with elevation of the temperature. It thus follows that the rate of a chemical reaction should also grow with elevation of the temperature. Indeed, chemical reactions do proceed faster when the temperature grows.

To better understand the accelerating action of the temperature on chemical reactions, let us see how the molecules of a substance are distributed by the value of their energy. Figure 63 shows such a distribution for a gas at a constant temperature. The energy E of one molecule of the gas is laid off along the horizontal axis. The fraction of the total number of molecules having an energy within the narrow interval from E to $E + \Delta E$ divided by the magnitude of this interval ΔE is laid off along the vertical axis. If the total number of molecules is N, and their fraction having an energy within the indicated interval is $\Delta N/N$, then the quantity laid off along the axis of ordinates will be $\Delta N/N\Delta E$.

Let us consider a column having a width of ΔE and a height equal to the ordinate of the curve (see Fig. 63). The area of this column is $\Delta E \cdot \Delta N/N\Delta E = \Delta N/N$, i.e. equals the fraction of the molecules whose energy is within the interval ΔE. Similarly, the area confined by the curve, two ordinates (for instance, by the ordinates corresponding to the energy values E_1 and E_2), and the axis of abscissas (area E_1ABE_2 in Fig. 63) equals the fraction of the gas molecules whose energy is within the given interval—in our case in the interval from E_1 to E_2. In exactly the same way, the area under the curve and confined at the left by an ordinate (for example, the ordinate corresponding to E_3) equals the fraction of molecules whose energy exceeds the value E_3 (the cross-hatched area in Fig. 63). The area confined by the entire curve and the axis of abscissas equals unity.

The curve in Fig. 63 shows that the molecules of a gas at a constant temperature have different energies. The majority of them have an

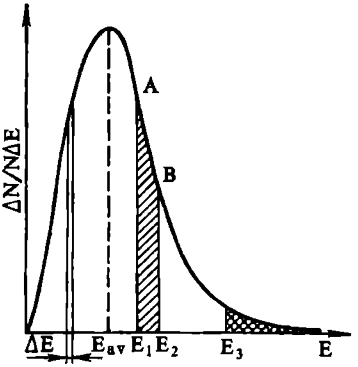


Fig. 63. Distribution of the molecules of a gas by kinetic energy.

Area E_1ABE_2 equals the fraction of the molecules whose energy is within the interval from E_1 to E_2. The cross-hatched area equals the fraction of the molecules whose energy exceeds E_3

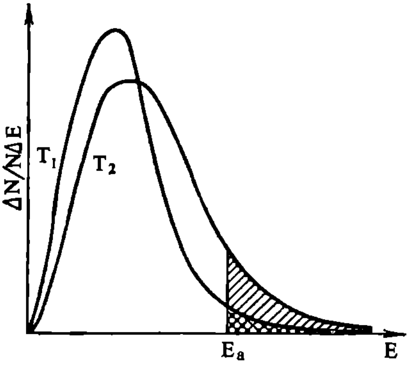


Fig. 64. Distribution of the molecules of a gas by kinetic energy for two temperatures T_1 and T_2 ($T_2 > T_1$).

E_a — activation energy. The hatched areas show the fractions of active molecules at the temperatures T_1 and T_2

energy equal to a certain average energy E_{av} or close to it. But there are molecules whose energy is higher or lower than E_{av}. The greater the energy differs from E_{av}, i.e. the farther a point on the curve is from the maximum, the smaller is the fraction of molecules of the gas having such an energy.

How does the curve change with the temperature? Figure 64 shows two curves corresponding to the same amount of a gas at the temperatures T_1 and T_2 (here T_2 is greater than T_1). A glance at the figure shows that the curve relating to the temperature T_2 is displaced to the right—in the direction of higher energies.

If in Fig. 64 we indicate the activation energy E_a of a reaction proceeding with participation of the given gas, then it will be evident that the fraction of the gas molecules whose energy exceeds E_a sharply grows with elevation of the temperature.

The growth in the rate of a reaction with increasing temperature is customarily characterized by the **temperature coefficient of the reaction rate**—a number showing how many times the rate of a given reaction grows when the temperature of the system increases by 10 kelvins. The temperature coefficient varies for different reactions. At conventional temperatures, its value for most reactions ranges from two to four. This small value of the temperature coefficient at first sight, however, underlies a great growth in the rate of a reaction upon a considerable elevation of the temperature. For example, if the temperature coefficient is 2.9, then when the temperature rises by 100 kelvins the rate of the reaction increases by 2.9^{10}, i.e. about 50 000 times.

The activation energy of different reactions is different. Its value is the factor by means of which the nature of the reactants affects the rate of a reaction. For some reactions, the activation energy is low, for others, on the contrary, it is high.

If the activation energy is very low (less than 40 kJ/mol), this signifies that a considerable part of the collisions between the particles of the reactants result in a reaction. The rate of such a reaction is high. An example of reactions whose activation energy is negligibly small are ionic reactions in solutions, usually consisting in the interaction of oppositely charged ions. Experiments show that such reactions proceed virtually instantaneously.

Conversely, if the activation energy is very high (above 120 kJ/mol), this means that only a very small fraction of the collisions between the interacting particles lead to a chemical reaction. The rate of such a reaction is very low. An example of a reaction with a high activation energy is that of ammonia synthesis:

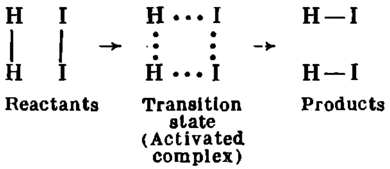
$$N_2 + 3H_2 = 2NH_3$$

At ordinary temperatures this reaction goes on so slowly that it is virtually impossible to notice it.

Finally, if the activation energy of a reaction is not very low and not very high, i.e. if it is moderate (40 to 120 kJ/mol), the reaction will proceed at a moderate rate. The rate of such a reaction can be measured. An example of a reaction occurring with a measurable rate is the reaction of decomposition of sodium thiosulphate by sulphuric acid mentioned on page 181.

Reactions requiring an appreciable activation energy begin with breaking or weakening of the bonds between the atoms in the molecules of the reactants. The latter pass over into an unstable intermediate state characterized by a great store of energy. This state is known as an **activated complex** (or a **transition state**). It is exactly for its formation that the activation energy is needed. The unstable activated complex exists for a very short time. It decomposes with the formation of the reaction products, and energy is evolved.

In the simplest case, the activated complex is a configuration of atoms in which the old bonds have become weaker and new bonds have started to form. An example is the scheme of hydrogen iodide synthesis:



$$\begin{array}{ccccc} \begin{array}{cc} H & I \\ | & | \\ H & I \end{array} & \rightarrow & \begin{array}{ccc} H & \cdots & I \\ \vdots & & \vdots \\ H & \cdots & I \end{array} & \rightarrow & \begin{array}{c} H-I \\ \\ H-I \end{array} \end{array}$$

The activated complex appears as an intermediate state in the course of both the forward and reverse reactions. From the energy viewpoint, it differs from the reactants by the value of the activation energy of the forward reaction, and from the products by the value of the activation energy of the reverse reaction. These relations are shown in Fig. 65. Inspection of this figure reveals that the difference between the activation energies of the forward and the reverse reaction equals the heat effect of the reaction.

60. Catalysis

Substances that are not consumed in a reaction, but affect its rate, are called **catalysts.** The phenomenon of the change in the rate of a reaction under the action of such substances is known as **catalysis.** Reactions proceeding under the action of catalysts are called **catalytic.**

The action of a catalyst in the majority of cases is explained by the fact that it lowers the activation energy of a reaction. In the presence of a catalyst a reaction proceeds through other intermediate stages than without it, and these stages are more accessible from the energy viewpoint. In other words, other activated complexes appear in the presence of a catalyst, and less energy is needed for their formation than for the formation of the activated complexes appearing without a catalyst. Thus, the activation energy of a reaction is lowered. Some molecules, whose energy was insufficient for active collisions, are now active.

The relationships between the activation energies of a reaction in the presence of a catalyst and without it are shown in Fig. 66. (For the notation see Fig. 65. The unprimed quantities are for a reaction without a catalyst, and the primed ones are for a reaction with a catalyst.) It is evident from Fig. 66 that a catalyst lowers the activation energy of the forward and the reverse reaction by the same amount. Hence, it follows that a catalyst accelerates both the forward and the reverse reaction the same number of times.

The relationship between the number of active molecules in the presence and in the absence of a catalyst is shown in Fig. 67.

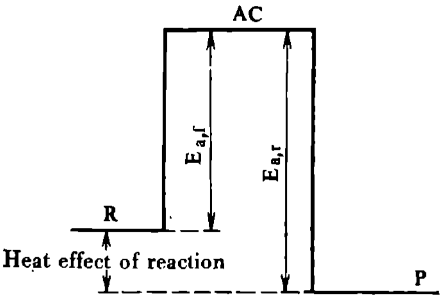


Fig. 65. Energy diagram of a reaction:
R = reactants; AC = activated complex; P = products of reaction; $E_{a,f}$ = = activation energy of forward reaction; $E_{a,r}$ = activation energy of reverse reaction

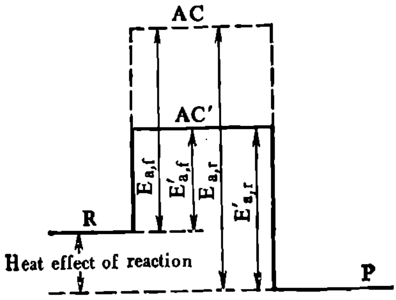


Fig. 66. Energy diagram of a reaction proceeding with the participation of a catalyst.
For the notation see Fig. 65. The unprimed quantities are for a reaction without a catalyst, and the primed ones are for a reaction with a catalyst

For a number of reactions, the intermediate compounds have been studied. As a rule, they are very active unstable products.

Catalysts are employed very broadly in the chemical industry. Catalysts accelerate reactions millions of times and more. Sometimes, such reactions may be initiated under the action of catalysts that in the given conditions do not virtually proceed at all.

Homogeneous catalysis and **heterogeneous** catalysis are distinguished.

In homogeneous catalysis, the catalyst and the reactants form a single phase (a gas or solution). In heterogeneous catalysis, the catalyst forms an independent phase.

An example of homogeneous catalysis is the catalytic decomposition of hydrogen peroxide in an aqueous solution into water and oxygen. The ions $Cr_2O_7^{2-}$, WO_4^{2-}, MoO_4^{2-} catalyzing the decomposition of hydrogen peroxide form intermediate compounds with it that further decompose with the liberation of oxygen.

Heterogeneous catalysis is in great favour in the chemical industry. At present, the major part of the products is manufactured by this industry with the aid of heterogeneous catalysis. In heterogeneous catalysis, the reaction proceeds on the surface of the catalyst. It thus follows that the activity of a catalyst depends on the size and properties of its surface. To have a greater ("developed") surface, a catalyst must have a porous structure or be in a greatly comminuted (highly dispersed) state. For practical use, a catalyst is usually applied onto a carrier (support) having a porous structure (pumice, asbestos, etc.)

As in homogeneous catalysis, in heterogeneous catalysis a reaction proceeds via active intermediate compounds (intermediates). But here, these intermediates are surface compounds of the catalyst with the reactants. After passing through a number of stages with the participation of these intermediates, the reaction terminates in the formation of the products, and the catalyst as a result is not consumed.

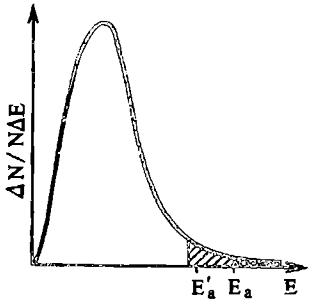


Fig. 67. Influence of a catalyst on the number of active molecules:

The area of the hatched section to the right of E_a equals the fraction of active molecules without a catalyst, and the area to the right of E'_a equals the fraction of active molecules in the presence of a catalyst

Examples of heterogeneous catalytic reactions are the oxidation of sulphur dioxide into the trioxide in the contact method of producing sulphuric acid, the synthesis of ammonia, and the oxidation of ammonia in the production of nitric acid.

Catalysis plays a very great role in biological systems. Most chemical reactions proceeding in the digestive system, in the blood and cells of animals and man are catalytic reactions. The catalysts, which in this case are known as enzymes, are simple or complex proteins. Thus, saliva contains the enzyme ptyaline, which catalyzes the transformation of starch into sugar. An enzyme in the stomach, pepsin, catalyzes the decomposition of proteins. The human organism contains about 30 000 various enzymes; each of them is an effective catalyst of the corresponding reaction.

61. Reaction Rate in Heterogeneous Systems

Heterogeneous reactions are of great significance in engineering. It is sufficient to remember that they include, for example, the combustion of solid fuel, and the corrosion of metals and alloys.

It is not difficult to see that heterogeneous reactions are closely associated with processes of transfer of a substance. Indeed, for a reaction, for instance, of coal combustion to proceed, it is essential that the carbon dioxide formed in this reaction be constantly removed from the surface of the coal, and that new amounts of oxygen be supplied to it. Both processes (the removal of the CO_2 from the surface of the coal and the supply of O_2 to it) are accomplished by convection (the movement of the mass of a gas or liquid) and diffusion.

Thus, at least three steps can be earmarked in the course of a heterogeneous reaction:

1. Supply of the reactant to the surface.
2. A chemical reaction on the surface.
3. Removal of the product from the surface.

In steady-state conditions of a reaction, all three steps proceed at equal rates. The activation energy of a reaction is often not great, and the second step (the chemical reaction proper) could proceed very rapidly if the supply of the reactant to the surface and the removal of the product from it were sufficiently rapid. Consequently, the rate of such reactions is determined by the rate of transfer of the relevant substances. It could be expected that with greater convection their rate would grow. Experiments confirm this assumption. For instance, the combustion of carbon

$$C + O_2 = CO_2$$

whose chemical step requires a low activation energy, proceeds at a faster rate when oxygen (or air) is supplied to the carbon more intensively.

The rate of a heterogeneous reaction is not always determined by the rate of transfer of a substance, however. The determining step of a reaction whose activation energy is high is the second step—the chemical reaction proper. It is quite natural that the rate of such reactions will not grow when stirring is improved. For example, the oxidation of iron by the oxygen in humid air does not accelerate when the supply of air to the surface of the metal is increased because here the activation energy of the chemical step of the process is considerable.

The step determining the rate of a reaction is called the **rate determining step.** In the first example, the transfer of the substance is the rate determining step, and in the second the chemical reaction proper.

62. Chain Reactions

Up to now, we dealt with chemical reactions proceeding comparatively simply. In such reactions, each elementary event of interaction—each collision between the active molecules of the reactants—occurs independently of the results of the preceding elementary events. The formation of macroscopic amounts of the product here is the result of a large number of these independent events.

There is a broad group of reactions, however, that proceed in a more complicated way. In these reactions, the possibility of the occurrence of each elementary event is associated with the successful outcome of the preceding event and, in turn, underlies the possibility of the following one. Here, the formation of macroscopic amounts of the product is the result of a chain of elementary events of interaction. Such reactions are known as **chain** ones.

Chain reactions proceed with the participation of **active centres**—atoms, ions, or **radicals** (fragments of molecules) having unpaired electrons and displaying, as a result, a very high reactivity. The role of the active centres can be played, for example, by the atoms $\mathrm{H}\cdot$, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\cdot$, $:\underset{\cdot}{\overset{\cdot}{\mathrm{O}}}:$ and by the groups of atoms* $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$, $\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot}{\mathrm{C}}}:\mathrm{H}$.

In the events of interaction of the active centres with molecules of the reactants, molecules of the product are formed, and also new active particles—new active centres capable of completing an interaction event. Thus, the active centres are the initiators of chains of consecutive transformations of substances.

A simple example of a chain reaction is the reaction of synthesis of hydrogen chloride

$$H_2+Cl_2=2HCl$$

This reaction is initiated by the action of light. The absorption by a chlorine molecule of a quantum of radiant energy $h\nu$ results in its excitation—in the appearance of energetic vibrations of the atoms

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* It is customary practice in designating active particles to indicate only unpaired electrons by dots, for instance $\mathrm{H}\cdot$, $\mathrm{Cl}\cdot$, $\underset{\cdot}{\overset{\cdot}{\mathrm{O}}}$, $\cdot\mathrm{OH}$, and $\cdot\mathrm{CH_3}$.

in it. If the energy of the vibrations exceeds the energy of the bond between the atoms, the molecule decomposes. This process of **photochemical dissociation** can be expressed by the equation

$$Cl_2 + h\nu = 2Cl\cdot$$

The chlorine atoms formed readily react with hydrogen molecules:

$$Cl\cdot + H_2 = HCl + H\cdot$$

Each hydrogen atom, in turn, readily reacts with a chlorine molecule:

$$H\cdot + Cl_2 = HCl + Cl\cdot$$

This sequence of processes continues: in the present example the number of cycles may reach 100 000. In other words, one absorbed quantum of light leads to the formation of up to one hundred thousand molecules of HCl. The chain terminates when a free atom collides with a wall of the vessel in which the reaction is proceeding. The chain may also terminate upon a collision of two active particles and one inactive one as a result of which the active particles combine into a molecule, and the energy evolved is carried off by the inactive particle. In such cases, **breaking of the chain** occurs.

This is the mechanism of an **unbranched** chain reaction: in each elementary interaction one active centre, in addition to a molecule of the product, gives birth to one new active centre.

In the twenties of the 20th century, N. Semenov* together with his collaborators, when studying the kinetics of various processes, discovered phenomena that could not be explained on the basis of the notions of the mechanism of chemical reactions existing at that time. To explain them, Semenov advanced the theory of **branching chain reactions** in the course of which the interaction of a free radical with a molecule of the reactant leads to the formation of two or more new active centres instead of one. One of them continues the old chain, while the others give birth to new ones. The chain branches out and the reaction progressively accelerates.

Branching chain reactions include, for example, the formation of water from simple substances. The following mechanism of this reaction has been established experimentally and confirmed by calculations. When a mixture of hydrogen with oxygen is heated or an electric discharge is passed through it, the molecules of these gases react to form two hydroxyl radicals:

$$H_2 + O_2 = \cdot OH + \cdot OH$$

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* Nikolai Nikolaevich Semenov (born 1896) is a Soviet academician, a winner of the Lenin, State, and Nobel prizes, and a Hero of Socialist Labour. He worked out and experimentally substantiated the theory of chain reactions and on its basis developed the theory of inflammation and explosions, which is of great practical significance.

The radicals $\cdot OH$ readily react with a hydrogen molecule

$$\cdot OH + H_2 = H_2O + H\cdot$$

which results in the formation of a molecule of water and a free hydrogen atom. The latter reacts with a molecule of O_2 producing two new active particles:

$$H\cdot + O_2 = \cdot OH + \underset{\bullet}{\overset{\bullet}{O}}$$

The oxygen atom, reacting with a molecule of H_2, in turn, can give birth to two new active centres:

$$\underset{\bullet}{\overset{\bullet}{O}} + H_2 = \cdot OH + H\cdot$$

Thus, a progressive increase in the number of active particles occurs, and, if breaking of the chains does not prevent this process, the rate of the reaction sharply grows.

The chain mechanism is followed by such important chemical reactions as burning, explosions, processes of oxidation of hydrocarbons (the preparation of alcohols, aldehydes, ketones, organic acids), and polymerization reactions. This is why the theory of chain reactions is the scientific foundation of a number of important branches of engineering and chemical technology.

Chain reactions also include **nuclear chain reactions** proceeding, for example, in atomic reactors or upon the explosion of an atomic bomb. Here the role of an active particle is played by a neutron whose penetration into the nucleus of an atom may result in decay of the latter attended by the evolving of a lot of energy and by the formation of new free neutrons continuing the chain of nuclear transformations.

63. Irreversible and Reversible Reactions. Chemical Equilibrium

All chemical reactions can be divided into two groups: **irreversible** and **reversible reactions**. Irreversible reactions proceed to the end—until one of the reactants is completely used up. Reversible reactions do not proceed to the end. In these reactions, none of the reactants is used up completely. This distinction is associated with the fact that an irreversible reaction can proceed only in one direction. A reversible reaction, on the contrary, can proceed either in the forward or in the reverse direction.

Let us consider two examples.

Example 1. The reaction between zinc and concentrated nitric acid proceeds according to the equation:

$$Zn + 4HNO_3 = Zn(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

With a sufficient amount of nitric acid, the reaction terminates only when the entire zinc dissolves. In addition, if we try to conduct this reaction in the reverse direction—if we pass nitrogen dioxide through a solution of zinc nitrate, no metallic zinc and nitric acid will be obtained—the given reaction cannot proceed in the reverse direction. Thus, the reaction of zinc with nitric acid is an irreversible reaction.

Example 2. The synthesis of ammonia proceeds according to the equation:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

If we mix one mole of nitrogen with three moles of hydrogen, provide conditions favourable for the reaction to proceed in the system, and analyse the gas mixture after sufficient time elapses, the results of the analysis will show that the system contains not only the product (ammonia), but also the reactants (nitrogen and hydrogen). If we now take ammonia as the reactant instead of the nitrogen-hydrogen mixture in the same conditions, we shall find that part of the ammonia decomposes into nitrogen and hydrogen, and the three substances will be in the same proportion finally as when we started with the mixture of nitrogen and hydrogen. Thus, the synthesis of ammonia is a reversible reaction.

In equations of reversible reactions, the equal sign may be replaced with arrows. They indicate that the reaction proceeds both in the forward and in the reverse direction.

Figure 68 shows how the rates of the forward and reverse reactions change with time. First, when the reactants are mixed, the rate of the forward reaction is high, while that of the reverse reaction is zero. As the reaction goes on, the reactants are used up, and their concentrations diminish. As a result, the rate of the forward reaction lowers. Simultaneously, the products appear, and their concentration grows. This causes the reverse reaction to begin, its rate gradually increasing. When the rates of the forward and reverse reactions become the same, **chemical equilibrium** sets in. For instance, in the last example, equilibrium sets in between the nitrogen, hydrogen, and ammonia.

Chemical equilibrium is called **dynamic** equilibrium. This stresses the fact that both the forward and reverse reactions proceed in equilibrium, but their rates are the same, and as a result no changes are noticeable in the system.

Chemical equilibrium is characterized quantitatively by a quantity known as the **chemical equilibrium constant.** Let us consider it taking as an example the synthesis of hydrogen iodide:

$$H_2 + I_2 \rightleftarrows 2HI$$

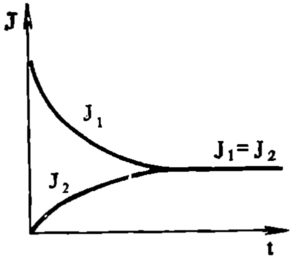

Fig. 68. Change in rate of forward (J_1) and reverse (J_2) reactions with time (t)

According to the law of mass action, the rates of the forward (J_1) and reverse (J_2) reactions are expressed by the equations*:

$$J_1 = k_1[H_2][I_2]$$
$$J_2 = k_2[HI]^2$$

At equilibrium, the rates of the forward and reverse reactions are equal, whence

$$k_1[H_2][I_2] = k_2[HI]^2$$

or

$$\frac{k_1}{k_2} = \frac{[HI]^2}{[H_2][I_2]}$$

The ratio of the rate constants of the forward and reverse reactions is also a constant. It is called the **equilibrium constant** (K) of a given reaction:

$$\frac{k_1}{k_2} = K$$

Hence, we finally get

$$\frac{[HI]^2}{[H_2][I_2]} = K$$

The left-hand side of this equation contains the concentrations of the reacting substances that set in at equilibrium—the **equilibrium concentrations.** The right-hand side of the equation is a constant (at a constant temperature) quantity.

It can be shown that in the general case of a reversible reaction

$$aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots$$

the equilibrium constant will be expressed by the equation

$$K = \frac{[P]^p[Q]^q \ldots}{[A]^a[B]^b \ldots}$$

Here the capital letters stand for the formulas of substances, and the small ones for the coefficients in the equation.

Thus, at a constant temperature, the equilibrium constant of a reversible reaction is a constant quantity showing the relationship between the concentrations of the products (the numerator) and the reactants (the denominator) that is established at equilibrium.

The equation of the equilibrium constant shows that in conditions of equilibrium, the concentrations of all the substances participating in a reaction are related to one another. A change in the concentration of any of these substances leads to changes in the concentrations of all the other substances. As a result, new concen-

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* The system is being considered at elevated temperatures when the iodine is in the vaporous state.

trations are established, but the relationship between them again corresponds to the equilibrium constant.

The numerical value of the equilibrium constant in the first approximation characterizes the yield* of the given reaction. For example, when $K \gg 1$, the yield of a reaction is high because

$$[P]^p [Q]^q \ldots \gg [A]^a [B]^b \ldots$$

i.e. at equilibrium, the concentrations of the products are much greater than those of the reactants, and this is exactly what signifies that the yield of the reaction is high. When $K \ll 1$ (for a similar reason), the yield of the reaction is low.

For heterogeneous reactions, the expression of the equilibrium constant, like the expression of the law of mass action (see Sec. 58), includes the concentrations of only the substances that are in the gaseous or liquid phase. For example, for the reaction

$$CO_2 + C = 2CO$$

the equilibrium constant has the form

$$K = \frac{[CO]^2}{[CO_2}$$

The magnitude of the equilibrium constant depends on the nature of the reacting substances and on the temperature. It does not depend on the presence of catalysts. We have already mentioned that the equilibrium constant equals the ratio of the rate constants of the forward and reverse reactions. Since a catalyst changes the activation energy of both the forward and reverse reactions by the same amount (see Sec. 60), it does not affect the ratio of their rate constants. Therefore, a catalyst does not affect the magnitude of the equilibrium constant and, consequently, cannot either increase or lower the yield of the reaction. It can only accelerate or retard the setting in of equilibrium.

64. Displacement of Chemical Equilibrium. Le Chatelier's Principle

A system will be in a state of equilibrium as long as the external conditions remain constant. If the conditions change, the system will no longer remain in equilibrium—the rates of the forward and reverse processes will change differently—a reaction will proceed. Of the greatest significance are cases of violation of equilibrium

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* The yield of a reaction is defined as the ratio of the amount of a substance produced to its amount that would have been produced if the reaction proceeded to the end.

owing to a change in the concentration of any of the substances participating in equilibrium, in the pressure or temperature.

Let us consider each of these cases.

Violation of Equilibrium Owing to a Change in the Concentration of One of the Substances Participating in the Reaction. Assume that hydrogen, hydrogen iodide, and iodine vapour are in equilibrium with one another at a definite temperature and pressure. Let us introduce a certain additional amount of hydrogen into the system. According to the law of mass action, the increase in the concentration of the hydrogen leads to an increase in the rate of the forward reaction—the synthesis of HI, while the rate of the reverse reaction does not change. The reaction will now proceed more rapidly in the forward direction than in the reverse one. The result will be diminishing of the concentrations of the hydrogen and iodine vapour, which will lead to retarding of the forward reaction, and a growth in the concentration of the HI, which will lead to acceleration of the reverse reaction. In a certain time, the rates of the forward and reverse reactions will again become equal—new equilibrium will set in. But now the concentration of the HI will be greater than it was before the addition of the H_2, while the concentration of the I_2 will be lower.

The process of a change in concentrations due to violation of equilibrium is called the displacement or shifting of equilibrium. If this is attended by an increase in the concentrations of the substances in the right-hand side of an equation (and, naturally, by a simultaneous decrease in the concentrations of the substances in the left-hand side), we say that **equilibrium shifts to the right**, i.e. in the direction of the forward reaction; when the concentrations change in the reverse direction, we say that **equilibrium shifts to the left**—in the direction of the reverse reaction. In the example considered above, equilibrium has shifted to the right. The substance (H_2) whose growth in concentration caused equilibrium to be violated entered into the reaction, and its concentration diminished.

Thus, *when the concentration of one of the substances participating in equilibrium increases, the equilibrium shifts in the direction of consumption of this substance; when the concentration of one of the substances decreases, the equilibrium shifts in the direction of the formation of this substance.*

Violation of Equilibrium Owing to a Change in Pressure (by diminishing or increasing the volume of the system). When gases participate in a reaction, equilibrium may be violated when the volume of the system is changed.

Let us see how the pressure affects the reaction between nitrogen monoxide NO and oxygen

$$2NO + O_2 \rightleftharpoons 2NO_2$$

Assume that a mixture of NO, O_2, and NO_2 was in equilibrium at a definite temperature. Without changing the temperature, let us reduce the volume of the system to one-half its initial value. At the first moment, the partial pressures and concentrations of all the gases will increase two-fold, but the ratio between the rates of the forward and reverse reactions will change—equilibrium is violated.

Indeed, before the increase in pressure, the concentrations of the gases had the equilibrium values $[NO]_{eq}$, $[O_2]_{eq}$, and $[NO_2]_{eq}$, and the rates of the forward and reverse reactions were determined by the equations:

$$J_1 = k_1 [O_2]_{eq} [NO]^2_{eq}$$
$$J_2 = k_2 [NO_2]^2_{eq}$$

At the first moment after compression, the concentrations of the gases will have the values $2[NO]_{eq}$, $2[O_2]_{eq}$, and $2[NO_2]_{eq}$. The rates of the forward and reverse reactions will be determined by the equations:

$$J'_1 = k_1 2 [O_2]_{eq} (2 [NO]_{eq})^2 = 8k_1 [O_2]_{eq} [NO]^2_{eq} = 8J_1$$
$$J'_2 = k_2 (2 [NO]_{eq})^2 = 4k_2 [NO_2]^2_{eq} = 4J_2$$

Thus, as a result of the increase in pressure, the rate of the forward reaction increased 8 times, and of the reverse one only 4 times. Equilibrium in the system will be violated—the forward reaction will predominate over the reverse one. After the rates become equal, equilibrium will again set in, but the amount of NO_2 in the system will increase—equilibrium shifts to the right.

It is not difficult to see that the different change in the rate of the forward and reverse reactions is associated with the fact that the number of gas molecules is different in the left-hand and right-hand sides of the reaction equation: one molecule of oxygen and two molecules of nitrogen monoxide (altogether *three* molecules of gases) transform into *two* molecules of nitrogen dioxide. The pressure of a gas is the result of collisions of its molecules against the walls of a vessel; other conditions being equal, the pressure of a gas is higher when more molecules are contained in a given volume of the gas. Consequently, a reaction proceeding with an increase in the number of molecules of the gases leads to a growth in pressure, while a reaction proceeding with lowering of the number of molecules of the gases leads to its dropping. Remembering this, we can formulate the conclusion on how the pressure affects chemical equilibrium as follows:

When the pressure is increased by compressing a system, equilibrium shifts in the direction of a reduction in the number of molecules of the gases, i.e., in the direction of lowering of the pressure; when the pressure is lowered, equilibrium shifts in the direction of a growth in the number *of molecules of the gases, i.e. in the direction of an increase in the pressure.*

When a reaction proceeds without a change in the number of molecules of the gases, equilibrium is not violated upon compression or expansion of the system. For example, in the system

$$H_2 + I_2 \rightleftharpoons 2HI$$

equilibrium is not violated when the volume changes; the yield of HI does not depend on the pressure.

Violation of Equilibrium Owing to a Change in Temperature. The equilibrium of the overwhelming majority of chemical reactions shifts when the temperature changes. The factor determining the direction of equilibrium displacement is the sign of the heat effect of the reaction. It can be shown that *upon elevation of the temperature, equilibrium shifts in the direction of the endothermic, and upon its lowering—in the direction of the exothermic reaction.*

The synthesis of ammonia, for instance, is an exothermic reaction:

$$N_2 + 3H_2 = 2NH_3 \qquad +92.4 \text{ kJ}$$

Hence, upon elevation of the temperature, equilibrium in the system H_2-N_2-NH_3 shifts to the left—in the direction of decomposition of ammonia, because this process goes on with the absorption of heat.

Conversely, the synthesis of nitrogen monoxide NO is an endothermic reaction:

$$N_2 + O_2 = 2NO \qquad -180.5 \text{ kJ}$$

Therefore, elevation of the temperature is attended by shifting of equilibrium in the system N_2-O_2-NO to the right, in the direction of formation of NO.

The regularities manifesting themselves in the above examples of the violation of chemical equilibrium are particular cases of the general principle determining the influence of various factors on equilibrium systems. This principle, known as **Le Chatelier's principle**, as applied to chemical equilibria can be formulated as follows:

> *If any change of conditions is imposed on a system in equilibrium, the system will alter in such a way as to counteract the imposed change.*

Indeed, when one of the substances participating in a reaction is introduced into the system, equilibrium shifts in the direction of consuming this substance. If the pressure is increased, it shifts so as to lower the pressure in the system; if the temperature is elevated, equilibrium shifts in the direction of the endothermic reaction—the temperature in the system drops.

Le Chatelier's principle relates not only to chemical, but also to various physicochemical equilibria. When the conditions of such processes as boiling, crystallization, and dissolution change, equilibrium shifts in accordance with Le Chatelier's principle.

65. Factors Determining the Direction of Chemical Reactions

In the preceding sections, we considered several examples showing that in definite conditions every chemical reaction spontaneously proceeds in a definite direction. For instance, at low temperatures, the exothermic reaction of formation of water vapour

$$2H_2 + O_2 = 2H_2O \quad +483.6 \text{ kJ}$$

proceeds virtually completely in the forward direction*. But at elevated temperatures, this reaction begins to proceed in the reverse direction: the water vapour decomposes into hydrogen and oxygen. A state of stable chemical equilibrium can always be achieved as a result of a reaction, but the position of equilibrium itself varies in different conditions.

The question arises: what is the reason for a definite direction of chemical processes, what factors cause a definite state of chemical equilibrium?

It is general knowledge that in mechanical systems stable equilibrium corresponds to a minimum of the potential energy of a system. For instance, a ball rolls spontaneously from position *a* on an inclined surface (Fig. 69), and its potential energy first transforms into the kinetic energy of motion of the ball as a whole, and then into the energy of thermal motion of the molecules. In position *b*, the ball is in equilibrium.

It is natural to assume that chemical processes too should spontaneously proceed in the direction of a decrease in the internal energy of the system, i.e. in a direction corresponding to a positive heat effect of the reaction. Indeed, experiments show that in ordinary conditions mainly exothermic reactions proceed spontaneously.

An attempt to explain the directivity of chemical processes *only* by their tendency to acquire a minimum internal energy results in contradictions with facts. For example already at ordinary tem-

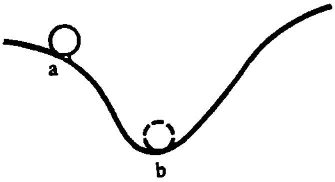

Fig. 69. The ball rolls spontaneously from position *a* to position *b*

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* In the absence of a catalyst, the rate of this reaction in ordinary conditions is extremely low. In the presence of a catalyst, however (for example platinized asbestos), the process of water formation goes on at a high rate.

peratures, the endothermic processes of dissolution of many salts and certain endothermic chemical reactions proceed spontaneously. With elevation of the temperature, a greater and greater number of reactions begin to proceed spontaneously in the direction of the endothermic process. Examples of such reactions are the above-mentioned decomposition of water or the synthesis of nitrogen monoxide NO proceeding at high temperatures:

$$\frac{1}{2}N_2+\frac{1}{2}O_2 \rightleftarrows NO \quad -90.4\ \text{kJ}$$

Moreover, the principle of the tendency to reduce the internal energy to a minimum requires that all exothermic reactions ought to proceed to the end, i.e. excludes the possibility of reversible reactions; however, such reactions actually exist.

Let us now remember that mechanical systems include ones whose behaviour also cannot be described only by the directivity of processes to the achievement of a minimum potential energy. These are systems consisting of a very great number of particles. For instance, the molecules forming air are distributed around the Earth as an atmosphere many kilometres thick, but they do not fall onto the Earth, although the lowest position of each molecule corresponds to the minimum of its potential energy.

Chemical systems also consist of an enormous number of particles. It is therefore not surprising that here too the tendency of achieving a minimum internal energy is not the only factor determining their behaviour.

To form an idea of the second factor affecting the direction of reactions, let us consider a spontaneously occurring process not attended by a heat effect. An example of such a process is the expansion of a rarefied gas.

Assume that part *A* of a vessel divided into two parts (Fig. 70) contains a rarefied gas. In this gas, the average distance between the molecules is great. In these conditions, the internal energy of the gas does not depend on the degree of its rarefaction. The second half of the vessel (*B*) contains no gas. If the cock connecting the two parts of the vessel is opened, the gas spontaneously diffuses through the

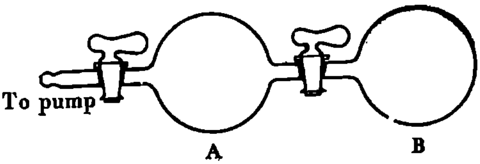

Fig. 70. A vessel consisting of two parts: part *A* contains a rarefied gas, and part *B*—a vacuum

entire vessel. The internal energy of the gas does not change. Nevertheless, it is exactly the process of gas expansion that occurs spontaneously, while the reverse process—spontaneous compression of the gas—does not occur.

The reasons for such a directivity of the process can be understood if we first consider a system containing a small number of molecules. Assume that the vessel contains altogether two molecules, which we shall designate *1* and *2*. The uniform distribution of the gas between the two parts of the vessel corresponding to a definite *macrostate* of the gas* can be achieved by two *microstates*:

A	*B*
1	2
2	1

The macrostate in which the entire gas is concentrated in one part of the vessel (for example, in part *A*) is achieved by a single microstate:

A	*B*
1, 2	—

It is evident that *the probability of a macrostate of a system grows with an increasing number of microstates in which it can be achieved.* In our example (two molecules), the uniform distribution of the gas over the vessel is twice as probable as the transition of the entire gas into part *A*.

Now assume that the vessel contains four molecules, which we shall again number. As previously, a single microstate corresponds to transition of all of the gas into part *A* of the vessel:

A	*B*
1, 2, 3, 4	—

Uniform distribution of the gas between both parts of the vessel, however, can now be achieved by means of six different microstates:

A	*B*	*A*	*B*
1,2	3,4	2,3	1,4
1,3	2,4	2,4	1,3
1,4	2,3	3,4	1,2

---

* A macrostate is the state of a substance characterized by definite values of its *macroscopic properties* (temperature, pressure, volume, etc.); a microstate is the state of a substance characterized by a definite state of *each particle* (molecule, atom). The same macrostate corresponds to a great number of various microstates.

Now, consequently, the probability of the uniform distribution of the gas molecules over the entire volume of the vessel is appreciably higher than the probability of their being concentrated in one of its parts. Naturally, the uniform distribution of the gas will be observed much more frequently than its complete concentration in one part of the vessel.

If the vessel contains six molecules, then only one microstate, as previously, corresponds to their all being in one part of the vessel (i.e. to the spontaneous compression of the gas to half of its initially occupied volume). But now already 20 possible combinations of the molecules, i.e. 20 different microstates, correspond to the uniform distribution of the gas between both parts of the vessel:

A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1, 2, 3	4, 5, 6	1, 3, 5	2, 4, 6	2, 3, 4	1, 5, 6	2, 5, 6	1, 3, 4
1, 2, 4	3, 5, 6	1, 3, 6	2, 4, 5	2, 3, 5	1, 4, 6	3, 4, 5	1, 2, 6
1, 2, 5	3, 4, 6	1, 4, 5	2, 3, 6	2, 3, 6	1, 4, 5	3, 4, 6	1, 2, 5
1, 2, 6	3, 4, 5	1, 4, 6	2, 3, 5	2, 4, 5	1, 3, 6	3, 5, 6	1, 2, 4
1, 3, 4	2, 5, 6	1, 5, 6	2, 3, 4	2, 4, 6	1, 3, 5	4, 5, 6	1, 2, 3

Now the phenomenon of the spontaneous compression of the gas, i.e. the concentration of all its molecules in one part of the vessel, will be observed still less frequently. Uniform distribution of the gas over the entire vessel, on the other hand, becomes still more probable.

Thus, with a growth in the number of molecules, the probability of chaotic uniform distribution of a gas in a vessel increases very rapidly, while the spontaneous compression of the gas becomes less and less probable. If we now remember that macroscopic quantities of a gas contain an enormous number of molecules, it becomes clear that in a real experiment, the spontaneous compression of a gas is a practically impossible process, and that the reverse process of expansion of the gas will proceed spontaneously. This process leads to the uniform chaotic distribution of its molecules over the entire volume of the vessel.

The phenomenon of the expansion of a gas which we have considered is an example illustrating the *principle of the direction of processes to the most probable state*, i.e. to a state which the maximum disorder in the distribution of the particles corresponds to. *The direction of the spontaneous proceeding of chemical reactions is determined by the combined action of two factors: by the tendency of a system to pass over to a state having the lowest internal energy, and by the tendency to achieve the most probable state.*

Thus, in the above example with air, the tendency to a minimum potential energy makes the molecules in the air drop to the Earth, while the tendency to the maximum probability makes them become distributed chaotically in space. The result is an equilibrium distribution of the molecules characterized by their higher concentration at the Earth's surface and a constantly growing rarefaction as the distance from the Earth increases.

In salt-water systems, a minimum of the internal energy in the majority of cases corresponds to the crystalline state of the salt. The most probable state of the system, however, is attained when the salt is distributed chaotically in liquid water. As a result of the combined action of these two factors, equilibrium sets in that corresponds to a definite concentration of the saturated salt solution.

In chemical reactions, owing to the principle of the direction of processes towards the minimum internal energy, the atoms combine into such molecules upon whose formation the greatest amount of energy is evolved. Owing to the principle of the direction of processes to the most probable state, on the other hand, such reactions proceed in which the number of particles grows (for instance, reactions of decomposition of molecules into atoms), or the number of possible states of the atoms increases.

Thus, for the reaction

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \quad +92.4 \text{ kJ}$$

the ammonia formed when the reaction proceeds to the right to the end corresponds to the minimum internal energy of the system. The nitrogen-hydrogen mixture formed upon the complete decomposition of the ammonia, however, corresponds to the most probable state of the system because the number of gas molecules doubles. Owing to the action of both factors, equilibrium sets in in the system that corresponds to a definite ratio between the concentrations of all the substances at the given temperature.

For the reaction

$$N_2 + O_2 \rightleftarrows 2NO \quad -180.8 \text{ kJ}$$

the nitrogen-oxygen mixture formed upon the complete decomposition of the nitrogen monoxide corresponds to the minimum internal energy. Since the number of particles does not change in the course of this reaction, its proceeding to the end both in the forward and in the reverse direction does not increase the probability of the state of the system. The number of possible states of the atoms also remains unchanged here: in the reactants each atom of both nitrogen and oxygen is bound to an atom of the same element (the molecules N_2 and O_2), while in the product each atom is bound to an atom of the other element (the molecule NO). Matters are different when the process occurs only partly in the forward or the reverse direction.

As a result of partial proceeding of the reaction, i.e. when the reactants and the products coexist, the nitrogen and oxygen atoms are in two states: part of them are bound into the molecules N_2 and O_2, and part into the molecules NO. Thus, the number of possible microstates of the system being considered and, consequently, the probability of its corresponding macrostate grow when the reaction proceeds partly. Thus, the tendency to a decrease in the internal energy facilitates the proceeding of the given reaction to the end in the reverse direction, while the tendency to an increase in the probability of the state causes it to partly proceed in the forward direction. Owing to the simultaneous action of both factors, part of the nitrogen-oxygen mixture when heated transforms into NO, and equilibrium sets in between the reactants and the products.

The tendency of the transition to the state with the lowest internal energy manifests itself at all temperatures to the same extent. The tendency of the achievement of the most probable state, however, manifests itself more with an increasing temperature. This is the reason why only the influence of the first of these tendencies tells at low temperatures in the majority of cases, and as a result reactions spontaneously proceed in the direction of the exothermic process. With elevation of the temperature, equilibrium in chemical systems shifts more and more in the direction of decomposition reactions or an increase in the number of states of the atoms. A state of equilibrium characterized by a definite ratio between the concentrations of the reactants and the products corresponds to each temperature.

Both factors considered above, as well as the result of their combined action, can be expressed quantitatively. The quantities involved are studied in the branch of physics called **thermodynamics** and are known as **thermodynamic quantities**. They include, particularly, the internal energy, the enthalpy, the entropy, and the Gibbs energy.

66. Thermodynamic Quantities. Internal Energy and Enthalpy

The **internal energy** *U* of a substance (or system) is the total energy of the particles forming the substance (see also Sec. 54). It consists of the kinetic and potential energies of the particles. The kinetic energy is the energy of translational, vibrational, and rotational motion of the particles; the potential energy is due to the forces of attraction and repulsion acting between the particles.

The internal energy depends on the state of a substance. The change in the internal energy of a system ΔU in a process can be determined. Assume that as a result of a process, a system passes from the initial state 1 to the final state 2, doing the work *W* and absorbing the heat Q from the surroundings*. It is evident that the internal energy of the system diminishes by the value of W, grows by the value of Q, and in the final state will be

$$U_2 = U_1 + Q - W$$

where U_1 and U_2 are the internal energy of the system in the initial (1) and the final (2) state, respectively. If we designate the difference $U_2 - U_1$ by ΔU, the equation can be written in the form

$$\Delta U = Q - W$$

This equation expresses the law of energy conservation according to which the change in the internal energy is independent of the way of conducting the process and is determined only by the initial and final states of a system. What part of the energy will go to do work and what part will transform into heat, however, depends on how the process is conducted: the relationship between the work and the heat may vary. Particularly, if no work is done in the course of a process, including work of expansion against the external pressure, i.e. if the volume of the system does not change, then

$$\Delta U = Q_V$$

where Q_V is the heat absorbed by the system in conditions of a constant volume.

The last equation allows us to determine the change in the internal energy in different processes. For instance, when a substance is heated at constant volume, the change in the internal energy is determined from the heat capacity of this substance:

$$\Delta U = Q_V = nC_V\Delta T$$

Here C_V is the molar heat capacity of the substance at constant volume, n is the number of moles of the substance, and ΔT is the difference between the final and initial temperatures.

For a chemical reaction proceeding without a change in the volume of the system, a change in the internal energy equals the heat effect of the reaction taken with the opposite sign.

Enthalpy. We have to do with processes occurring at a constant pressure more often in chemistry, however. Here it is convenient to use the quantity called the **enthalpy** H determined by the relationship

$$H = U + pV$$

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* In thermochemical equations (see Sec. 55), the heat liberated by a system is considered to be positive. In equations of thermodynamics, the opposite condition has been adopted: the heat absorbed by a system is considered to be positive.

At constant pressure and provided that only the work of expansion ($W = p\Delta V$)* is performed in the course of a process, we have

$$\Delta H = \Delta U + p\Delta V$$

or

$$\Delta U = \Delta H - p\Delta V$$

Comparing the last equation with the equation for the internal energy

$$\Delta U = Q - W$$

we see that in the conditions indicated above

$$\Delta H = Q_p$$

where Q_p is the heat absorbed by the system at constant pressure.

The last equation allows us to determine the change in the enthalpy in different processes. Such determinations are similar to those of the internal energy, the only difference being that all the measurements must be conducted in conditions of a constant pressure. Thus, when a substance is heated, the change in its enthalpy is determined from the heat capacity of this substance at constant pressure

$$\Delta H = Q_p = nC_p\Delta T$$

where n is the number of moles of the substance, and C_p is its molar heat capacity at constant pressure.

Upon changes in the state of aggregation of a substance and in allotropic transitions, the change in the enthalpy is equal in magnitude, but opposite in sign, to the heat of the relevant transformation (fusion, boiling, transformation from one modification into another). Finally, in a chemical reaction, *the change in the enthalpy equals the heat effect of the reaction conducted at a constant temperature and constant pressure taken with the opposite sign.*

The enthalpy, like the internal energy, characterizes the energy state of a substance, but includes the energy spent to overcome the external pressure, i.e. to do the work of expansion. Like the internal energy, the enthalpy is determined by the state of a system and does not depend on how this state was reached. For gases, the difference between ΔU and ΔH in the course of a process may be considerable. For systems containing no gases, the changes in the internal energy and enthalpy attending a process are close to each other. The explanation is that the changes in the volume (ΔV) in processes occurring with substances in condensed (i.e. in the solid or liquid) states are usually very small, and the quantity $p\Delta V$ is small in comparison with ΔH.

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* The work (W) against the force of external pressure equals the magnitude of this force (F) multiplied by the path (Δl), i.e. $W = F\Delta l$. But the force equals the pressure (p) multiplied by the area (A) which it acts on: $F = pA$, whence $W = pA\Delta l$, or $W = p\Delta V$.

67. Thermodynamic Quantities. Entropy and Gibbs Energy

We have already indicated in Sec. 65 that the probability of a macrostate of a system is greater when the number of microstates in which it can be achieved increases. The number of microstates corresponding to a macrostate of a system is usually very great because the number of particles in macroscopic amounts of a substance is colossal, while their positions and velocities at ordinary temperatures are exceedingly diverse.

It was found more convenient to characterize the state of a system in this sense not by the probability itself of achieving a given macrostate, but by a quantity proportional to its logarithm. This quantity is called the entropy. The **entropy** (S) is related to the number (P) of equally probable microscopic states by means of which the given macroscopic state of a system can be achieved by the equation

$$S = \mathrm{k} \log P$$

where k is a proportionality constant.

Crystals with an ideally regular structure at absolute zero have the smallest entropy. The entropy of a crystal whose structure has irregularities is somewhat greater already at absolute zero because the ideal structure may be violated in more than a single way. The entropy always grows with increasing temperature because the intensity of motion of the particles grows, and, consequently, the number of ways in which they can arrange themselves grows. It also grows when a substance transforms from the crystalline state to the liquid one and, especially, when it transforms from the liquid state to the gaseous one. The entropy also changes when chemical processes occur. These changes are especially great in reactions leading to a change in the number of molecules of gases: an increase in the number of gas molecules results in a growth in the entropy, a decrease—in its diminishing.

Like the internal energy and enthalpy, the entropy depends only on the state of a system. But unlike these two functions, the relationship between the change in the entropy and the heat depends on how a process is conducted—on its rate.

We have already mentioned that the relationship between the heat and the work done in the course of a process may be different. But the difference between these quantities equal to the change in the internal energy of a system does not depend on how the process is conducted. When a process is conducted rapidly, the work is small, and when it is conducted slowly, the work grows. In an infinitely slow process—when it is conducted in infinitely small steps from one equilibrium state to another infinitely close to the preceding state—the work takes on the maximum possible value. A process conducted in this way is called a **thermodynamically reversible**, or simply a reversible one*.

The reversible conducting of a process can sometimes be approached in experimental conditions with a high accuracy. In a laboratory, oxidation-reduction reactions in galvanic cells (see Sec. 98), the melting of a solid, and the evaporation of a liquid can be conducted practically reversibly.

If a process is also conducted reversibly at a constant temperature (isothermally), the change in entropy is related to the heat absorbed by the equation

$$\Delta S = \frac{Q_{\text{rev}}}{T}$$

where Q_{rev} is the amount of heat absorbed by the system in an isothermal reversible process, and T is the absolute temperature.

This equation can be used, for example, to determine the change in the entropy in the melting and boiling of substances.

The last equation shows that when a certain amount of heat is absorbed, the entropy of a system grows the more, the lower is the temperature at which the heat is absorbed. This can be explained as follows. Let us supply the same amount of heat to two identical portions of a given substance. Let one of the portions be at a low temperature, for instance 1 K, and the other at a high temperature, for instance 1000 K. It is evident that the relative growth in the velocity of the particles and the increase in the degree of their randomness—and, therefore, the growth in the entropy—will be greater in the first case than in the second.

The entropy has the dimension of energy divided by temperature. It is usually expressed in J/K.

It is shown in thermodynamics that functions can be introduced which show how the direction of a process is affected both by the tendency to diminishing of the internal energy and by the tendency to achieve the most probable state of a system. The sign of the change in such a function in a reaction can be a criterion of the possibility of the reaction proceeding spontaneously. For isothermal reactions proceeding at a constant pressure, the **Gibbs energy**** G is such a function (other names of this function are the **isobaric-isothermal potential**, the **isobaric potential**, and the **free energy at constant pressure**).

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[*] Do not confuse thermodynamic reversibility as a way of conducting a process with chemical reversibility—the ability of a reaction to proceed both in the forward and in the reverse direction.

[**] Named after Josiah Willard Gibbs (1839-1903)—an outstanding American scientist, one of the founders of chemical thermodynamics and statistical physics.

The Gibbs energy is related to the enthalpy, entropy, and temperature by the equation

$$G = H - TS$$

If a reaction is conducted at constant pressure and temperature (such a process is called an **isobaric-isothermal** one), then the change in the Gibbs energy in the reaction will be

$$\Delta G = \Delta H - T\,\Delta S$$

In the reversible and isothermal conducting of a process, ΔG is equal in magnitude, but opposite in sign, to the maximum useful work that the system does in the given process:

$$\Delta G = -W_{\max}$$

By useful work is meant all the work done in the course of a process less the work of expansion $p\,\Delta V$.

It can be proved that *in conditions of a constant temperature and pressure, reactions proceed spontaneously in the direction of diminishing of the Gibbs energy.* Since ΔG is equal in magnitude but opposite in sign to the maximum useful work of a process, what has been said above can be worded differently: *only those reactions can proceed spontaneously at the expense of whose energy useful work can be performed.*

For a rough assessment of the direction in which a reaction will proceed at low and at high temperatures, approximate equations of the Gibbs energy of a reaction can be used. For low temperatures, the factor T is small and the absolute value of the product $T\,\Delta S$ is also small. In this case for reactions having a considerable heat effect, $|\Delta H| \gg |T\,\Delta S|$. Hence in the expression

$$\Delta G = \Delta H - T\,\Delta S$$

the second term may be ignored. This yields

$$\Delta G \approx \Delta H$$

For sufficiently high temperatures (the factor T is large), we have the opposite relationship:

$$|\Delta H| \ll |T\,\Delta S|$$

Ignoring now the first term in the expression of the Gibbs energy, we get

$$\Delta G \approx -T\,\Delta S$$

These approximate equations show that for low temperatures the criterion of the direction in which a reaction proceeds simultaneously in a first approximation is the sign of the heat effect of the reaction, and for high temperatures is the sign of the change in the entropy.

This signifies that at low temperatures exothermic reactions can proceed spontaneously, and at high temperatures—reactions attended by an increase in the entropy.

We must add to what has been said above that a negative value of ΔG for a reaction points only to the possibility of its occurring. Actually, the reaction may not be observed. The matter is that its rate may be low; hence, notwithstanding observance of the condition $\Delta G < 0$, the reaction will virtually not proceed. In these cases, an appropriate catalyst must be found to increase the rate of the reaction. Such cases are especially frequent at low temperatures.

68. Standard Thermodynamic Quantities. Chemico-Thermodynamic Calculations

The value of the change in the Gibbs energy in a reaction depends on the temperature, and also on the nature and concentrations of the reactants and products. For convenience of comparing different reactions, it is customary practice to compare the values of ΔG for **standard** conditions, i.e. at identical concentrations of the substances (a pure state for individual substances, a concentration equal to 1 mole in 1000 g of the solvent for solutions, and a partial pressure equal to standard atmospheric pressure for gases). The state of a substance in standard conditions is called its **standard state.**

Thermodynamic quantities characterizing a substance in its standard state are called **standard quantities.** Changes in thermodynamic quantities in a reaction where the reactants in the standard state transform into the products also in the standard state are called **standard changes** in the relevant quantities. Standard quantities and their changes are customarily designated by means of the superscript "°". For instance, the standard entropy is designated by the symbol S°, the standard change in the enthalpy by ΔH°, and the standard change in the Gibbs energy by ΔG°.

The standard change in the Gibbs energy of a reaction is related to the equilibrium constant of the reaction by the equation

$$\Delta G^\circ = -2.3RT \log K$$

If we introduce the value of the molar gas constant $R = 8.31$ J/(mol·K) into the above equation, we get

$$\Delta G^\circ = -2.3 \times 8.31T \log K = -19.1 \log K \text{ J/mol}$$

or

$$\Delta G^\circ = -0.0191T \log K \text{ kJ/mol}$$

This equation makes it possible to calculate the equilibrium constant if we know ΔG° and, conversely, to determine ΔG° for a reaction using the experimentally found value of the equilibrium constant.

It holds for any temperature, but is used most often for 25 °C (298 K); this temperature has been adopted as the standard one. The temperature is indicated in the form of a subscript:

$$\Delta G^\circ_{298} = -0.0191 \times 298 \log K_{298} \text{ kJ/mol}$$

or

$$\Delta G^\circ_{298} = -5.69 \log K_{298} \text{ kJ/mol}$$

In calculating the standard changes in the enthalpy and Gibbs energy for reactions, the standard enthalpies and Gibbs energies of formation of the relevant substances are generally used. These quantities are ΔH° and ΔG° for the reactions of formation of a given substance from simple ones in standard conditions. If an element forms several simple substances, the most stable of them (in the given conditions) is taken. The enthalpy of formation and the Gibbs energy of formation of the most stable simple substances are taken equal to zero.

According to Hess's law, *the standard change in the enthalpy of a reaction* (or simply the standard enthalpy of a reaction) *equals the sum of the standard enthalpies of formation of the products less the sum of the standard enthalpies of formation of the reactants.* Similarly, *the standard change in the Gibbs energy of a reaction* (or simply the standard Gibbs energy of a reaction) *equals the sum of the standard Gibbs energies of formation of the products less the sum of the standard Gibbs energies of formation of the reactants.* All summations are performed with account taken of the number of moles of the substances participating in the reaction in accordance with its equation.

Table 7 gives the values of the standard enthalpies and Gibbs energies of formation of selected substances at 25 °C (298 K).

More complete data of this kind can be found in reference and other books, for example in M. Kh. Karapetyants, *Chemical Thermodynamics*. Trans. by G. Leib. Moscow, Mir Publishers (1978), pp. 604-624*.

Example 1. Calculate ΔH°_{298}, the heat effect at 298 K and constant pressure, and ΔG°_{298} for the reaction:

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

Calculation of ΔH°_{298} and the heat effect of the reaction. In Table 7, we find $\Delta H^\circ_{\text{form}}$ for Fe_2O_3 (—822.2 kJ/mol) and Al_2O_3 (—1676 kJ/mol) at 298 K and

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* Some reference books give the values of the standard enthalpy of formation ($\Delta H^\circ_{\text{form}}$) and the standard entropy (S°) of substances. To calculate the standard Gibbs energy of formation ($\Delta G^\circ_{\text{form}}$) of a substance, it is necessary to first compute the standard entropy of formation ($\Delta S^\circ_{\text{form}}$) of the substance, and then use the formula

$$\Delta G^\circ_{\text{form}} = \Delta H^\circ_{\text{form}} - T\,\Delta S^\circ_{\text{form}}$$

Table 7

Standard Enthalpy of Formation and Standard Gibbs Energy of Formation of Selected Substances at 298 K (25 °C)

The symbols used to denote the states of aggregation of the substances are: g — gaseous, lq — liquid, c — crystalline

Substance	$\Delta H^\circ_{\text{form}}$, kJ/mol	$\Delta G^\circ_{\text{form}}$, kJ/mol	Substance	$\Delta H^\circ_{\text{form}}$, kJ/mol	$\Delta G^\circ_{\text{form}}$, kJ/mol
Al_2O_3 (corundum)	—1676	—1582	HBr (g)	—34.1	—51.2
			HI (g)	+26.6	+1.8
CH_4 (g)	—74.9	—50.8	H_2O (g)	—241.8	—228.6
C_2H_2 (g)	+226.8	+208.4	H_2O (lq)	—285.8	—237.2
C_2H_4 (g)	+52.3	+68.2	H_2S (g)	—20.9	—33.6
CO (g)	—110.5	—137.1	MgO (c)	—601.8	—569.6
CO_2 (g)	—393.5	—394.4	NH_3 (g)	—46.2	—16.7
CaO (c)	—635.5	—604.2	NH_4Cl (c)	—314.2	—203.2
ClO_2 (g)	+105	+122.3	NO (g)	+90.2	+86.6
Cl_2O (g)	+75.7	+93.4	NO_2 (g)	+33	+51.5
Cl_2O_7 (lq)	+251	...	N_2O (g)	+82.0	+104.1
Cr_2O_3 (c)	—1141	—1059	OF_2 (g)	+25.1	+42.5
CuO (c)	—162.0	—129.4	SO_2 (g)	—296.9	—300.2
FeO (c)	—264.8	—244.3	SO_3 (g)	—395.8	—371.2
Fe_2O_3 (c)	—822.2	—740.3	SiO_2 (α-quartz)	—910.9	—856.7
HF (g)	—270.7	—272.8			
HCl (g)	—91.8	—94.8			

perform algebraic summation:

$$\Delta H^\circ_{298} = -1676 - (-822.2) = -853.8 \text{ kJ}$$

Since the change in the enthalpy of a reaction is equal in magnitude, but opposite in sign, to its heat effect at constant temperature and pressure (see p. 207), the thermochemical equation of the reaction can be written as follows:

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe \quad +853.8 \text{ kJ}$$

For low temperatures, the sign of the change in the enthalpy of a reaction can serve for a preliminary determination of the possible direction of the reaction. The negative value of ΔH° obtained for the reaction being considered means that it can be spontaneous at sufficiently low temperatures; the high absolute value of ΔH° makes it possible with sufficient probability to assume that in conditions differing not very greatly from standard ones this reaction can also proceed in the forward direction.

Calculation of ΔG°_{298} of the reaction. In Table 7, we find $\Delta G^\circ_{\text{form}}$ for Fe_2O_3 (—740.3 kJ/mol) and Al_2O_3 (—1582 kJ/mol) at 298 K and perform summation:

$$\Delta G^\circ_{298} = -1582 - (-740.3) = -831.7 \text{ kJ}$$

The negative value obtained for ΔG°_{298} confirms the conclusion made on the basis of the assessment of ΔH°_{298} of the reaction. The closeness of the found values of ΔH°_{298} and ΔG°_{298} is associated, in particular, with the fact that when the reaction proceeds, the number of molecules of the gases does not change (in our example neither the reactants nor the products are gases). When the number of molecules of the gases changes, however, the entropy of the system may change quite appreciably (the transition to the gaseous state is attended by a great growth in the molecular randomness!), owing to which the values of ΔH° and ΔG° may not only noticeably differ in their magnitude, but even have different signs (see Example 2). Therefore, in such cases, the sign of ΔH°_{298} cannot be a definite criterion of the direction of the spontaneous proceeding of a reaction.

The high absolute value of ΔG°_{298} found for the reaction being considered makes it possible with sufficient probability to speak of the possibility of this reaction proceeding in the forward direction not only at the standard temperature (25 °C), but also at other temperatures. Such a conclusion cannot be made for low absolute values of ΔG°_{298}, and also for reactions proceeding with a change in the number of gas molecules: in such cases we must know how ΔG° depends on the temperature.

Example 2. Calculate ΔH°_{298}, the heat effect at 298 K and constant pressure, and ΔG°_{298} for the reaction:

$$CuO + C = Cu + CO$$

Calculation of ΔH°_{298} *of the reaction.* In Table 7, we find ΔH°_{form} for CuO (—162.0 kJ/mol) and CO (—110.5 kJ/mol) at 298 K and perform summation:

$$\Delta H^\circ_{298} = -110.5 - (-162.0) = 51.5 \text{ kJ}$$

Thus,

$$CuO + C = Cu + CO \quad -51.5 \text{ kJ}$$

The found value of ΔH°_{298} is positive, but small in absolute value. Therefore, it cannot be a criterion of the direction of the reaction even at moderate temperatures, moreover because in the case being considered the number of gas molecules changes as a result of the reaction.

Calculation of ΔG°_{298} *of the reaction.* In Table 7, we find ΔG°_{form} for CuO (—129.4 kJ/mol) and CO (—137.1 kJ/mol) at 298 K and perform summation:

$$\Delta G^\circ_{298} = -137.1 - (-129.4) = -7.7 \text{ kJ}$$

The obtained value of ΔG°_{298} is also small in absolute value, but negative. It shows that the reaction may occur in the forward direction in standard conditions, but gives no grounds for conclusions on its direction in conditions differing from standard ones.

In the given example, the different signs of ΔH°_{298} and ΔG°_{298} are explained by the growth in the number of gas molecules in the course of the reaction and the corresponding increase in the entropy. It is exactly for this reason that the spontaneous proceeding of the endothermic reaction of copper reduction is possible.

Example 3. Calculate the equilibrium constant for the reaction

$$NH_3 + HCl = NH_4Cl$$

First of all, we determine ΔG°_{298} of the reaction. For this purpose, in Table 7, we find ΔG°_{form} for NH_3 (—16.7 kJ/mol), HCl (—94.8 kJ/mol), and NH_4Cl

(—203.2 kJ/mol) at 298 K, and perform summation:

$$\Delta G^\circ_{298} = -203.2 - (-16.7 - 94.8) = -91.7 \text{ kJ}$$

Now, we introduce the found value of ΔG°_{298} into the equation $\Delta G^\circ_{298} = -5.69 \log K_{298}$ (see p. 212). We get

$$-91.7 = -5.69 \log K_{298}$$

Hence

$$\log K_{298} \approx 16$$

that is

$$K_{298} = \frac{1}{[NH_3][HCl]} \approx 10^{16}$$

The high value of the constant we have found shows that at the standard temperature the equilibrium

$$NH_3 + HCl \rightleftharpoons NH_4Cl$$

is greatly shifted to the right; in other words, at 25 °C ammonium chloride is a stable compound.

7

WATER. SOLUTIONS

WATER

69. Water in Nature

Water is a very widespread substance on the Earth. Almost three-fourths of our globe's surface is covered with water that forms the oceans, seas, rivers, and lakes. The atmosphere contains a lot of water in the gaseous state in the form of vapour. The peaks of high mountains and polar countries are covered the year around with enormous masses of water in the form of snow and ice. The interior of the Earth also contains water; it impregnates the soil and rocks.

Natural water is never absolutely pure. Rain water is the closest to the pure state, but it too contains insignificant amounts of various impurities entrapped from the air.

The amount of impurities in fresh water usually ranges from 0.01 to 0.1% (mass). Ocean water contains 3.5% (mass) of dissolved substances, the main mass of which is sodium chloride (table salt).

Water containing a considerable amount of calcium and magnesium salts is called **hard** in contrast to **soft** water, for example rain water. Hard water gives only a small amount of suds with soap, and forms scale on the walls of boilers (and in tea-kettles). The hardness of water will be considered in greater detail in Vol. 2, Sec. 98.

To free natural water from particles suspended in it, it is filtered through a layer of a porous substance, for example charcoal or burnt clay. Sand and gravel filters are used to purify large quantities of water. The filters also retain a major part of the bacteria. In addition, potable water is disinfected by chlorination; not over 0.7 g of chlorine per tonne of water is needed for its complete sterilization.

Only insoluble impurities can be removed from water by filtration. Solutes are removed from it by distillation or ion exchange (see Vol. 2, Sec. 98).

Water is very important in the life of plants, animals, and man. According to modern notions, the origin of life itself is associated with the ocean. In any organism, water is the medium in which the chemical processes ensuring the vital activity of the organism occur. In addition, it itself participates in numerous biochemical reactions.

70. The Physical Properties of Water

Pure water is a colourless transparent liquid. The density of water when it transforms from the solid state to the liquid one does not diminish, as it does in almost all other substances, but grows. When water is heated from 0 to 4 °C, its density also increases. At 4 °C, water has the maximum density, and only upon further heating does its density diminish.

If in lowering of the temperature and in a transition from the liquid to the solid state, the density of water would change in the same way as in the overwhelming majority of substances, then when cold weather sets in, the surface layers of bodies of water in nature would cool to 0 °C and sink to the bottom, freeing place for the warmer layers. This would continue until the entire mass of the body of water would acquire a temperature of 0 °C. Next, the water would begin to freeze, the ice floes formed would sink to the bottom, and the body of water would freeze through its entire depth. Many forms of life in water would be impossible. But since water reaches its greatest density at 4 °C, the displacement of its layers due to cooling terminates when this temperature is reached. Upon further lowering of the temperature, the cooled layer, having a lower density, remains on the surface, freezes, and thus protects the lower layers from further cooling and freezing.

The circumstance that water has an anomalously high heat capacity [4.18 J/(g·K)]* is of great significance in the life of nature. For this reason, at night, and also when cold weather sets in, water cools slowly, while in the daytime, or when warm weather sets in, it warms just as slowly, thus being a governor of the temperature on the globe.

Since when ice melts, the volume occupied by the water diminishes, the application of pressure lowers the melting point of ice. This follows from Le Chatelier's principle. Indeed, assume that ice and liquid water are in equilibrium at 0 °C. When the pressure is increased, equilibrium, according to Le Chatelier's principle, shifts in the direction of formation of the phase which occupies a smaller volume at the same temperature. In the given case, this phase is the liquid. Thus, an increase in the pressure at 0 °C causes ice to transform into a liquid, and this signifies that the melting point of ice lowers.

A water molecule has a V-shaped structure. The nuclei in it form an isosceles triangle in whose base there are two protons, while its

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* We shall indicate for comparison the values of the specific heat capacity for some other substances [in J/(g · K)]: sand 0.79, lime 0.88, sodium chloride 0.88, glycerine 2.43, ethyl alcohol 2.85.

apex accommodates the nucleus of an oxygen atom. The internuclear distances O—H are close to 0.1 nm, and the distance between the nuclei of the hydrogen atoms is about 0.15 nm. Of the eight electrons forming the outer electron layer of the oxygen atom in a water molecule

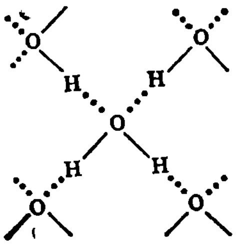
$$\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}$$

two electron pairs form covalent bonds O—H, while the other four electrons are two unshared electron pairs.

As we indicated on p. 144, the oxygen atom in a water molecule is in the state of sp^3 hybridization. Therefore, the valence angle HOH (104.5 deg) is close to the tetrahedral one (109.5 deg). The electrons forming the O—H bonds are displaced towards the more electronegative oxygen atom, and as a result the hydrogen atoms acquire effective positive charges (Fig. 71). The unshared electron pairs in the sp^3 hybrid orbitals are displaced relative to the nucleus of the oxygen atom and set up two negative poles.

The molecular mass of vaporous water is 18 and corresponds to its empirical formula. But the molecular mass of liquid water determined by studying its solutions in other solvents (see Sec. 80) is higher. This indicates that the molecules in liquid water **associate**, i.e. combine into more complex aggregations. This conclusion is also confirmed by the anomalously high values of the melting and boiling points of water (see Fig. 57 on p. 163). As we have already mentioned in Sec. 47, the association of water molecules is due to the formation of hydrogen bonds between them.

In solid water (ice), the oxygen atom in each molecule participates in the formation of two hydrogen bonds with the neighbouring molecules of water according to the scheme



in which the hydrogen bonds are shown by dotted lines. The volume structure of ice is shown schematically in Fig. 72. The formation of hydrogen bonds results in an arrangement of the water molecules such that their opposite poles are in contact with one another. The molecules form layers, and each of them is bound to three molecules belonging to the same layer and to one molecule from the adjacent layer. The structure of ice is the least dense, and it has voids whose size is somewhat greater than that of a water molecule.

When ice melts, its structure is demolished. But in liquid water too the hydrogen bonds between the molecules are retained: associates—fragments of the ice structure—are formed each consisting of a certain number of water molecules. Unlike ice, however, each associate exists a very short time: the destruction of some aggregates and the formation of others are constantly taking place. The voids of such "ice" aggregates can accommodate single molecules of water, and the packing of the water molecules becomes denser. This is exactly the reason why when ice melts the volume occupied by the formed water diminishes, and its density grows.

When the water is heated, the number of fragments of the ice structure in it becomes smaller and smaller, which leads to a further increase in the density of the water. In the temperature interval from 0 to 4 °C, this effect predominates over thermal expansion, so that the density of the water continues to grow. Upon further heating above 4 °C, however, the influence of the increase in the thermal motion of the molecules predominates, and the density of the water diminishes. This is why water has the maximum density at 4 °C.

When water is heated, part of the heat is used to break the hydrogen bonds (the bond dissociation energy of the hydrogen bond in water is about 25 kJ/mol). This explains the high heat capacity of water.

The hydrogen bonds between water molecules are broken completely only when the water transforms into vapour. At 20 °C, about a half of the hydrogen bonds still remain in liquid water.

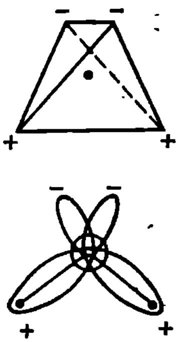


Fig. 71. Structure of water molecule

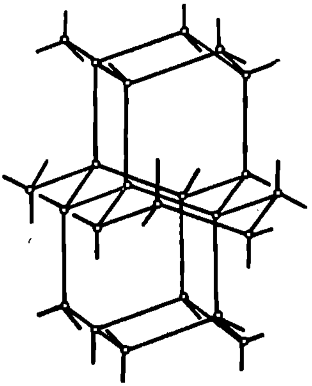


Fig. 72. Structure of ice

71. Phase Diagram of Water

A phase diagram is a graphical illustration of the relationship between quantities characterizing the state of a system, and the phase transitions in the system (the transition from the solid to the liquid state, from the liquid to the gaseous state, etc.). Phase diagrams are widely used in chemistry. Diagrams showing how the phase transitions depend on the temperature and pressure are customarily used for one-component systems; they are known as **phase diagrams in *p-T* coordinates.**

Figure 73 depicts a phase diagram of water schematically (without strict observance of the scale). Definite values of the temperature and pressure correspond to any point in the diagram.

The diagram shows the states of water that are thermodynamically stable at definite values of the temperature and pressure. It consists of three curves dividing all possible temperatures and pressures into three regions corresponding to ice, liquid, and vapour.

Let us consider each of the curves in greater detail. We shall begin with curve *OA* separating the vapour region from the region of the liquid state. Let us imagine a cylinder from which air has been evacuated, and a certain amount of pure water free of solutes, including gases, has been introduced into it. The cylinder is provided with a piston fixed in a certain position (Fig. 74). After some time, part of the water will evaporate, and saturated vapour will be above its surface. We can measure the pressure and see that it does not change with time and does not depend on the position of the piston. If we raise the temperature of the entire system and again measure the pressure of the saturated vapour, we shall find that it has grown. Repeating such measurements at different temperatures, we shall find how the pressure of saturated water vapour depends on the tem-

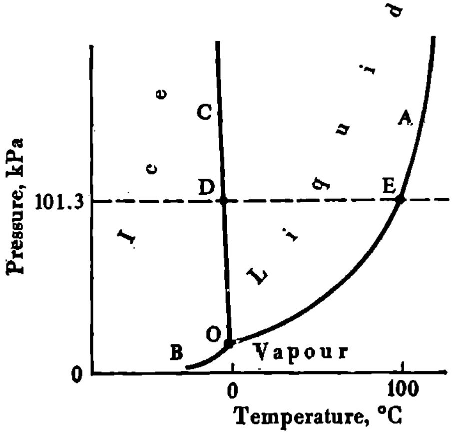


Fig. 73. Phase diagram of water in region of low pressures

perature. Curve OA shows this dependence: points on the curve give the pairs of values of the temperature and pressure at which liquid water and water vapour are in equilibrium with each other—they coexist. Curve OA is called a liquid-vapour equilibrium curve or a boiling curve. Table 8 gives the values of the pressure of saturated water vapour at several temperatures.

Table 8

Pressure of Saturated Water Vapour at Different Temperatures

Temperature, °C	Saturated vapour pressure		Temperature, °C	Saturated vapour pressure	
	kPa	mmHg		kPa	mmHg
0	0.61	4.6	50	12.3	92.5
10	1.23	9.2	60	19.9	149
20	2.34	17.5	70	31.2	234
30	4.24	31.8	80	47.4	355
40	7.37	55.3	100	101.3	760

Let us try to achieve in the cylinder a pressure other than the equilibrium one, for instance lower than the equilibrium value. To do this, we shall release the piston and lift it. At the first moment, the pressure in the cylinder will indeed drop, but soon equilibrium will be restored: a certain amount of water will additionally evaporate, and the pressure will again reach its equilibrium value. Only when the water evaporates completely can a pressure below the equilibrium value be achieved. It thus follows that the points in the phase diagram below or to the right of curve OA correspond to the vapour region. We can produce a pressure exceeding the equilibrium value only by lowering the piston to the surface of the water. In other words, the region of the liquid state corresponds to the points in the diagram above or to the left of curve OA.

How far to the left do the regions of the liquid and gaseous states extent? Let us earmark a point in each of these regions and move from them horizontally to the left. Cooling of the liquid or vapour at constant pressure corresponds to this move-

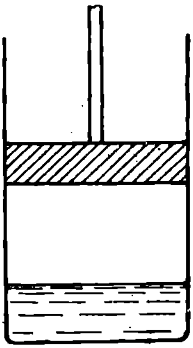


Fig. 74. Vessel with water in equilibrium with water vapour

ment of the points in the diagram. We know that if water is cooled at standard atmospheric pressure, when 0° C is reached, the water will begin to freeze. Performing similar experiments at other pressures, we shall arrive at curve *OC* separating the region of liquid water from that of ice. This curve—the curve of solid-liquid equilibrium or the **melting (freezing) curve**—shows the pairs of temperature and pressure values at which ice and liquid water are in equilibrium.

Moving horizontally to the left in the vapour region (in the lower part of the diagram), we arrive in a similar way at curve *OB*. This is a curve of solid-vapour equilibrium, or a **sublimation curve.** The pairs of temperature and pressure values at which ice and water vapour are in equilibrium correspond to it.

All three curves intersect at point *O*. The coordinates of this point are the single pair of temperature and pressure values at which all three phases (ice, liquid water, and vapour) can be in equilibrium. It is known as the **triple point.**

The melting curve has been investigated up to very high pressures. In this region, several modifications of ice have been found (they are not shown in the diagram).

The boiling curve terminates at the right at the **critical point**. At the temperature corresponding to this point—the **critical temperature**—the quantities characterizing the physical properties of the liquid and vapour become the same, so that the distinction between the liquid and vapour states vanishes.

The existence of the critical temperature was established in 1860 by D. Mendeleev in studying the properties of liquids. He showed that at temperatures above the critical one a substance cannot be in the liquid state. In 1869, T. Andrews, in studying the properties of gases, arrived at a similar conclusion.

The critical temperature and pressure are different for different substances. For instance, for hydrogen, $t_{cr} = -239.9$ °C and $p_{cr} = 1.30$ MPa, for chlorine, $t_{cr} = 144$ °C and $p_{cr} = 7.71$ MPa, and for water, $t_{cr} = 374.2$ °C and $p_{cr} = 22.12$ MPa.

One of the features of water distinguishing it from other substances is the lowering of the melting point of ice with a growth in the pressure (see Sec. 70). This is reflected in the phase diagram. Melting curve *OC* in the phase diagram of water extends upwards to the left, whereas for almost all other substances it extends upwards to the right.

The transformations occurring with water at atmospheric pressure are shown in the diagram by points or segments on the horizontal line corresponding to 101.3 kPa (760 mmHg). For instance, the melting of ice or the freezing of water corresponds to point *D* (see Fig. 73), the boiling of water to point *E*, and the heating or cooling of water to segment *DE*.

Phase diagrams have been studied for a number of substances having a scientific or practical significance. In principle, they are similar to the phase diagram of water considered above. The phase diagrams of various substances, however, may have special features. For instance, substances are known whose triple point corresponds to a pressure greater than atmospheric pressure. In this case, heating of crystals at atmospheric pressure results not in melting of the substance, but in its **sublimation**—the transformation of the solid phase directly into the gaseous one.

72. The Chemical Properties of Water

Water molecules are distinguished by their high stability when heated. At temperatures above 1000 °C, however, water vapour (or steam, as water vapour is usually called at temperatures equal to or above the boiling point) begins to decompose into hydrogen and oxygen:

$$2H_2O \rightleftharpoons 2H_2 + O_2$$

The process of decomposition of a substance due to heating is called **thermal dissociation.** The thermal dissociation of water proceeds with the absorption of heat. Therefore, according to Le Chatelier's principle, water decomposes to a greater extent with elevation of the temperature. Even at 2000 °C, however, the degree of thermal dissociation of water does not exceed 2%, i.e. equilibrium between gaseous water and the products of its dissociation—hydrogen and oxygen—still remains shifted towards the side of water. Upon cooling to below 1000 °C, equilibrium shifts virtually completely in this direction.

A variety of methods are used to determine the degree of thermal dissociation of a substance. One of them is based on the so-called "freezing of equilibrium". If the dissociation products formed at a high temperature are rapidly cooled, equilibrium does not have time to shift immediately, and does not shift later owing to the extremely low rate of the reaction at a low temperature. Thus, the ratio between the substances that existed at the high temperature is retained. This ratio can be determined by analysis.

Water is a highly reactive substance. The oxides of many metals and non-metals combine with water to form bases and acids. Some salts form crystal hydrates (see Sec. 75) with water. The most active metals react with water with the liberation of hydrogen.

Water also has a catalytic ability. Some ordinary reactions do not virtually proceed in the absence of traces of moisture. For instance, chlorine does not react with metals, hydrogen fluoride does not erode glass, and sodium does not oxidize in an atmosphere of air.

Water is capable of forming compounds with a number of substances that are in the gaseous state in ordinary conditions and usually do not display a high chemical activity. Examples are the hydrates $Xe \cdot 6H_2O$, $CH_4 \cdot 6H_2O$, and $C_2H_5Cl \cdot 15H_2O$. Such compounds are formed when the gas molecules fill the intermolecular spaces in the structure of water and are known as **inclusion** or **clathrate compounds.** The latter are unstable and can exist at comparatively low temperatures.

Heavy Water. In the electrolysis of ordinary water, which in addition to H_2O molecules contains an insignificant amount of D_2O molecules formed by the heavy isotope of hydrogen, the molecules of H_2O are mainly decomposed. Consequently, when a portion of water is electrolyzed for a long time, the residue is gradually enriched in D_2O molecules. In 1933, after the repetition of electrolysis many times, a small amount of water consisting of almost 100% of D_2O molecules was obtained for the first time. It was called heavy water.

Heavy water appreciably differs from ordinary water in its properties (Table 9). Reactions with heavy water proceed more slowly than with its ordinary counterpart. Heavy water is used as a neutron moderator in nuclear reactors.

Table 9

Selected Constants of Ordinary and Heavy Water

Constant	H_2O	D_2O
Molecular mass	18	20
Freezing point, °C	0	3.8
Boiling point, °C	100	101.4
Density at 25 °C, g/cm^3	0.9971	1.1042
Temperature of maximum density, °C	4	11.6

SOLUTIONS

Solutions are of great importance in the life and practical activities of man. For example, the processes of food assimilation by man and animals involve the transfer of nutrient substances into a solution. All the most important physiological liquids (blood, lymph, etc.) are solutions. Industrial processes based on chemical reactions are generally associated with the use of solution.

73. A Characteristic of Solutions. The Dissolving Process

A solution is defined as a solid or liquid homogeneous system consisting of two or more components (constituent parts) whose relative amounts may vary within broad limits. Liquid solutions are the most important kinds of solution, and the present section is devoted to their consideration.

A solution consists of one or more dissolved substances called **solutes**, and the medium in which the solutes are uniformly distributed in the form of molecules or ions, called the **solvent**. Usually, the component which in the pure form exists in the same state of aggregation as the solution obtained is considered to be the solvent (for example, if we consider an aqueous solution of a salt, the solvent is naturally water). If both components were in the same state of aggregation prior to dissolution (for instance, alcohol and water), then the component that is in the greater amount is considered to be the solvent.

The homogeneity of solutions makes them very similar to chemical compounds. The evolution of heat when some substances dissolve also points to the chemical interaction between the solvent and the solute. Solutions differ from chemical compounds in that the composition of a solution can change within broad limits. Moreover, the properties of a solution display many properties of its individual components, which is not observed for a chemical compound. The variability of the composition of solutions brings them close to mechanical mixtures, but they differ sharply from the latter in their homogeneity. Solutions are thus intermediate between mechanical mixtures and chemical compounds.

A crystal dissolves in a liquid as follows. When the crystal is introduced into a liquid in which it can dissolve, separate molecules break away from its surface and owing to diffusion (see p. 235) become uniformly distributed throughout the entire volume of the solvent. The separation of the molecules from the surface of the solid is due, on the one hand, to their intrinsic vibrational motion, and, on the other, to attraction by the solvent molecules. This process ought to proceed up to complete dissolution of any amount of crystals if the reverse process—crystallization—did not proceed simultaneously. The molecules that have passed into the solution collide with the surface of the still undissolved substance, are again attracted to it, and enter the composition of its crystals. It is quite obvious that the molecules will leave the solution at a faster rate when their concentration in the solution is higher. And since the latter grows as the substance dissolves, a moment finally sets in when the rate of dissolution becomes equal to that of crystallization. We now have dynamic equilibrium, when the same number of molecules dissolves in unit time that crystallizes from the solution. A solution in equilibrium with the dissolving substance is called a **saturated solution**.

74. Concentration of Solutions

One has to use saturated solutions comparatively rarely. In the majority of cases what is used are **unsaturated** solutions, i.e. ones having a lower solute concentration than a saturated solution does.

By the concentration of a solution is meant the amount of solute contained in a definite amount of solution or solvent. Solutions with a high solute concentration are called **concentrated**, and those with a low one, **dilute**.

The concentration of a solution can be expressed in different ways. The following are in the greatest favour among chemists:

1. *By the number of mass units (for example, the number of grams) of solute dissolved in 100 units of mass (for example, in 100 grams) of solution (per cent concentration by mass).* For instance, a 15% solution of sodium chloride is a solution 100 g of which contain 15 g of NaCl and 85 g of water.

2. *By the number of moles of solute dissolved in one litre of solution.* The concentration expressed in this way is known as the molar-volume concentration or the molarity and is designated by the symbol M. For instance, $2\,M$ H_2SO_4 signifies a solution of sulphuric acid each litre of which contains two moles, i.e. 196 g, of H_2SO_4.

3. *By the number of solute equivalents in one litre of solution.* The concentration expressed in this way is called the **equivalent concentration** or the **normality** and is designated by the symbol N. Thus, $2\,N$ H_2SO_4 stands for a solution of sulphuric acid each litre of which contains two equivalents, i.e. 98 g, of H_2SO_4.

4. *By the number of moles of solute dissolved in 1000 g of solvent.* The concentration expressed in this way is called the molal concentration or the **molality** and is designated by the symbol m. For instance, $2\,m$ H_2SO_4 indicates a solution of sulphuric acid in which 1000 g of water contain two moles of H_2SO_4. The molality of a solution, unlike its molarity, does not change with a change in the temperature.

5. *By the ratio of the number of moles of a substance to the total number of moles of all the substances in the solution.* The concentration expressed in this way is called the **mole fraction** of a substance. It is usually designated by the symbol x_1 for the solvent and x_2, x_3, etc. for the solutes. For a solution of one substance in another, the mole fraction of the solute x_2 is

$$x_2 = \frac{n_2}{n_1 + n_2}$$

where n_1 and n_2 are the numbers of moles of the solvent and solute, respectively.

When using solutions whose concentration is expressed by the normality, it is easy to calculate beforehand the volume ratios in which they should be mixed for the solutes to react without any residue. Assume that V_1 litres of a solution of substance 1 having the normality N_1 react with V_2 litres of a solution of substance 2 with the normality N_2. This signifies that N_1V_1 equivalents of substance 1 and N_2V_2 equivalents of substance 2 have entered into the reaction. But the substances react in equivalent amounts, therefore

$$V_1N_1 = V_2N_2$$

or

$$V_1 : V_2 = N_2 : N_1$$

Thus, *the volumes of the reactant solutions are inversely proportional to their normalities for no residues to be formed.*

This relationship makes it possible not only to calculate the volumes of solutions needed for conducting reactions, but also, conversely, to find the concentrations of solutions by their volumes used for a reaction.

Example 1. How many millilitres of a 0.3 N solution of sodium chloride have to be added to 150 ml of a 0.16 N solution of silver nitrate to precipitate all the silver in the solution as silver chloride?

Introducing the data of the example into the last equation, we get

$$\frac{150}{V} = \frac{0.3}{0.16}$$

whence

$$V_2 = \frac{0.16 \times 150}{0.3} = 80 \text{ ml}$$

Example 2. To neutralize 40 ml of a solution of sulphuric acid, 24 ml of a 0.2 N solution of an alkali had to be added to it. Find the normality of the H_2SO_4 solution taken.

Denoting the unknown normality of the sulphuric acid solution by x, we have

$$40 : 24 = 0.2 : x$$

whence

$$x = \frac{24 \times 0.2}{40} = 0.12\ N$$

75. Hydrates and Crystal Hydrates

Most substances in the crystalline state dissolve in liquids with the absorption of heat. The temperature rises appreciably, however, when sodium hydroxide, potassium carbonate, anhydrous copper(II) sulphate, and many other substances dissolve in water. Heat is also evolved when some liquids and all gases dissolve in water.

The amount of heat absorbed (or evolved) when one mole of a substance is dissolved is called its heat of solution.

The heat of solution is negative if heat is absorbed in dissolution, and positive if heat is evolved. For instance, the heat of solution of ammonium nitrate is —26.4 kJ/mol, and of potassium hydroxide +55.6 kJ/mol*.

The process of dissolution is attended by a considerable growth in the entropy of a system because its number of microstates sharply grows as a result of the uniform distribution of the particles of one substance in the other. Consequently, notwithstanding the endothermic nature of the dissolving of most crystals, the change in the Gibbs energy of a system in dissolution is negative and the process goes on spontaneously.

When crystals dissolve, they are destroyed, which requires the expenditure of energy. Therefore, dissolution ought to be attended by the absorption of heat. If the opposite effect is observed, however, this shows that simultaneously with dissolution, some kind of interaction occurs between the solvent and the solute in which more energy is evolved in the form of heat than is spent on the destruction of the crystal lattice.

Indeed, it has been established at present that when many substances dissolve, their molecules (or ions) become bound to molecules of the solvent and form compounds called **solvates**. The process itself is known as **solvation**. In the particular case when the solvent is water, these compounds are called **hydrates**, and the process of their formation is known as **hydration**.

Solvates can be formed in different ways depending on the nature of the solute. For instance, when substances having an ionic structure are dissolved, the solvent molecules are kept near the ions by forces of electrostatic attraction. In this case, we speak of ion-dipole interaction. In addition, donor-acceptor interaction may occur. Here the solute ions usually play the role of acceptors, and the solvent molecules, the part of donors of electron pairs. It is clear that solvents whose molecules have unshared electron pairs (for instance, water and ammonia) can participate in such interaction. The hydrates formed as a result of donor-acceptor interaction are a particular case of complex compounds treated in Vol. 2, Chap. 8 (aquacomplexes—see Vol. 2, Sec. 90).

When substances having a molecular structure are dissolved, solvates are formed owing to dipole-dipole interaction. The solute dipoles may be permanent (in substances with polar molecules) or induced (in substances with non-polar molecules).

The assumption that hydrates exist in aqueous solutions was advanced and substantiated in the eighties of the 19th century by Mendeleev who considered that dissolution is not only a physical, but also

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* The values of the heats of solution vary depending on the amount of solvent used and the temperature at which dissolution occurs. The values given here relate to a temperature of from 18 to 20 °C and a large amount of water (one mole of solute per 200 to 800 moles of water).

a chemical process, and that substances dissolving in water form compounds with it. This is witnessed first of all by studying the heats of solution.

The chemical nature of dissolution is also confirmed by the fact that many substances separate from aqueous solutions in the form of crystals containing the water of crystallization (see below), and a definite number of water molecules falls to each solute molecule. "This," wrote Mendeleev, "gives us every reason to believe that the solutions themselves contain identical or similar compounds of the solutes and the solvent, but only in the liquid (and partly in the decomposed) form."

Hydrates, as a rule, are unstable compounds that often decompose already when the solutions are evaporated. But hydrates are sometimes so strong that when the solute separates from the solution, water enters the composition of its crystals. Substances whose crystals contain molecules of water are known as **crystal hydrates**, and the water contained in them as the **water of crystallization.**

The composition of crystal hydrates is customarily depicted by formulas showing the amount of water of crystallization contained by a crystal hydrate. For instance, the crystal hydrate of copper(II) sulphate (blue vitriol) containing five moles of water per mole of $CuSO_4$ is depicted by the formula $CuSO_4 \cdot 5H_2O$, the crystal hydrate of sodium sulphate (Glauber salt)—by the formula $Na_2SO_4 \cdot 10H_2O$.

The strength of the bond between the substance and the water of crystallization in crystal hydrates is different. Many of them lose their water of crystallization even at room temperature. For instance, the transparent crystals of soda ($Na_2CO_3 \cdot 10H_2O$) easily "disintegrate". They lose their water of crystallization, become dull, and gradually crumble into a powder. The dehydration of other crystal hydrates requires quite strong heating.

Hydrates are formed with the evolution of heat. When a substance subjected to hydration dissolves, the total heat effect consists of the heat effect of dissolution proper and that of hydration. Since the first of these processes is endothermic, and the second is exothermic, the total heat effect of a dissolution process equals the algebraic sum of the heat effects of the individual processes and may be either positive or negative.

76. Solubility

By solubility is meant the ability of a substance to dissolve in a solvent. *The solubility of a substance in given conditions is measured by the concentration of its saturated solution.* Consequently, solubility can be expressed numerically in the same ways as the concentration, for example by the per cent ratio of the mass of solute to that of saturated solution, or by the number of moles of solute in one litre of the saturated solution. Solubility is also frequently expressed by the number of mass units of the anhydrous substance saturating 100 mass units of solvent in the given conditions. The solubility expressed in this way is sometimes called the **solubility coefficient.**

The solubility of various substances in water changes within broad limits. If more than 10 g of a substance dissolves in 100 g of water, the substance is said to have a good solubility; if less than 1 g of a substance dissolves, it is said to have a low solubility, and, finally, if less than 0.01 g of a substance dissolves, it is virtually insoluble.

The principles making it possible to predict the solubility of a substance are meanwhile not known. But usually substances consisting of polar molecules and substances with an ionic type of bond dissolve better in polar solvents (water, alcohols, liquid ammonia), and non-polar substances—in non-polar solvents (benzene, carbon disulphide).

The dissolution of most solids is attended by the absorption of heat. This is explained by the expenditure of a considerable amount of energy to destroy the crystal lattice of the solid, which is usually not completely compensated by the energy liberated in the formation of hydrates (solvates). Applying Le Chatelier's principle to the equilibrium between a substance in the crystalline state and its saturated solution:

$$\text{Crystal} + \text{Solvent} \rightleftarrows \text{Saturated solution} \pm Q$$

we arrive at the conclusion that when a substance dissolves with the absorption of energy, elevation of the temperature must lead to an increase in its solubility. If, however, the energy of hydration (solvation) is sufficiently high for the formation of a solution to be attended by the evolution of energy, the solubility diminishes with increasing temperature. This is what occurs, for instance, when alkalies and many salts of lithium, magnesium, and aluminium dissolve in water.

It is very convenient to depict the relationship between the solubility and the temperature graphically, in the form of solubility curves. To do this, the temperature is laid off along the horizontal axis, and the solubility of the substance at the corresponding temperature along the vertical one.

Figure 75 gives several characteristic solubility curves. The sharply rising curves showing the solubility of silver, potassium, and lead nitrates indicate that the solubility of these substances grows greatly with elevation of the temperature. The solubility of sodium chloride grows only insignificantly with elevation of the temperature, which is shown by the almost horizontal solubility curve of this salt. The solubility curve of sodium sulphate (Fig. 76) has a more intricate shape. Up to 32 °C, this curve steeply rises, which points to a rapid growth in the solubility. At 32 °C, a sharp break occurs in the curve, after which it descends somewhat. Consequently, sodium sulphate has the highest solubility at 32 °C. The presence of a peak on the solubility curve of sodium sulphate is explained by the fact that below 32 °C the crystal hydrate $Na_2SO_4 \cdot 10H_2O$, whose dissolution is attended by the absorption of heat, is in equilibrium with the saturated solution. At higher temperatures, the solid phase in equilibrium with the saturated solution is the anhydrous salt Na_2SO_4 that dissolves with the evolution of heat.

When solid bodies dissolve in water, the volume of the system generally changes insignificantly. Therefore, the solubility of solid substances does not virtually depend on the pressure.

Liquids can also dissolve in liquids. Some of them can dissolve without any limit in each other, i.e. mix with each other in any proportions as, for instance, alcohol and water, while others can dissolve in each other only up to a certain limit. For example, if we agitate diethyl ether with water, two layers are formed: the upper one is a saturated solution of water in ether, and the lower one is a saturated solution of ether in water. In the majority of such cases, the mutual solubility of the liquids grows with increasing temperature until a temperature is reached at which both liquids mix in any proportions.

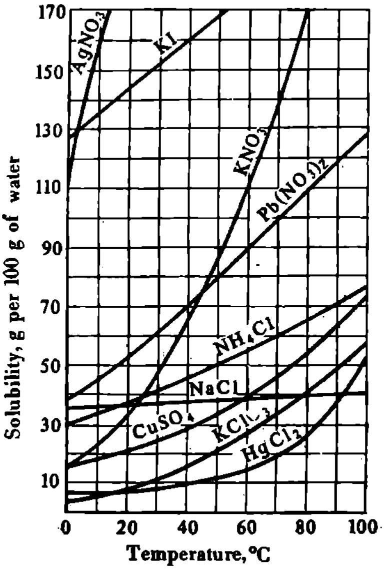

Fig. 75 Temperature dependence of solubility in water of selected salts

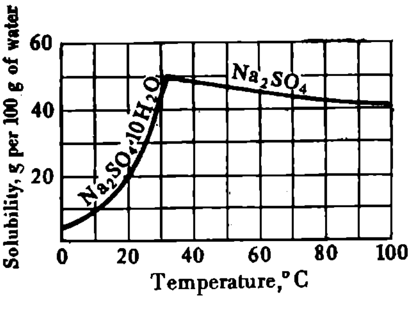

Fig. 76. Temperature dependence of solubility in water of sodium sulphate

The temperature at which the limited mutual solubility of liquids changes into unlimited solubility is called the **critical solution temperature.** For instance, at a temperature below 66.4°C, phenol dissolves limitedly in water, and water dissolves limitedly in phenol. The temperature 66.4 °C is the critical solution temperature for the system water-phenol: beginning from this temperature, both liquids dissolve unlimitedly in each other.

As in the dissolution of solids, the mutual dissolution of liquids is not usually attended by a considerable change in volume. Therefore, the mutual solubility of liquids depends only slightly on the pressure and grows appreciably only at very high pressures (of the order of thousands of atmospheres).

If into a system consisting of two immiscible liquids there is introduced a third substance capable of dissolving in each of these liquids, then the solute will be distributed between the two liquids in proportion to its solubility in each of them. Hence follows the **distribution** or **partition law,** according to which *a substance capable of dissolving in two immiscible solvents is distributed between them so that the ratio of its concentrations in these solvents at constant temperature remains constant regardless of the total amount of solute*:

$$\frac{c_1}{c_2} = K$$

Here c_1 and c_2 are the concentrations of the solute in the first and second solvents, respectively, and K is the **partition coefficient.**

For example, the partition coefficient for iodine in water and chloroform is 130. If to water containing dissolved iodine we add chloroform that is immiscible with water, shake the system and let it stand, then after equilibrium sets in, the concentration of the iodine in the chloroform will be 130 times greater than in the water, regardless of the total amount of dissolved iodine. Thus, we can use chloroform to **extract** from water the predominating part of iodine dissolved in it. Such a method of **extraction** of a solute from a solution with the aid of a second solvent immiscible with the first one based on the distribution law is widely used in laboratory practice and in the chemical industry.

The dissolving of gases in water is an exothermic process. Consequently, the solubility of gases diminishes with elevation of the temperature. If we let a glass with cold water stand in a warm room, its inside walls become covered with gas bubbles—the air that was dissolved in the water leaves it owing to the rising of the temperature. All the air dissolved in water can be separated from it by boiling.

The dissolving of gases in organic liquids, however, is sometimes attended by the absorption of heat; in these cases, the solubility of the gas grows with increasing temperature.

When a gas dissolves in a liquid, equilibrium sets in:

$$\text{Gas} + \text{Liquid} \rightleftharpoons \text{Saturated solution of gas in liquid}$$

The volume of the system appreciably diminishes. Hence, an increase in the pressure should lead to shifting of the equilibrium to the right, i.e. to an increase in the solubility of the gas.

We can arrive at the same conclusion proceeding from the dynamic nature of the equilibrium between a gas and its solution in a liquid. The molecules of a gas over a liquid in a closed vessel bombard the surface of the liquid and dissolve in it at a rate that is proportional to the gas concentration. The molecules that have passed into the solution, in turn, collide with the surface of the liquid from inside and fly out from time to time. As the concentration of the dissolved molecules grows owing to dissolution, the rate of their escaping, i.e. the number of molecules leaving the solution in unit time, will also grow until, finally, it becomes equal to the rate of dissolution. As a result, a state of equilibrium sets in, i.e. the liquid will become saturated with the gas.

If we now increase the pressure of the gas, for instance two-fold, the concentration of its molecules over the liquid and, consequently, the rate of dissolving of the gas, will increase the same number of times. Equilibrium will be violated. For equilibrium to set in again at the new pressure, the concentration of the dissolved molecules should also evidently increase two-fold.

We thus arrive at a conclusion known by the name of Henry's law:

> *The mass of a gas that dissolves at a constant temperature in a given volume of a liquid is directly proportional to the partial pressure of the gas.*

Henry's law can be expressed by the equation

$$c = kp$$

where c is the mass concentration of the gas in a saturated solution, p is the partial pressure, and k is a proportionality constant known as **Henry's law constant** (or **Henry's coefficient**).

We must note an important corollary of Henry's law. Assume that one volume of a gas containing m grams of the gas dissolves at a given pressure in a certain volume of a liquid. Without changing the temperature, let us increase the pressure n times. According to Boyle's law, the volume occupied by the gas will diminish to $1/n$th its original value. Hence, the mass of the gas in unit volume will grow n times and will be nm grams. On the other hand, in accordance with Henry's law, the mass of the gas dissolving in a definite volume of the liquid will also grow n times, i.e. it will also become equal to nm grams. In other words, one volume of the gas will dissolve in the given volume of the liquid as previously.

Consequently, *the volume of a gas dissolving at constant temperature in a given volume of a liquid does not depend on its partial pressure.* It is exactly for this reason that the solubility of gases is customarily expressed not in grams, but in millilitres, indicating the volume of gas dissolving in 100 ml of the solvent.

The solubility of selected gases in water at 0 and at 20 °C is given in Table 10.

Table 10

Solubility of Selected Gases in Water

Gas	Solubility of gas in 100 ml of water,		Gas	Solubility of gas in 100 ml of water,	
	at 0 °C	at 20 °C		at 0 °C	at 20 °C
Hydrogen	2.15	1.8	Carbon dioxide	171	87.8
Oxygen	4.9	3.1	Chlorine	461	236
Nitrogen	2.35	1.5	Methane	5.5	3.3

If a mixture of several gases is over a liquid, the solubility of each of them is determined by its partial pressure. This must be taken into consideration in calculating the solubility of gases in a mixture with other gases.

Gases obey Henry's law at not very high pressures and then only if they do not enter into a chemical reaction with the solvent. At high pressures, when the behaviour of all gases appreciably differs from the ideal behaviour, deviations from Henry's law are also observed for gases that do not react chemically with the solvent.

77. Supersaturated Solutions

The solubility of the majority of substances diminishes with lowering of the temperature. Consequently, when hot saturated solutions are cooled, the excess solute usually crystallizes from the solution. If cooling is conducted carefully and slowly, however, and the solution is protected from solute particles getting into it from outside, crystallization may fail to occur. Now the solution obtained contains considerably more solute than is needed for saturation at the given temperature. This phenomenon was discovered and studied in detail by the Russian academician T. Lovits (1794). He called such solutions **supersaturated** ones. When left undisturbed, they can remain unchanged for years. But it is sufficient to throw a minute crystal of the substance contained in the solution into it, and immediately other crystals begin to grow around it. In a short time, the entire excess amount of the solute crystallizes out of the solution. Crystallization sometimes begins if the solution is jolted, and also as a result of friction of a glass rod against the walls of the vessel containing the solution. A considerable amount of heat is evolved in crystallization, so that the vessel with the solution becomes noticeably heated. Supersaturated solutions are formed very easily by $Na_2SO_4 \cdot 10H_2O$ (Glauber's salt), $Na_2B_2O_7 \cdot 10H_2O$ (borax), and $Na_2S_2O_3 \cdot 5H_2O$ (sodium thiosulphate).

It follows from the above that supersaturated solutions are unstable systems capable of existing only in the absence of solid particles of the solute in the system. The possibility of such solutions existing for a long time is explained by the difficulty of the initial appearance of the very minute "seed" crystals, the **centres of crystallization**, from which crystallization spreads to the entire body of the solution.

78. Osmosis

We have already mentioned on a previous page that a solution is a homogeneous system. The particles of the solute and the solvent are in chaotic thermal motion and are uniformly distributed through the entire volume of the solution.

If we place a concentrated solution of a substance, for instance sugar, into a cylindrical flask and then carefully pour a more dilute sugar solution over it, then initially the sugar and water will be distributed unevenly throughout the volume of the solution. After a certain time elapses, however, the sugar and the water will again be uniformly distributed throughout the entire volume of the liquid. This occurs because the molecules of sugar, moving chaotically, penetrate both from the concentrated solution into the dilute one and in the opposite direction. But during any time interval, more sugar molecules pass from the concentrated solution into the dilute one than from the dilute solution into the concentrated one. In exactly the same way, the water molecules move in different directions, but more molecules of water will pass from the dilute solution icher in water into the concentrated one than in the opposite direction during the same time. Thus, a directed motion appears of the sugar from the concentrated solution into the dilute one and of the water in the opposite direction. Each substance is transferred to where its concentration is lower. Such a spontaneous process of motion of a substance leading to levelling out of its concentration is called **diffusion**.

In the course of diffusion, a certain initial order in the distribution of the substances (a high concentration of a substance in one part of the system and a low one in the other part) is replaced by total disorder in their distribution. The entropy of the system grows.

When the concentration of the solution levels out throughout its volume, the entropy reaches a maximum, and diffusion stops.

Diffusion can be observed if we pour a coloured solution, for instance a solution of $KMnO_4$, into a cylindrical vessel and carefully pour in water over it so as not to cause mixing. First a sharp boundary will be noticeable, but it will gradually become blurred. After a certain time, the solute will become uniformly distributed throughout the entire volume of the solution, and the entire liquid will acquire the same colour.

In the above example, the particles of the solvent and the solute diffuse in opposite directions. This is called counter or two-directional diffusion. Matters will be different if a partition is placed between two solutions that lets the solvent pass through and retains the solute. Such partitions, called **semipermeable membranes**, exist in nature, and can also be obtained artificially. For example, if a porous clay cylinder is impregnated with a solution of copper(II) sulphate, and then immersed in a solution of potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$), copper hexacyanoferrate(II) will be deposited in the pores of the cylinder. A cylinder treated in this way has the properties of a semipermeable membrane: molecules of water can pass through its walls, but they are impervious to the solute molecules.

If we pour a solution of a substance, for instance sugar, into such a cylinder and immerse it in water, the concentrations will level out only owing to the motion of the water molecules. The latter will diffuse in a greater number into the solution than in the opposite direction. The volume of the solution will gradually grow, while the concentration of the sugar in it will diminish. Such unidirectional diffusion through a semipermeable membrane is called **osmosis**.

Let us take vessel *2* with semipermeable walls transforming on top into narrow vertical tube *3* (Fig. 77), fill it with a sugar solution, and immerse it in vessel *1* with water. Owing to osmosis, the volume of the solution will gradually increase, and the solu-

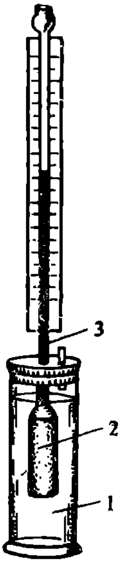

Fig. 77. Schematic view of arrangement for measuring osmotic pressure:
1—vessel with water; *2*—vessel with semipermeable walls; *3*—tube

tion will begin to fill the vertical tube. As the level of the solution rises, a surplus pressure of the water column will be created in the tube (a hydrostatic pressure) measured by the difference between the levels of the liquid and counteracting the penetration of the water molecules into the solution. When the hydrostatic pressure reaches a definite value, the osmosis stops—equilibrium sets in. The hydrostatic pressure will become equal to the pressure that is a quantitative characteristic of osmosis—the **osmotic pressure of the solution.** By measuring the hydrostatic pressure in such equilibrium, we can determine the magnitude of the osmotic pressure*.

The phenomenon of osmosis plays a very important role in the life of animal and vegetable organisms. The envelopes of cells are membranes that are permeable for water, but almost impermeable for the substances dissolved in the liquid inside the cells. Penetrating into the cells, water produces an excess pressure in them that slightly stretches the envelopes of the cells and keeps them in a stressed state. This is why the soft organs of plants such as grassy stalks, leaves and flower petals are elastic. If we cut a plant, then owing to evaporation of the water, the volume of the liquid inside a cell diminishes, the envelopes of the cells subside and become flabby—the plant wilts. But as soon as we put a plant that has begun to wilt in water, osmosis begins, the envelopes of the cells again become stressed, and the plant acquires its previous appearance.

Osmosis is also one of the reasons underlying the rising of water along the stem of a plant, the supply of food to cells, and many other phenomena.

Measurements of the osmotic pressure of various solutions showed that the magnitude of the osmotic pressure depends on the concentration of the solution and on its temperature, but does not depend on the nature of the solute or on that of the solvent. In 1886, J. van't Hoff** showed that for solutions of non-electrolytes with moderate concentrations the dependence of the osmotic pressure on the concentration and temperature of the solution is expressed by the equation

$$p = 1000cRT$$

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* The osmotic pressure measured in this way relates not to the initial solution, but to a solution diluted somewhat with water as a result of the osmosis proceeding in the course of the experiment. With a large volume of the solution and a small tube diameter, however, this dilution changes the concentration of the initial solution only insignificantly.

** **Jacobus Henricus van't Hoff** (1852-1911) was an outstanding Dutch physicochemist. He studied the laws of chemical reactions, chemical equilibrium, the properties of solutions. He advanced and developed the idea of directional valence bonds in a carbon atom, and developed the fundamentals of **stereochemistry**—the science dealing with the spatial arrangements of the atoms in a molecule.

Here p is the osmotic pressure of the solution, Pa; c is its molar-volume concentration (molarity), mol/l; R is the molar gas constant, 8.314 J/(mol·K); and T is the absolute temperature of the solution, K.

The molarity c of a solution is the ratio of the number of solute moles n to the volume of the solution V (litres):

$$c=\frac{n}{V}$$

while the number of moles of a substance equals its mass m divided by the molar mass M. Hence for the molarity of a solution, we get:

$$c=\frac{m}{MV}$$

Using this value of c in van't Hoff's equation, we obtain:

$$pV=1000\frac{m}{M}RT$$

The equation obtained is similar in its form to the Clapeyron-Mendeleev equation of state of an ideal gas. It allows us to determine the molar mass (and, consequently, the relative molecular mass) of a solute from the value of the osmotic pressure of a solution.

Example. The osmotic pressure of a solution, 250 ml of which contains 3 g of sugar, is 83.14 kPa at 12 °C. Find the relative molecular mass of sugar.

Introducing these data into the last equation, we get

$$83.14\times 10^3\times 0.25=1000\times\frac{3}{M}\times 8.314\,(273+12)$$

whence M = 342 g/mol. The relative molecular mass of sugar is 342 amu.

79. Vapour Pressure of Solutions

At a given temperature, the pressure of the saturated vapour over every liquid is a constant quantity. Experiments show that when a substance is dissolved in a liquid, the saturated vapour pressure of this liquid lowers. Thus, *the saturated vapour pressure of the solvent over a solution is always lower than that over the pure solvent at the same temperature*. The difference between these quantities is called the **vapour pressure depression** over the solution (or the depression of the vapour pressure of the solution). The ratio of the magnitude of this depression to the saturated vapour pressure over the pure solvent is called the **relative vapour pressure depression** over the solution.

Let us designate the saturated vapour pressure of the solvent over the pure solvent by p_0, and over a solution by p. Hence, the relative vapour pressure depression over a solution will be the fraction

$$\frac{p_0-p}{p_0}$$

In 1887, the French physicist F. Raoult, in studying solutions of various non-volatile* liquids and solid substances, established a law relating the vapour pressure depression over dilute solutions of non-electrolytes and the concentration:

> *The relative depression of the saturated vapour pressure of a solvent over a solution equals the mole fraction of the solute.*

The following equation is a mathematical expression of Raoult's law:

$$\frac{p_0-p}{p_0}=x_2$$

Here x_2 is the mole fraction of the solute.

The phenomenon of the depression of the saturated vapour pressure over a solution follows from Le Chatelier's principle. Let us imagine equilibrium between a liquid, for instance water, and its vapour. This equilibrium, which a definite pressure of the saturated vapour corresponds to, can be expressed by the equation

$$(H_2O)_{lq} \rightleftarrows (H_2O)_{vap}$$

If we now dissolve a certain amount of a substance in the water, then the concentration of the water molecules in the liquid will lower, and a process will go on that increases it—condensation of the vapour. New equilibrium will set in at a lower pressure of the saturated vapour.

The lowering of the vapour pressure over a solution is reflected in the phase diagram. Figure 78 depicts a phase diagram of water and

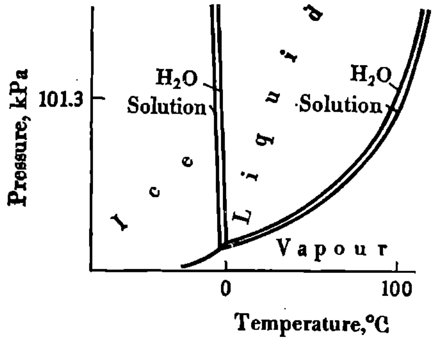

Fig. 78. Phase diagram of water and an aqueous solution of a non-volatile substance

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* The law is of a more complicated nature for solutions of volatile substances because there is a mixture of the solute and solvent vapours over the solution.

an aqueous solution of a non-volatile substance. According to Raoult's law, the pressure of the water vapour over the aqueous solution is lower than over water. Therefore, the boiling curve for the solution is lower than for water. The position of the melting curve also changes when passing from water to the solution. Both the boiling curve and the melting curve for the solution will be farther from the relevant curves for water when the concentration of the solution grows.

80. Freezing and Boiling of Solutions

Individual substances are characterized by strictly definite temperatures of their transitions from one state of aggregation to another (the boiling point and the melting or freezing point). For example, water at standard atmospheric pressure (101.3 kPa) freezes at a temperature of 0 °C and boils at 100 °C.

Matters are different with solutions. The presence of a solute raises the boiling point and lowers the freezing point of the solvent. These changes grow when the concentration of the solution increases. In the majority of cases, only the solvent freezes out (in freezing) or boils out (in boiling) from a solution. Consequently, the concentration of a solution increases in the course of its freezing or boiling. This, in turn, results in still greater elevation of the boiling point and depression of the freezing point. Thus, a solution freezes and boils not at a definite temperature, but within a certain temperature interval. The temperature of the beginning of freezing and of the beginning of boiling of a given solution is called its freezing point and its boiling point.

The difference between the boiling point of a solution and that of the pure solvent is called the **elevation of the boiling point of the solution** (Δt_b). The difference between the freezing point of the pure solvent and that of a solution is called the **depression of the freezing point of the solution** (Δt_{fr}). Denoting the boiling and freezing points of a solution by t'_b and t'_{fr}, and the same quantities for the pure solvent by t_b and t_{fr}, we have:

$$\Delta t_b = t'_b - t_b$$

$$\Delta t_{fr} = t'_{fr} - t_{fr}$$

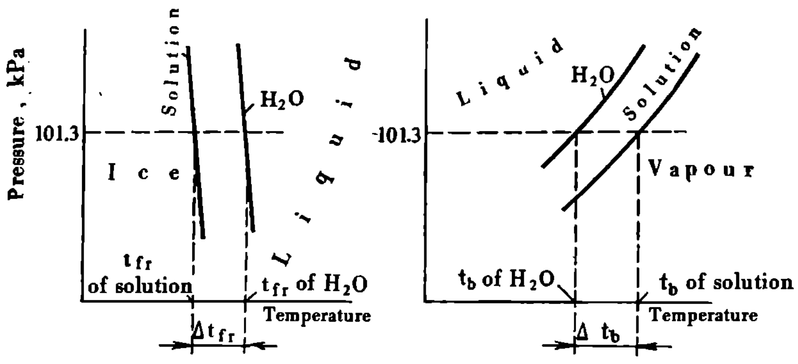
A liquid begins to boil at the temperature at which its saturated vapour pressure reaches the magnitude of the external pressure. For example, water under a pressure of 101.3 kPa boils at 100 °C because at this temperature the pressure of water vapour is exactly equal to 101.3 kPa. If we dissolve a non-volatile substance in water, its vapour pressure will lower. To bring the vapour pressure of the solution obtained up to 101.3 kPa, we must heat the solution to above 100 °C. It thus follows that the boiling point of a solution is always higher than the boiling point of the pure solvent. The depression of the freezing point of solutions is explained in a similar way.

The elevation of the boiling point and the depression of the freezing point of solutions are in agreement with Le Chatelier's principle. Let us consider the freezing of a solution from this angle of view. Assume that there is equilibrium between a liquid and its solid phase, for instance equilibrium between water and ice at 0 °C. It can be expressed by the equation

$$(H_2O)_s \rightleftharpoons (H_2O)_{lq}$$

If we dissolve a certain amount of a substance in water, the concentration of the water molecules in the liquid will diminish, and a process increasing it—melting of the ice—will occur. For new equilibrium to set in, the temperature must be lowered.

The elevation of the boiling point and the depression of the freezing point are reflected in a phase diagram. Figure 79 shows a part of a phase diagram for water and a solution in the region of pressures close to standard atmospheric pressure (101.3 kPa). The segments are intersected by a horizontal line corresponding to a pressure of 101.3 kPa (the scale of the drawing has been increased in comparison with Figs. 73 and 78). Inspection of the figure shows that the points of intersection of this horizontal line with the melting and boiling curves for water and for the solution are different. The abscissas of these points—the freezing point and the boiling point—are 0 and 100 °C for water, while for the solution they are below 0 °C and above 100 °C, respectively. The curves corresponding to the solution will be farther from the corresponding curves for water when the concentration of the solution is higher. Therefore, the difference between the



(a) (b)

Fig. 79. Part of phase diagram for water and a solution in the region of pressures close to 101.3 kPa (shown schematically):
a—melting curves; *b*—boiling curves

boiling points or freezing points of water and the solution is also greater when the concentration of the solution is higher.

In studying the freezing and boiling of solutions, Raoult found that for dilute solutions of non-electrolytes, the elevation of the boiling point and the depression of the freezing point are proportional to the concentration of the solution:

$$\Delta t_b = Em$$

$$\Delta t_{fr} = Km$$

Here m is the molar mass concentration (the molality); E and K are the **ebullioscopic*** constant (or molal boiling point elevation) and the **cryoscopic**** constant (or molal freezing point depression), respectively. These two constants depend only on the nature of the solvent, but do not depend on that of the solute. For water, the cryoscopic constant K is 1.86, and the ebullioscopic constant E is 0.52. For benzene, $K = 5.07$, and $E = 2.6$.

Measurements of the boiling and freezing points of solutions underly the **ebullioscopic** and **cryoscopic methods** of determining the molecular masses of substances. Both methods are widely used in chemistry because the molecular masses of a variety of substances can be determined by using different solvents.

Example. When 2.76 g of glycerine were dissolved in 200 g of water, the freezing point lowered by 0.279 degree. Determine the molecular mass of glycerine.

We find the number of grams of glycerine in the solution per 1000 g of water:

$$\mu = \frac{2.76 \times 1000}{200} = 13.8 \text{ g}$$

We express the molality of the solution (m) through the mass of the glycerine (μ) per 1000 g of water and its molar mass (M):

$$m = \frac{\mu}{M} = \frac{13.8}{M}$$

We introduce the data into the equation $\Delta t_{fr} = Km$:

$$0.279 = 1.86 \times \frac{13.8}{M}$$

Hence, the molar mass of glycerine is $M = 92$ g/mol, and its molecular mass is 92 amu.

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* From the Latin "ebullire"—to boil out.

** From the Greek "kryos"—cold.

8

SOLUTIONS OF ELECTROLYTES

81. Features of Solutions of Salts, Acids, and Bases

In Chapter 7, we became acquainted with the laws obeyed by dilute solutions. The truth of these laws is confirmed by the results of many experiments. Substances exist, however, whose solutions greatly deviate from these laws. Such substances include salts, acids, and alkalies. The osmotic pressure, depression of the vapour pressure, and the changes in the boiling and freezing points are always greater for them than they ought to be for the given concentration of the solution.

For instance, the depression of the freezing point of a solution containing 1 g of NaCl in 100 g of water is almost double the value of Δt_{fr} calculated according to Raoult's law. The osmotic pressure of this solution is greater than the theoretical value by the same amount.

As we have indicated in Sec. 78, the magnitude of the osmotic pressure is expressed by the equation

$$p = 1000cRT$$

To extend this equation to solutions with an "abnormal" osmotic pressure, van't Hoff introduced the correction coefficient *i* (the **isotonic* coefficient**) into it. This coefficient shows how many times the osmotic pressure of a given solution is greater than the "normal" value:

$$p = 1000icRT$$

The coefficient *i* is determined for each solution experimentally—for example, from the depression of the vapour pressure, or from the depression of the freezing point, or from the elevation of the boiling point.

Let p' stand for the osmotic pressure of a solution, $\Delta t'_{fr}$ for the depression of the freezing point of the solution, $\Delta t'_{b}$ for the elevation of the boiling point of the solution not obeying van't Hoff's and Raoult's laws, and p, Δt_{fr} and Δt_{b} for the values of the same quan-

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* From the Greek "isos"—equal and "tonos"—stress, pressure.

tities calculated theoretically according to the concentration of the solution. Since the osmotic pressure and the changes in the freezing and boiling points are proportional to the number of solute particles in a solution, the coefficient i can be expressed by the relations

$$i = \frac{p'}{p} = \frac{\Delta t'_b}{\Delta t_b} = \frac{\Delta t'_{fr}}{\Delta t_{fr}}$$

The values of the coefficient i found by van't Hoff for 0.2 N solutions of selected salts according to the depression of their freezing points are given in Table 11.

Table 11

Values of Coefficient *i* for 0.2 *N* Solutions of Selected Salts

Salt	Formula	Depression of freezing point		$i = \frac{\Delta t'_{fr}}{\Delta t_{fr}}$
		observed ($\Delta t'_{fr}$)	calculated by Raoult's formula (Δt_{fr})	
Potassium chloride	KCl	0.673	0.372	1.81
Potassium nitrate	KNO_3	0.664	0.372	1.78
Magnesium chloride	$MgCl_2$	0.519	0.186	2.79
Calcium nitrate	$Ca(NO_3)_2$	0.461	0.186	2.48

The data of Table 11 show that the coefficient i varies for different salts. It grows with dilution of a solution, approaching the integers 2, 3, and 4. These values are identical for salts of a similar composition. For example, for all salts formed by monovalent metals and monobasic acids, with sufficient dilution of their solutions, the coefficient i approaches 2; for salts formed by divalent metals and monobasic acids, it approaches 3.

Thus, salts, acids, and bases upon dissolving in water produce a considerably greater osmotic pressure than equimolecular amounts of all other substances. How can this phenomenon be explained?

We shall note that a similar phenomenon is observed with respect to certain gases or substances passing over into the gaseous state. For example, the vapours of phosphorus pentachloride PCl_5, iodine, and some other substances when heated in a closed vessel acquire a higher pressure than follows from Gay-Lussac's law.

For gases, this phenomenon is explained by dissociation. If, for example, PCl_5 completely decomposes into PCl_3 and Cl_2, it is quite obvious that at a constant volume the pressure, which depends on the number of particles, should double. In incomplete dissociation, when only a part of the molecules decompose, the pressure also increases, but less than two-fold.

It was natural to assume that in solutions having an abnormally high osmotic pressure, the solute molecules also decompose into smaller particles so that the total number of particles in the solution grows. And since the osmotic pressure depends on the number of solute particles per unit volume of the solution, when this number increases, it also grows. Such an assumption was advanced for the first time in 1887 by the Swedish scientist S. Arrhenius* and was the cornerstone of his theory explaining the behaviour of salts, acids, and bases in aqueous solutions.

Aqueous solutions of salts, acids, and bases have another feature—they conduct an electric current. Anhydrous solid salts and bases, and also anhydrous acids do not conduct a current; pure water also does not practically conduct a current. It is evident that when such substances dissolve in water, they undergo deep changes that give rise to the electrical conductivity of the solutions obtained. We shall see below that these changes consist in the dissociation of the relevant substances into ions (ionization).

Substances decomposing in solutions or melts into ions are called **electrolytes**. They include salts, acids, and bases.

82. The Theory of Electrolytic Dissociation

Arrhenius gave attention to the close relationship between the ability of solutions of salts, acids, and bases to conduct an electric current and the deviations of the solutions of these substances from van't Hoff's and Raoult's laws. He showed that the electrical conductivity of a solution could be used to calculate the value of its osmotic pressure and, consequently, the isotonic coefficient i. The values of i which he calculated from the electrical conductivity coincided quite well with those found for the same solutions in other ways.

The cause of the exceedingly high osmotic pressure of electrolyte solutions is, according to Arrhenius, the dissociation of electrolytes into ions. The result of this, on the one hand, is an increase in the total number of particles in a solution and, consequently, an increase in the osmotic pressure, in the depression of the vapour pressure, and in the changes in the boiling and freezing points, and on the other, the acquiring by the solution of an ability to conduct an electric current owing to the formation of ions.

These assumptions were later developed into a harmonious theory known as the **theory of electrolytic dissociation**. According to this theory, when electrolytes dissolve in water, they decompose (dissociate) into positively and negatively charged ions. The positively

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* **Svante August Arrhenius** (1859-1927) was a professor at the Stockholm University and the Director of the Nobel Institute. He proposed a theory explaining the properties of solutions of salts, acids, and bases and called the theory of electrolytic dissociation. He was also the author of a number of studies in astronomy, cosmic physics, and in the field of the application of physicochemical laws to biological processes.

charged ions are called **cations**. They include, for example, the ions of hydrogen and metals. The negatively charged ions are called **anions**. They include the ions of acid residues and hydroxide ions. Like the solvent molecules, ions in a solution are in a state of disordered thermal motion.

The process of electrolytic dissociation is depicted with the aid of chemical equations. For instance, the dissociation of HCl is expressed by the equation

$$HCl = H^+ + Cl^-$$

The dissociation of electrolytes into ions (ionization) explains the deviations from van't Hoff's and Raoult's laws mentioned at the beginning of this chapter. We showed as an example the depression of the freezing point of a solution of NaCl. Now it is not difficult to understand why it is so great. Sodium chloride passes into a solution in the form of the ions Na^+ and Cl^-. From one mole of NaCl, we get not 6.02×10^{23} particles, but twice this number. Hence, the depression of the freezing point in a solution of NaCl must be double that in a solution of a non-electrolyte having the same concentration.

In exactly the same way, the osmotic pressure in a very dilute solution of barium chloride, dissociating according to the equation

$$BaCl_2 = Ba^{2+} + 2Cl^-$$

is three times greater than that computed according to van't Hoff's law because the number of particles in the solution is three times greater than if the barium chloride were in it in the form of the molecule $BaCl_2$.

Thus, the features of aqueous solutions of electrolytes that at first sight contradicted van't Hoff's and Raoult's laws were explained on the basis of these same laws.

Arrhenius's theory, however, did not take into account all the intricate features of the phenomena in solutions. Particularly, it treated ions as free particles not depending on the solvent molecules. Arrhenius's theory was opposed to the chemical, or hydrate theory of solutions advanced by Mendeleev that is based on the notion of solvent-solute interaction. Great merit for surmounting the seeming contradiction between the two theories belongs to the Russian scientist I. Kablukov* who was the first to advance the assumption on the hydration of ions. The development of this idea later resulted in combination of Arrhenius's and Mendeleev's theories.

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* **Ivan Alekseevich Kablukov** (1857-1942) was involved in studying the electrical conductivity of solutions. His work "Modern Theories of Solutions (of van't Hoff and Arrhenius) in Relation to the Science of Chemical Equilibrium" had a great influence on the development of physical chemistry in Russia and furthered the development of the theory of electrolytic dissociation.

83. The Dissociation Process

The dissociation of the solute proceeds differently depending on its structure in the anhydrous state. Two cases are the most typical. One of them is the dissociation of dissolving salts, i.e. crystals having an ionic structure, and the second is dissociation when acids, i.e. substances consisting of polar molecules, dissolve.

When a crystal of a salt, for instance, potassium chloride, gets into water, the ions on its surface attract the polar molecules of the water (ion-dipole interaction). The water molecules are attracted to the potassium ions by their negative poles, and to the chloride ions by their positive ones (Fig. 80). But if the ions attract water molecules, then the water molecules attract the ions too with the same force. At the same time, the attracted molecules of water experience impacts on the part of other molecules that are in motion. These impacts together with the thermal vibrations of the ions in a crystal are sufficient for separation of the ions from the crystal and their transition into the solution. After the first layer of ions, the second one passes into the solution, and in this way the gradual dissolving of the crystal takes place.

The dissociation of polar molecules (Fig. 81) occurs in a different way. The water molecules attracted to the ends of a polar molecule

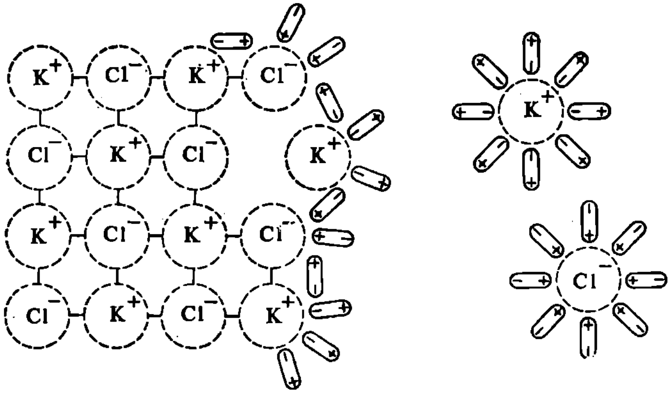

Fig. 80. Dissolving of a salt

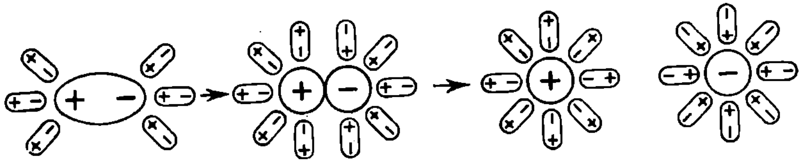

Fig. 81. Dissociation of polar molecules in a solution

(dipole-dipole interaction) cause its poles to move apart—they polarize the molecule. This polarization together with the vibrational thermal motion of the atoms in the molecule being considered, and also together with the continuous thermal motion of the water molecules surrounding it leads in the long run to ionization of the polar molecule. As in the dissolving of an ionic crystal, these ions become hydrated. The hydrogen ion H^+ (i.e. a proton) firmly combines with a water molecule into the hydroxonium ion H_3O^+. For instance, when hydrogen chloride dissolves in water, a process occurs that can be shown schematically by the equation

$$H_2O + HCl = H_3O^+ + Cl^-$$

As a result of this process, the molecule HCl decomposes in such a way that the shared pair of electrons remains in the chlorine atom, which transforms into the chloride ion Cl^-, while the proton, penetrating into the electron shell of the oxygen atom in a water molecule, forms the hydroxonium ion H_3O^+.

Similar processes occur when other acids, for instance nitric acid, dissolve in water:

$$H_2O + HNO_3 = H_3O^+ + NO_3^-$$

The ions that have passed into the solution remain bound to the water molecules and form ion **hydrates.** In other words, what is formed as a result of dissociation are not free ions, but compounds of ions with molecules of the solvent. In the general case of any solvent, these compounds are called ion **solvates.** But it is customary practice to write the formulas of the ions instead of their hydrates or solvates in equations of dissociation, moreover since the number of molecules of the solvent bound to the ions changes depending on the concentration of the solution and on other conditions.

The polarity of the solvent molecules promotes the dissociation of substances both of an ionic and a molecular structure. Consequently, not only water, but also other liquids consisting of polar molecules (formic acid, ethyl alcohol, ammonia, etc.) are ionizing solvents: salts, acids, and bases dissolved in these liquids dissociate into ions.

84. Degree of Dissociation. Strength of Electrolytes

If electrolytes completely dissociated into ions, the osmotic pressure (and other quantities proportional to it) would always be an integral number of times greater than the values observed in solutions of non-electrolytes. But already van't Hoff established that the coefficient *i* is expressed by fractions that grow when the solution is diluted, approaching integers.

Arrhenius explained this by the fact that only a part of an electrolyte dissociates into ions in a solution, and introduced the concept of the **degree of dissociation.** *By the degree of dissociation of an electrolyte is meant the ratio of the number of its molecules that have broken up into ions in the given solution to the total number of its molecules in the solution.*

It was later found that electrolytes can be divided into two groups—strong and weak ones. Strong electrolytes dissociate virtually completely in aqueous solutions. The concept of the degree of dissociation cannot in essence be applied to them, and the deviation of the isotonic coefficient i from integral values is explained by other reasons (see Sec. 86). Weak electrolytes dissociate only partly in aqueous solutions, and dynamic equilibrium sets in between the undissociated molecules and the ions in the solution.

Virtually all salts belong to strong electrolytes. Among the most important acids and bases, the following are strong electrolytes: HNO_3, $HClO_4$, HCl, HBr, HI, KOH, $NaOH$, $Ba(OH)_2$, and $Ca(OH)_2$.

Weak electrolytes include most of the organic acids, and the following important inorganic compounds: H_2CO_3, H_2S, HCN, H_2SiO_3, and NH_4OH.

The degree of dissociation is designated by the Greek letter α and is customarily expressed either in fractions of unity or as a percentage. For instance, for a 0.1 N solution of CH_3COOH, $\alpha = 0.013$ (or 1.3%), and for a 0.1 N solution of HCN, $\alpha = 10^{-4}$ (or 0.01%).

85. Dissociation Constant

We can apply the laws of chemical equilibrium to the equilibrium that sets in between the molecules and ions in a solution of a weak electrolyte, and write the expression for the equilibrium constant. For instance, for the dissociation of acetic acid

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

the equilibrium constant has the form

$$K = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Here the numerator of the fraction contains the concentrations of the ions that are the dissociation products, and the denominator contains the concentration of the undissociated molecules.

The equilibrium constant corresponding to the dissociation of a weak electrolyte is known as the **dissociation** (or **ionization**) **constant.** The value of K depends on the nature of the electrolyte and solvent, and also on the temperature, but does not depend on the concentration of the solution. It characterizes the ability of a given acid or given base to break up into ions: the greater is K, the more easily does the electrolyte dissociate.

Polybasic acids, and also bases of di- and polyvalent metals dissociate in steps. Complicated equilibria are attained in the solutions of these substances in which ions having different charges participate. For example, carbonic acid dissociates in two steps:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

The first equilibrium—**dissociation in the first step**—is characterized by the dissociation constant denoted by K_1:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

and the second one—**dissociation in the second step**—is characterized by the dissociation constant K_2:

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

The summary dissociation constant K:

$$K = \frac{[H^+]^2\,[CO_3^{2-}]}{[H_2CO_3]}$$

corresponds to the summary equilibrium

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

The quantities K, K_1, and K_2 are related to one another by the expression

$$K = K_1K_2$$

Similar relations characterize the stepwise dissociation of bases of polyvalent metals. For example, for the two steps of dissociation of iron(II) hydroxide

$$Fe(OH)_2 \rightleftharpoons FeOH^+ + OH^-$$
$$FeOH^+ \rightleftharpoons Fe^{2+} + OH^-$$

we get the dissociation constants

$$K_1 = \frac{[FeOH^+][OH^-]}{[Fe(OH)_2]} \quad \text{and} \quad K_2 = \frac{[Fe^{2+}][OH^-]}{[FeOH^+]}$$

The constant

$$K = \frac{[Fe^{2+}][OH^-]^2}{[Fe(OH)_2]}$$

corresponds to the summary dissociation

$$Fe(OH)_2 \rightleftharpoons Fe^{2+} + 2OH^-$$

Here

$$K = K_1K_2$$

In the stepwise dissociation of substances, the decomposition in a following step always occurs to a smaller degree than in the preceding one (in the second one it is less than in the first one, and so on). In other words, the inequality

$$K_1 > K_2 > K_3 \ldots$$

is observed.

The explanation is that the energy that must be spent for breaking away an ion is minimum when it is detached from a neutral molecule and becomes higher upon dissociation in each following step.

If we denote the concentration of an electrolyte dissociating into two ions by c, and the degree of its dissociation in the given solution by α, then the concentration of each of the ions will be $c\alpha$, and the concentration of the undissociated molecules will be $c(1-\alpha)$. Hence, the equation of the dissociation constant acquires the form

$$K = \frac{(c\alpha)^2}{c(1-\alpha)} \quad \text{or} \quad K = \frac{\alpha^2}{1-\alpha}c$$

This equation expresses W. Ostwald's **dilution law.** It permits us to calculate the degree of dissociation for different concentrations of an electrolyte if we know its dissociation constant. Using this equation, we can also calculate the dissociation constant of an electrolyte knowing its degree of dissociation at the relevant concentration.

For solutions in which the dissociation of an electrolyte is very small, the equation of Ostwald's law is simplified. Since in these cases $\alpha \ll 1$, we may disregard the quantity α in the denominator of the right-hand side of the equation. Hence, the equation acquires the form

$$K \approx \alpha^2 c \quad \text{or} \quad \alpha \approx \sqrt{\frac{K}{c}}$$

This equation clearly shows the relationship existing between the concentration of a weak electrolyte and the degree of its dissociation: *the degree of dissociation increases upon dilution of a solution.*

The conclusion obtained follows from the nature of the phenomenon of dissociation. Like any chemical equilibrium, equilibrium in a solution of a weak electrolyte is dynamic, i.e. when it sets in, two processes go on at different rates: the process of ionization and the reverse process of molecule formation from ions. Dilution of a solution does not hinder the first of these processes—ionization. The process of molecule formation from ions, however, becomes more difficult as a result of dilution: for a molecule to form, the relevant ions must collide, and the probability of such a collision diminishes with dilution.

Table 12 gives the values of the dissociation constants for selected weak electrolytes.

Table 12

Dissociation Constants of Selected Weak Electrolytes in Aqueous Solutions at 25 °C

Electrolyte		Dissociation constant
Name	Formula	
Acetic acid	CH_3COOH	2×10^{-5}
Ammonium hydroxide	NH_4OH	2×10^{-5}
Carbonic acid	H_2CO_3	$K_1 = 4.5 \times 10^{-7}$ $K_2 = 4.7 \times 10^{-11}$
Hydrogen cyanide (prussic acid)	HCN	8×10^{-10}
Hydrogen fluoride	HF	7×10^{-4}
Hydrogen peroxide	H_2O_2	$K_1 \approx 10^{-12}$ $K_2 \approx 10^{-25}$
Hydrogen sulphide	H_2S	$K_1 = 6 \times 10^{-8}$ $K_2 = 10^{-14}$
Nitrous acid	HNO_2	4×10^{-4}
Orthophosphoric acid	H_3PO_4	$K_1 = 8 \times 10^{-3}$ $K_2 = 6 \times 10^{-8}$ $K_3 = 1 \times 10^{-12}$
Silicic acid	H_2SiO_3	$K_1 \approx 10^{-10}$ $K_2 \approx 10^{-12}$
Sulphurous acid	H_2SO_3	$K_1 = 2 \times 10^{-2}$ $K_2 = 6 \times 10^{-8}$

86. Strong Electrolytes

Strong electrolytes are usually completely dissociated in aqueous solutions. Therefore, the number of ions in them is greater than in solutions of weak electrolytes of the same concentration. And if in solutions of weak electrolytes the concentration of the ions is small, the distances between them are great, and the interaction of the ions with one another is insignificant, then in not very dilute solutions of strong electrolytes the average distance between ions is comparatively small owing to the considerable concentration. For instance, in a saturated solution of sodium chloride, the average distance between the ions is only double that in NaCl crystals. The forces of interionic attraction and repulsion are quite great. In such solutions, the ions are not entirely free, their motion is hampered by their mutual attraction. Owing to this attraction, each ion is surrounded, as it were, with a spherical cluster of oppositely charged ions that has been named an "ionic atmosphere".

In the absence of an external electric field, an ionic atmosphere is symmetrical, and the forces exerted on the central ion mutually balance one another. If, however, we apply a constant electric field to a solution, oppositely charged ions will travel in opposite directions. Each ion will tend to travel in one direction, and the ionic atmosphere surrounding it in the opposite one. As a result, the directed motion of the ion is retarded, and, consequently, the number of ions passing through the solution in unit time, i.e. the current, diminishes. When the concentration of the solution increases, the retarding action of the ionic atmosphere on the electrical conductivity of the solution manifests itself to a greater extent. The values of the degree of dissociation of potassium chloride calculated for 18 °C according to the electrical conductivity of its solutions show that α diminishes with a growth in the concentration:

Concentration of KCl, N	0.01	0.1	1	2
α, %	94.2	86.2	75.6	71.2

The drop in the degree of dissociation, however, is explained not by the formation of molecules, but by an increase in the retarding action of the ionic atmosphere. In this connection, the value of the degree of dissociation of strong electrolytes determined from the electrical conductivity (or by other methods) is called the **apparent degree of dissociation.**

Similarly, the forces of interionic attraction and repulsion also affect the magnitude of the osmotic pressure, which, notwithstanding the complete dissociation, is lower than ought to be expected with a double, triple, and greater number of particles. Consequently, all the properties of an electrolyte solution depending on the concentration of the ions manifest themselves as if the number of ions in the solution were smaller than in the complete dissociation of the electrolyte.

The state of the ions in a solution is assessed with the aid of a quantity called the **activity.**

By the activity of an ion is meant its effective, conditional concentration according to which it acts in chemical reactions. The activity of an ion a equals its concentration c multiplied by the **activity coefficient** f:

$$a = fc$$

The activity coefficients of various ions are different. In addition, they change upon a change in the conditions, particularly when the concentration of the solution changes. The activity coefficient is usually less than unity for concentrated solutions, and it approaches unity in very dilute solutions. A value of f less than unity points to interaction between the ions resulting in their mutual combination. An activity coefficient close to unity points to the weak interaction between ions. Indeed, in very dilute solutions, the average distances between ions are so great that the interionic forces do not virtually manifest themselves.

In dilute solutions, the nature of ions only slightly affects the values of their activity coefficients. We can state approximately that the activity coefficient of a given ion depends only on its charge and on the **ionic strength** I of the relevant solution. The latter is defined as the half-sum of the products of the concentrations of all the ions in the solution and the square of their charge:

$$I=\frac{1}{2}(c_1z_1^2+c_2z_2^2+\ldots+c_nz_n^2)$$

Let us calculate, for example, the ionic strength of a solution containing 0.1 mol/l of sodium chloride and 0.1 mol/l of barium chloride. Here the concentration of the Na^+ ions (c_1) is 0.1 mol/l, $z_1 = 1$; the concentration of the Ba^{2+} ions (c_2) is 0.1 mol/l, $z_2 = 2$; the total concentration of the chloride ions (c_3) is $0.1 + 0.1 \times 2 =$ $= 0.3$ mol/l, $z_3 = -1$. Thus,

$$I=\frac{1}{2}[0.1\times 1^2+0.1\times 2^2+0.3(-1)^2]=$$

$$=\frac{1}{2}(0.1+0.4+0.3)=0.4$$

Table 13 gives the values of the activity coefficients for ions having a different charge at different ionic strengths of the solution. Using the data of this table, it is not difficult, for instance, to find that in the solution mentioned above, the activity coefficients of the singly charged ions Na^+ and Cl^- are the same and equal 0.82, while the activity coefficient of the doubly charged ion Ba^{2+} equals 0.45.

Table 13

Activity Coefficients f of Ions at Different Ionic Strengths of a Solution

Ionic strength of solution I	Charge of ion z			Ionic strength of solution I	Charge of ion z		
	±1	±2	±3		±1	±2	±3
0.05	0.84	0.50	0.21	0.3	0.81	0.42	0.14
0.1	0.81	0.44	0.16	0.4	0.82	0.45	0.17
0.2	0.80	0.41	0.14	0.5	0.84	0.50	0.21

If the values of the activities are used, the laws of chemical equilibrium may also be applied to strong electrolytes. Particularly, we can obtain the values of the dissociation constants for strong acids. The activities will be used in the expression for the dissociation constant instead of the concentrations of the ions and undissociated molecules. Notwithstanding a certain formality of such constants, they are helpful because they make it possible to compare the properties of strong acids. Table 14 gives the dissociation constants of selected strong acids expressed through the activities.

Table 14

Dissociation Constants of Selected Strong Acids in Aqueous Solutions at 25 °C

Acid	Formula	Dissociation constant K
Hydrobromic	HBr	10^9
Hydrochloric	HCl	10^7
Hydriodic	HI	10^{11}
Nitric	HNO_3	43.6
Permanganic	$HMnO_4$	200
Sulphuric	H_2SO_4	$K_1=1000,\ K_2=10^{-2}$

87. Properties of Acids, Bases, and Salts from the Viewpoint of the Theory of Electrolytic Dissociation

Let us consider the properties of substances that display the properties of electrolytes in aqueous solutions from the viewpoint of the theory of electrolytic dissociation.

Acids. Acids are characterized by the following general properties:

(a) the ability to react with bases and form salts;

(b) the ability to react with certain metals with the evolution of hydrogen;

(c) the ability to change the colour of indicators, particularly to cause litmus to turn red;

(d) a sour taste.

Hydrogen ions are formed in the dissociation of any acid. We must therefore explain all the properties that are common for aqueous solutions of acids by the presence of hydrated hydrogen ions. They are exactly what causes litmus to turn red, imparts a sour taste to acids, and so on. With the elimination of hydrogen ions, for example in neutralization, the acid properties also vanish. Consequently, the theory of electrolytic dissociation defines *acids as electrolytes dissociating in solutions with the formation of hydrogen ions.*

Strong acids, which dissociate completely, display the properties of acids to a greater extent, and **weak** acids, to a smaller one. The better an acid dissociates, i.e. the higher its dissociation constant, the stronger it is.

Comparing the data given in Tables 12 and 14, we can note that the values of the dissociation constants of acids vary within very broad limits. Particularly, the dissociation constant of hydrogen cyanide is much smaller than that of acetic acid. And although both these acids are weak, acetic acid is considerably stronger than hydrogen cyanide. The values of the first and second dissociation constants of sulphuric acid show that with respect to the first dissociation step H_2SO_4 is a strong acid, and with respect to the second step—a weak one. Acids whose dissociation constants range from 10^{-4} to 10^{-2} are sometimes called acids of a **medium** or **moderate strength**. They include, particularly, orthophosphoric and sulphurous acids (with respect to the first step dissociation).

Bases. Aqueous solutions of bases have the following general properties:

(a) the ability to react with acids to form salts;

(b) the ability to change the colour of indicators in a different way than acids do (for example, they colour litmus blue);

(c) a peculiar soapy or slippery feeling.

Since a common feature of all base solutions is the presence of hydroxide ions in them, it is quite obvious that the hydroxide ion is a carrier of the basic properties. Consequently, from the viewpoint of the theory of electrolytic dissociation, *bases are electrolytes dissociating in solutions with the detachment of hydroxide ions.*

The strength of bases, like that of acids, depends on the magnitude of the dissociation constant. *The greater the dissociation constant of a given base, the stronger is the base.*

There are hydroxides that are capable of entering into a reaction to form salts not only with acids, but also with bases. Such hydroxides include zinc hydroxide. When it reacts, for example, with hydrochloric acid, zinc chloride is obtained:

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

and when it reacts with sodium hydroxide, sodium zincate is produced:

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

Hydroxides having this property are known as **amphoteric hydroxides** or **amphoteric electrolytes.** In addition to zinc hydroxide, they include, among others, aluminium and chromium hydroxides.

The phenomenon of amphoterism is explained by the fact that the strength of the bond between the metal and oxygen in molecules of amphoteric electrolytes differs insignificantly from the strength of the bond between the oxygen and hydrogen. Dissociation of such molecules is possible, consequently, at the sites of both bonds. If we designate an amphoteric electrolyte by the formula ROH, then its dissociation can be depicted as follows:

$$H^+ + RO^- \rightleftharpoons ROH \rightleftharpoons R^+ + OH^-$$

Hence, there is complicated equilibrium in a solution of an amphoteric electrolyte, and products of both the acid- and base-type dissociation participate in it.

Amphoteric properties are also observed among certain organic compounds. They play an important role in biological chemistry; for instance, proteins are amphoteric electrolytes.

Salts. Salts can be defined as electrolytes that dissociate when dissolved in water, detaching positive ions other than hydrogen ions and negative ions other than hydroxide ions. There are no ions that would be common for aqueous solutions of all salts; for this reason, salts do not have common properties. Salts dissociate quite well, as a rule, and the better, the smaller are the charges of the ions forming the salt.

When **acid** salts dissolve, metal cations, complex anions of the acid residue, and also ions that are the products of dissociation of this complex acid residue, including H^+ ions, are formed in the solution. For instance, when sodium hydrogen carbonate (sodium bicarbonate) dissolves, dissociation proceeds according to the following equations:

$$NaHCO_3 = Na^+ + HCO_3^-$$
$$HCO_3^- = H^+ + CO_3^{2-}$$

When **basic** salts dissociate, anions of an acid and complex cations consisting of a metal and hydroxyl groups are formed. These complex cations are also capable of dissociation. This is why OH^- ions are present in a solution of a basic salt. For example, when magnesium chloride hydroxide dissolves, dissociation proceeds according to the equations

$$MgOHCl = MgOH^+ + Cl^-$$
$$MgOH^+ = Mg^{2+} + OH^-$$

Thus, the theory of electrolytic dissociation explains the common properties of acids by the presence of hydrogen ions in their solutions, and the common properties of bases by the presence of hydroxide ions in their solutions. This explanation is not general, however. Chemical reactions proceeding with the participation of acids and bases are known which the theory of electrolytic dissociation cannot be applied to. Particularly, acids and bases can react with one another without being ionized. For example, anhydrous hydrogen chloride consisting only of molecules reacts quite readily with anhydrous bases. In addition, substances are known that do not contain hydroxyl groups, but display the properties of bases. For example, ammonia reacts with acids and forms salts (ammonium salts), although it contains no OH groups. With hydrogen chloride, for instance, it forms a typical salt—ammonium chloride:

$$NH_3 + HCl = NH_4Cl$$

The studying of such reactions, and also of reactions proceeding in non-aqueous media led to the appearance of more general concepts of acids and bases. Among the most important theories of acids and bases is the **proton theory**, proposed independently in 1923 by J. Brönsted and T. Lowry.

According to this theory, an acid is a **proton donor**, i.e. a particle (molecule or ion) that is capable of giving up a hydrogen ion—a proton, and a base is a **proton acceptor**, i.e. a particle (molecule or ion) that is capable of attaching a proton. The relationship between an acid and a base is determined by the equation:

$$\text{Base} + \text{Proton} \rightleftharpoons \text{Acid}$$

An acid and a base related by this equation are called **conjugate** (a **conjugate acid-base pair**). For instance, the ion HSO_4^- is the conjugate base of the acid H_2SO_4.

The proton theory represents the reaction between an acid and a base by the equation:

$$(\text{Acid})_1 + (\text{Base})_2 = (\text{Acid})_2 + (\text{Base})_1$$

For example, in the reaction

$$HCl + NH_3 = NH_4^+ + Cl^-$$

the ion Cl^- is the conjugate base of the acid HCl, and the ion NH_4^+ is the conjugate acid of the base NH_3.

Of significance in the proton theory is the proposition that a substance behaves like an acid or a base depending on what other substance it enters into a reaction with. A very important factor here is the bond energy of the substance with a proton. For instance, in the series NH_3-H_2O-HF, this energy is maximum for NH_3 and minimum for HF. Therefore, when mixed with NH_3, water functions as an acid, and when mixed with HF, as a base:

$$NH_3 + H_2O = NH_4^+ + OH^-$$
$$HF + H_2O = F^- + H_3O^+$$

88. Net Ionic Equations

When any strong acid is neutralized with any strong base, about 57.6 kJ of heat are evolved per mole of water formed:

$$HCl + NaOH = NaCl + H_2O \quad +57.53 \text{ kJ}$$
$$HNO_3 + KOH = KNO_3 + H_2O \quad +57.61 \text{ kJ}$$

This indicates that such reactions are a single process. We shall get the equation of this process if we consider one of the above reactions, for instance the first one, in greater detail. Let us rewrite its equation, putting the strong electrolytes in the ionic form because they exist in the solution in the form of ions, and the weak ones in the molecular form because they are in the solution mainly in the form of molecules (water is a very weak electrolyte, see Sec. 90):

$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O$$

Examining the equation obtained, we see that the Na^+ and Cl^- ions have remained unchanged in the course of the reaction. We shall therefore rewrite the equation again, excluding these "spectator" ions from both sides of the equation. We get:

$$H^+ + OH^- = H_2O$$

Thus, the reaction of neutralization of any strong acid with any strong base consists in the same process—in the formation of water molecules from hydrogen and hydroxide ions. It is clear that the heat effects of these reactions must also be the same.

Strictly speaking, the reaction of water formation from ions is reversible, which can be expressed by the equation

$$H^+ + OH^- \rightleftharpoons H_2O$$

We shall see below, however, that water is a very weak electrolyte and dissociates only to a negligibly small extent. In other words, equilibrium between the water molecules and the ions shifts greatly in the direction of molecule formation. For this reason, a reaction of neutralization of a strong acid with a strong base goes practically to completion.

When a solution of a silver salt is mixed with hydrochloric acid or a solution of any of its salts, a characteristic white curdy precipitate of silver chloride is formed:

$$AgNO_3 + HCl = AgCl\downarrow + HNO_3$$
$$Ag_2SO_4 + CuCl_2 = 2AgCl\downarrow + CuSO_4$$

Such reactions are also a single process. To obtain its net ionic equation, let us rewrite, for example, the equation of the first reaction, putting the strong electrolytes, as in the preceding example, in the ionic form, and the substance in the precipitate in the molecular one:

$$Ag^+ + NO_3^- + H^+ + Cl^- = AgCl\downarrow + H^+ + NO_3^-$$

We can see that the H^+ and NO_3^- ions are spectators of the reaction. We shall therefore exclude them and rewrite the equation again:

$$Ag^+ + Cl^- = AgCl\downarrow$$

This is exactly the net ionic equation of the process being considered.

Here it must also be borne in mind that the silver chloride precipitate is in equilibrium with the Ag^+ and Cl^- ions in the solution, so that the process expressed by the last equation is reversible:

$$Ag^+ + Cl^- \rightleftharpoons AgCl\downarrow$$

Owing to the low solubility of silver chloride, however, this equilibrium shifts very greatly to the right. We can therefore consider that the reaction of AgCl formation from ions goes virtually to completion.

The formation of a precipitate of AgCl will always be observed when a solution has a considerable concentration of the Ag^+ and Cl^- ions. Hence, silver ions can be used to detect the presence of chloride ions in a solution, and, conversely, chloride ions can be used to detect the presence of silver ions. The Cl^- ion can be a reagent for the Ag^+ ion, and the Ag^+ ion a reagent for the Cl^- ion.

In the following, we shall widely use the net ionic form of writing equations of reactions with the participation of electrolytes.

To compile net ionic equations, we must know which salts are soluble in water and which are virtually insoluble. A general characteristic of the solubility of the most important salts in water is given in Table 15.

Table 15

Solubility of Most Important Salts in Water

Anions and cations	Solubility of salts
NO_3^-	All salts are soluble
Cl^-	All salts are soluble except for AgCl, CuCl, $PbCl_2$, and Hg_2Cl_2
SO_4^{2-}	All salts are soluble except for $BaSO_4$, $SrSO_4$, and $PbSO_4$; $CaSO_4$ is poorly soluble
CO_3^{2-}	Of the neutral salts, only those of sodium, potassium, and ammonium are soluble
PO_4^{3-}	Ditto
Na^+, K^+, NH_4^+	Virtually all salts are soluble

Net ionic equations help us to understand the features of reactions between electrolytes. Let us consider as an example several reactions proceeding with the participation of weak acids and bases.

We have already mentioned that the neutralization of any strong acid with any strong base is attended by the same heat effect, so that it consists in the same process—the formation of water molecules from hydrogen and hydroxide ions. But in the neutralization of a strong acid with a weak base, or of a weak acid with a strong or a weak base, the heat effects vary. Let us write the net ionic equations for such reactions.

Neutralization of a weak acid (acetic acid) **with a strong base** (sodium hydroxide):

$$CH_3COOH + NaOH = CH_3COONa + H_2O$$

Here sodium hydroxide and the salt formed are strong electrolytes, and the acid and water are weak ones:

$$CH_3COOH + Na^+ + OH^- = CH_3COO^- + Na^+ + H_2O$$

It can be seen that only the sodium ions are spectators of the reaction. The net ionic equation therefore has the form:

$$CH_3COOH + OH^- = CH_3COO^- + H_2O$$

Neutralization of a strong acid (nitric acid) **with a weak base** (ammonium hydroxide):

$$HNO_3 + NH_4OH = NH_4NO_3 + H_2O$$

Here we must write the acid and the salt formed as ions, and the ammonium hydroxide and water as molecules:

$$H^+ + NO_3^- + NH_4OH = NH_4^+ + NO_3^- + H_2O$$

The ions NO_3^- do not change. Omitting them, we get the following net ionic equation:

$$H^+ + NH_4OH = NH_4^+ + H_2O$$

Neutralization of a weak acid (acetic acid) **with a weak base** (ammonium hydroxide):

$$CH_3COOH + NH_4OH = CH_3COONH_4 + H_2O$$

In this reaction, all the substances except for the salt formed are weak electrolytes. Consequently, the net ionic form of the equation is:

$$CH_3COOH + NH_4OH = CH_3COO^- + NH_4^+ + H_2O$$

Comparing the obtained net ionic equations, we see that they are all different. It is therefore evident that the heat effects of the considered reactions are also different.

We have already indicated that the reactions of neutralization of strong acids with strong bases in the course of which hydrogen and hydroxide ions combine into water molecules proceed virtually to the end. On the other hand, neutralization reactions in which at least one of the reactants is a weak electrolyte and in which molecules of poorly dissociating substances are present not only in the right-hand, but also in the left-hand side of the net ionic equation, do not go to completion. They reach a state of equilibrium in which the salt coexists with the acid and base from which it was formed. It will therefore be more proper to write the equations of such reactions as reversible ones:

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

$$H^+ + NH_4OH \rightleftharpoons NH_4^+ + H_2O$$

$$CH_3COOH + NH_4OH \rightleftharpoons CH_3COO^- + NH_4^+ + H_2O$$

89. Solubility Product

We know (Sec. 73) that when a solid dissolves in water, dissolving stops when a saturated solution is obtained, i.e. when equilibrium sets in between the solute and the molecules of the same substance in the solution. When an electrolyte dissolves, for instance a salt, not molecules, but ions pass into the solution. Hence, equilibrium in a saturated solution will also set in between the solid salt and the ions that have passed into the solution. For example, in a saturated solution of calcium sulphate, the following equilibrium will set in:

$$\underset{\text{Solid salt}}{CaSO_4} \rightleftharpoons \underset{\text{Ions in solution}}{Ca^{2+} + SO_4^{2-}}$$

The equilibrium constant for this process is

$$K = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4]}$$

The denominator of the fraction—the concentration of the solid salt—is a constant quantity that can be introduced into the equilibrium constant. Hence, introducing the symbol

$$K[CaSO_4] = K'$$

we obtain

$$[Ca^{2+}][SO_4^{2-}] = K'$$

Thus, *in a saturated solution of an electrolyte, the product of the concentrations of its ions is a constant quantity at the given temperature.* This quantity characterizes the ability of an electrolyte to dissolve from a quantitative viewpoint. It is known as the **solubility product** (or the **solubility product constant**) of an electrolyte and is designated by the symbol K_{sp}.

Using $K_{sp}(CaSO_4)$ instead of K', we have:

$$K_{sp}(CaSO_4) = [Ca^{2+}][SO_4^{2-}]$$

It is not difficult to find the solubility product of an electrolyte knowing its solubility. For instance, the solubility of calcium sulphate at 20 °C is 1.5×10^{-2} mol/l. This signifies that in a saturated solution the concentration of each of the ions Ca^{2+} and SO_4^{2-} is 1.5×10^{-2} mol/l. Consequently, the solubility product of this salt is

$$K_{sp}(CaSO_4) = [Ca^{2+}][SO_4^{2-}] = (1.5 \times 10^{-2})^2 = 2.25 \times 10^{-4}$$

The above calculation, performed on the basis of the classical theory of electrolytic dissociation, is not completely accurate because no account is taken here of the influence of the electrostatic forces acting between the ions on the solubility of the electrolyte. If we take this influence into consideration, i.e. if instead of the concentrations of Ca^{2+} and SO_4^{2-} we multiply their activities in a saturated solution of $CaSO_4$, the magnitude of the solubility product will lower somewhat; the precised value of $K_{sp}(CaSO_4)$ is 1.3×10^{-4}. When dealing with very slightly soluble electrolytes, the influence of the above forces may be disregarded.

When an electrolyte contains two or more common ions, the concentrations of these ions must be raised to the relevant powers in calculating the solubility product. For example:

$$K_{sp}(PbI_2) = [Pb^{2+}][I^-]^2$$

A knowledge of the solubility product makes it possible to solve problems related with the formation or dissolving of precipitates in chemical reactions, which is of special importance for analytical chemistry. It must be borne in mind, however, that *the solubility product calculated without account taken of the activity coefficients is a constant quantity only for poorly soluble electrolytes*, and provided that the concentrations of the other ions in the solution are not high. The explanation is that the activity coefficients are close to unity only in very dilute solutions (see p. 253). For well soluble electrolytes, the value of the product of the ion concentrations in a saturated solution may vary greatly in the presence of other substances. This occurs owing to the change in the activity coefficients of the ions. Hence, calculations performed using the solubility product without taking the activity coefficients into consideration lead to incorrect results in these cases.

Table 16 gives the values of the solubility product for selected compounds having a low solubility in water.

Table 16

Solubility Products of Selected Substances at 25 °C

Compound	Solubility product	Compound	Solubility product
AgCl	1.8×10^{-10}	$CaCO_3$	5×10^{-9}
AgBr	6×10^{-13}	CuS	6×10^{-36}
AgI	1×10^{-16}	Cu_2S	1×10^{-48}
$Cu(OH)_2$	2.2×10^{-20}	FeS	5×10^{-18}
$Zn(OH)_2$	1×10^{-17}	HgS	10^{-52}
$BaSO_4$	1.1×10^{-10}	MnS	2.5×10^{-10}
$CaSO_4$	1.3×10^{-4}	ZnS	10^{-23}

90. Dissociation of Water. pH

Pure water conducts an electric current very poorly, but nevertheless it has a measurable electrical conductivity that is explained by the slight dissociation of water into hydrogen and hydroxide ions:

$$H_2O \rightleftharpoons H^+ + OH^-$$

The electrical conductivity of pure water can be used to calculate the concentration of hydrogen and hydroxide ions in water. At 25 °C, it is 10^{-7} mol/l.

Let us write an expression for the dissociation constant of water:

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

We can rewrite this equation as follows:

$$[H^+][OH^-] = [H_2O]K$$

Since the degree of dissociation of water is very low, the concentration of undissociated molecules of H_2O in water virtually equals the total concentration of water, i.e. 55.55 mol/l (1 litre contains 1000 grams of water, i.e. 100:18.02 = 55.55 moles). The concentration of water can be considered the same in dilute aqueous solutions. Therefore, replacing the product $[H_2O]K$ in the last equation with the new constant K_w, we have:

$$[H^+][OH^-] = K_w$$

The obtained equation shows that *for water and dilute aqueous solutions at a constant temperature, the product of the hydrogen ion and hydroxide ion concentrations is a constant quantity.* The latter is called the **ion product of water.** It is not difficult to obtain its numerical value by introducing into the last equation the concentrations of the hydrogen and hydroxide ions. For pure water at 25 °C, we have $[H^+] = [OH^-] = 1 \times 10^{-7}$ mol/l. Hence, for this temperature*:

$$K_w = 10^{-7} \times 10^{-7} = 10^{-14}$$

Solutions in which the concentrations of the hydrogen ions and hydroxide ions are the same are called neutral solutions. At 25 °C, as we have already indicated, the concentration of both hydrogen ions and hydroxide ions in neutral solutions is 10^{-7} mol/l. In acid solutions, the hydrogen ion concentration is greater, and in alkali ones—the hydroxide ion concentration. But no matter how the solution reacts, the product of the concentrations of the hydrogen ions and hydroxide ions remains constant.

If, for instance, we add so much acid to pure water that the hydrogen ion concentration grows to 10^{-3} mol/l, then the hydroxide ion concentration will diminish so that the product $[H^+][OH^-]$ remains equal to 10^{-14}. Consequently, in this solution, the hydroxide ion concentration will be

$$[OH^-] = \frac{10^{-14}}{10^{-3}} = 10^{-11} \text{ mol/l}$$

Conversely, if we add an alkali to water and thus raise the hydroxide ion concentration, for example to 10^{-5} mol/l, the hydrogen ion

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* The value of the ion product of water grows with the temperature. At 100 °C, it reaches a value of 5.5×10^{-13}.

concentration will be

$$[H^+] = \frac{10^{-14}}{10^{-5}} = 10^{-9}\ \text{mol/l}$$

These examples show that if the hydrogen ion concentration in an aqueous solution is known, this determines the hydroxide ion concentration. Therefore, both the degree of acidity and the degree of alkalinity of a solution can be characterized quantitatively by the hydrogen ion concentration:

Neutral solution — $[H^+] = 10^{-7}$ mol/l
Acid solution — $[H^+] > 10^{-7}$ mol/l
Alkaline solution — $[H^+] < 10^{-7}$ mol/l

The acidity or alkalinity of a solution can be expressed in another, more convenient way: instead of the hydrogen ion concentration, its common logarithm is taken with the reverse sign. The latter quantity is named the **hydrogen ion index**, but most chemists call it the **pH-value***, or simply the pH, which is its symbol:

$$pH = -\log [H^+]$$

For instance, if $[H^+] = 10^{-5}$ mol/l, then pH = 5, if $[H^+] = 10^{-9}$ mol/l, then pH = 9, and so on. It is thus clear that for a neutral solution ($[H^+] = 10^{-7}$ mol/l), pH = 7 (at a temperature of 25 °C). For acid solutions, $pH < 7$, and diminishes with an increasing acidity of the solution. Conversely, for alkaline solutions, $pH > 7$, and grows with an increasing alkalinity of the solution.

There are different ways of measuring the pH. The reaction of a solution can be determined approximately with the aid of special

Table 17

Most Important Indicators

Indicator	Colour of indicator in different solutions		
	acid solution	neutral solution	basic solution
Methyl orange	Red ($pH < 3.1$)	Orange ($3.1 < pH < 4.4$)	Yellow ($pH > 4.4$)
Methyl red	Red ($pH < 4.2$)	Orange ($4.2 < pH < 6.3$)	Yellow ($pH > 6.3$)
Phenolphthalein	Colourless ($pH < 8.0$)	Pale crimson ($8.0 < pH < 9.8$)	Crimson ($pH > 9.8$)
Litmus	Red ($pH < 5$)	Violet ($5 < pH < 8$)	Blue ($pH > 8$)

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* The notation "pH" was introduced by the Danish biochemist Sören P. L. Sörensen in 1909 as an abbreviation of "power of hydrogen".

reagents called **indicators** whose colour changes depending on the hydrogen ion concentration. The most widespread indicators are methyl orange, methyl red, and phenolphthalein. Table 17 characterizes the most important indicators.

The pH is of great significance for many processes. For example, the pH of the blood of human beings and animals has a strictly constant value. Plants can grow normally only when the pH of the soil solution is within a definite interval characteristic of a given species of plant. The properties of natural water, particularly its corrosion activity, depends greatly on the pH.

91. Shift of Ionic Equilibria

Equilibrium in solutions of electrolytes, like any chemical equilibrium, remains unchanged until the conditions determining it change. A change in the conditions leads to violation of equilibrium.

For instance, equilibrium is violated when the concentration of one of the ions participating in this equilibrium changes. When the concentration grows, a process occurs during which these ions become bound. For example, if we introduce into a solution of acetic acid dissociating according to the equation

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

a salt of this acid and thus increase the CH_3COO^- ion concentration, then according to Le Chatelier's principle, equilibrium will shift to the left, i.e. the degree of dissociation of the acetic acid diminishes. Hence, it follows that *the introduction of ions in common with one of the electrolyte ions into a solution of a weak electrolyte lowers the degree of dissociation of the electrolyte.* Conversely, a reduction in the concentration of one of the ions results in the dissociation of a new number of molecules. For example, when hydroxide ions binding the hydrogen ions are introduced into a solution of the above-mentioned acid, its dissociation grows.

Equilibrium is violated in a similar way in a sparingly soluble electrolyte: as soon as the product of the ion concentrations of a poorly soluble electrolyte in a solution exceeds the value of the solubility product, a precipitate is formed. For instance, if to a saturated solution of calcium sulphate we add another well soluble electrolyte containing a common ion, for example, potassium sulphate, then owing to the growth in the concentration of the SO_4^{2-} ions equilibrium will shift in the direction of formation of $CaSO_4$ crystals; the ions Ca^{2+} and SO_4^{2-} will leave the solution, forming a precipitate. The process will go on until the product of the concentrations of these ions becomes equal to the solubility product of $CaSO_4$. As a result, the amount of calcium sulphate in the solution will diminish.

Thus, *the solubility of an electrolyte diminishes as a result of the introduction of common ions into the solution.* The cases when one of the ions in the solution combines with the introduced ions into more complicated (complex) ions (see Vol. 2, Chap. 8) are an exception.

The above examples allow us to arrive at the following general conclusion.

An essential condition for reactions between electrolytes to go on is the removal from the solution of some species of the ions, for example owing to the formation of poorly dissociating substances, or substances liberated from the solution as a precipitate or gas. In other words, reactions in solutions of electrolytes always proceed in the direction of formation of the least dissociated or least soluble substances.

It follows from this conclusion, in particular, that strong acids displace weak ones from solutions of their salts. For instance, when sodium acetate reacts with hydrochloric acid, the reaction proceeds virtually to the end with the formation of acetic acid:

$$CH_3COONa + HCl = CH_3COOH + NaCl$$

or in the net ionic form:

$$CH_3COO^- + H^+ = CH_3COOH$$

Reactions between strong bases and the salts of weak bases proceed in a similar way. For instance, when sodium hydroxide acts on iron(II) sulphate, iron(II) hydroxide precipitates:

$$FeSO_4 + 2NaOH = Na_2SO_4 + Fe(OH)_2\downarrow$$

or in the net ionic form:

$$Fe^{2+} + 2OH^- = Fe(OH)_2\downarrow$$

The last reaction is an example of the formation not only of a weak, but also of a poorly soluble electrolyte.

From the viewpoint considered above, the difference between the neutralization of a strong acid with a strong base and the neutralization when at least one of the reactants is a weak electrolyte now becomes clear. When a strong acid is neutralized with a strong base, only one weak electrolyte—water—is formed in the solution. The equilibrium

$$H^+ + OH^- \rightleftharpoons H_2O$$

shifts greatly to the right, and the reaction in this case goes virtually to completion. In neutralization of a weak acid or a weak base, on the other hand, the solution contains at least two weak electrolytes—water and a weak acid or a weak base. For example, when acetic acid is neutralized with a strong base, two equilibria set in in the solution:

$$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

A hydrogen ion can thus combine with the relevant ion into a molecule of acetic acid or into a water molecule. The ions CH_3COO^- and OH^- compete with each other, as it were, to combine with a hydrogen ion. Therefore, the reaction of neutralization goes not to completion here, but to a state of equilibrium:

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

This equilibrium, however, shifts greatly to the right because water is a considerably weaker electrolyte than acetic acid so that the H^+ ions combine more completely into water molecules than into acetic acid ones.

When a weak base—ammonium hydroxide—is neutralized with a strong acid, two equilibria also set in in the solution:

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

Here, competition is between the ions NH_4^+ and H^+ combining with the hydroxide ions to form undissociated molecules. As a result, this reaction also fails to go to completion, but goes on to a state of equilibrium:

$$H^+ + NH_4OH \rightleftharpoons NH_4^+ + H_2O$$

But since water is a considerably weaker electrolyte than NH_4OH, equilibrium shifts greatly to the right.

Similar processes also occur in reactions during which a poorly soluble substance transforms into a soluble, but only slightly dissociating product. Such reactions include, for instance, the dissolving of the sulphides of certain metals in hydrochloric acid. For example, the reaction of manganese sulphide with hydrochloric acid is expressed by the equation

$$MnS(c) + 2HCl = MnCl_2 + H_2S$$

or

$$MnS(c) + 2H^+ = Mn^{2+} + H_2S$$

The presence among the reactants of a poorly soluble electrolyte (MnS) upon whose formation the S^{2-} ions become bound induces the reaction to proceed to the left. On the other hand, when a weak electrolyte (H_2S) is formed, the S^{2-} ions are also bound, which facilitates proceeding of the reaction to the right. Thus, the S^{2-} ions participate in two competing processes that result in the establishment of two equilibria:

$$S^{2-} + Mn^{2+} \rightleftharpoons MnS(c)$$

and

$$S^{2-} + 2H^+ \rightleftharpoons H_2S$$

The direction of the reaction considered depends on which of the two substances—H_2S or MnS—combines with the S^{2-} ions to a greater extent. The summary dissociation constant of hydrogen sulphide is $K = K_1K_2 = 6 \times 10^{-22}$ (see Table 12). The solubility product of MnS, on the other hand, is 2.5×10^{-10} (see Table 16). It is thus obvious that the combination of the S^{2-} ions into hydrogen sulphide molecules takes place more completely than into MnS. Therefore, the reaction considered proceeds to the right—the manganese sulphide dissolves in the hydrochloric acid.

Two similar equilibria set in in the hydrochloric acid-copper(II) sulphide system. But the solubility product of CuS is very low, it equals 6×10^{-36} (see Table 16). Therefore, the S^{2-} ions combine more completely into CuS than into hydrogen sulphide molecules, and equilibrium in the system

$$CuS(c) + 2HCl \rightleftharpoons CuCl_2 + H_2S$$

shifts to the left; copper(II) sulphide is insoluble in hydrochloric acid.

The regularities considered make it possible to understand the behaviour of amphoteric hydroxides. For instance, equilibrium between a zinc hydroxide precipitate and its solution is violated when either an acid or an alkali is added. In this case, equilibrium can be written in the form*:

$$\begin{array}{ccccc} 2H^+ + ZnO_2^{2-} & \rightleftharpoons & Zn(OH)_2 & \rightleftharpoons & Zn^{2+} + 2OH^- \\ & & \text{solution} & & \\ & & \updownarrows & & \\ & & Zn(OH)_2 & & \\ & & \text{precipitate} & & \end{array}$$

When an acid is added to the zinc hydroxide, the hydrogen ion concentration grows. The product $[H^+][OH^-]$ becomes greater than the ion product of water—the process of formation of H_2O molecules from ions goes on; equilibrium is also violated in the system $Zn(OH)_2$. According to Le Chatelier's principle, owing to the growth in the H^+ ion concentration and in the consumption of the OH^- ion, the dissociation of $Zn(OH)_2$ according to the acid type is suppressed, and according to the base type increases. As a result, the $Zn(OH)_2$

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* Actually, the equilibrium being considered is more complicated. First, the dissociation proceeds in steps, and second, complex ions (see Vol. 2, Sec. 100) are also formed in addition to the simple ones. A strict treatment of these processes, however, does not alter the conclusions arrived at on the basis of our simplified scheme.

precipitate dissolves, and a salt is formed in which zinc is a cation. For example, with hydrochloric acid, the following reaction proceeds:

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

When an alkali is added to the zinc hydroxide, the OH^- ion concentration grows. In this case, the process goes on in the direction of combination of the hydrogen ions. Equilibrium in the system is violated, but now dissociation of $Zn(OH)_2$ according to the acid type predominates. As a result, the $Zn(OH)_2$ precipitate dissolves, and a salt is formed in which the zinc is in the anion. For example, when NaOH is added, the following reaction proceeds:

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

The process is possible in both cases and occurs because the combination of the H^+ and OH^- ions into water molecules proceeds to a greater extent than into molecules of $Zn(OH)_2$.

92. Hydrolysis of Salts

By hydrolysis is meant the reaction of a substance with water in which the constituent parts of the substance combine with the constituent parts of water.* An example of hydrolysis is the reaction of phosphorus trichloride PCl_3 with water. It results in the formation of phosphorous acid H_3PO_3 and hydrochloric acid:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

Compounds of various classes are subjected to hydrolysis. In the present section, we treat one of the most important cases—the hydrolysis of salts.

We have already mentioned that in neutralization in which weak acids and bases participate, the reactions do not proceed to the end. Consequently, to a certain extent, the reverse reaction (the reaction of the salt with water) also proceeds and results in the formation of an acid and a base. This is the hydrolysis of the salt.

Salts formed by a weak acid and a weak base, or by a weak acid and a strong base, or by a weak base and a strong acid, enter into reactions of hydrolysis. Salts formed by a strong acid and a strong base do not undergo hydrolysis; here neutralization consists in the process

$$H^+ + OH^- = H_2O$$

while the reverse reaction—the ionization of a water molecule—proceeds to a negligibly small extent.

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* Hydrolysis literally means "decomposition by water".

Let us consider the hydrolysis of a salt formed by a monobasic acid and a monovalent metal. We shall take as an example sodium acetate—a salt of a weak acid and a strong base. The equation of hydrolysis of this salt is

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

or in the net ionic form:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

The equation shows that in this case the anion of the salt is hydrolyzed and that the reaction is attended by the formation of OH^- ions. But since the ion product of water $[H^+][OH^-]$ is a constant quantity, when OH^- ions accumulate, the hydrogen ion concentration diminishes. Hence, *solutions of salts formed by a weak acid and a strong base are basic.*

Similarly, in a salt formed by a weak base and a strong acid, the cation of the salt is hydrolyzed, and the reaction is attended by the formation of H^+ ions; for example

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

or

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Accumulation of the H^+ ion leads to diminishing of the OH^- ion concentration. Thus, *solutions of salts formed by a weak base and a strong acid are acidic.*

In the above cases, not all the salt in the solution, but only a part of it is hydrolyzed. In other words, equilibrium sets in in the solution between the salt and the acid and base forming it. The fraction of a substance subjected to hydrolysis—the **degree of hydrolysis**—depends on the constant of this equilibrium, and also on the temperature and the salt concentration.

Let us write the equation of hydrolysis in the general form. Let HA be an acid and MOH a base. The salt they form is MA. The equation of hydrolysis will thus have the form

$$MA + H_2O \rightleftharpoons HA + MOH$$

The following constant corresponds to this equilibrium:

$$K = \frac{[HA][MOH]}{[MA][H_2O]}$$

The concentration of water in dilute solutions is virtually a constant quantity. Introducing the symbol

$$K[H_2O] = K_h$$

we get

$$K_h = \frac{[HA][MOH]}{[MA]}$$

The quantity K_h is known as the **hydrolysis constant** of a salt. Its value characterizes the ability of the given salt to be hydrolyzed. An increase in K_h is attended by a greater (at the same temperature and salt concentration) degree of hydrolysis.

For a salt formed by a weak acid and a strong base, the hydrolysis constant is related to the dissociation constant of the acid K_{acid} by the expression

$$K_h = \frac{K_W}{K_{acid}}$$

This equation shows that K_h grows when K_{acid} decreases. In other words, *the weaker an acid, the greater is the degree of hydrolysis of its salts.*

For a salt formed by a weak base and a strong acid, a similar expression relates the hydrolysis constant to the dissociation constant of the base K_{base}:

$$K_h = \frac{K_W}{K_{base}}$$

Therefore, *the weaker a base, the greater is the degree of hydrolysis of the salts it forms.*

For a salt formed by a weak acid and a weak base, the hydrolysis constant is related to the dissociation constants of the acid and the base by the following expression:

$$K_h = \frac{K_W}{K_{acid}K_{base}}$$

The expressions relating the hydrolysis constant to the dissociation constants of an acid and a base are easily obtained from the expression for the hydrolysis constant. Let us derive the first of them relating to the formation of a salt by a weak acid and a strong base. We shall take into account that the base MOH from which the salt MA has been formed is a strong one, i.e. dissociates completely. Hence,

$$[MOH] = [OH^-]$$

The salt itself also dissociates completely. Hence,

$$[MA] = [A^-]$$

We shall express the concentration of the acid, disregarding its dissociated part, through the dissociation constant of the acid K_{acid}:

$$K_{acid} = \frac{[H^+][A^-]}{[HA]} \quad \text{or} \quad [HA] = \frac{[H^+][A^-]}{K_{acid}}$$

We use the found values of the concentrations of MOH, MA, and HA in the expression for the hydrolysis constant:.

$$K_h = \frac{[HA][MOH]}{[MA]} = \frac{[H^+][A^-][OH^-]}{K_{acid}[A^-]} = \frac{[H^+][OH^-]}{K_{acid}}$$

Taking into consideration that $[H^+][OH^-]$ is the ion product of water, we finally get

$$K_h = \frac{K_w}{K_{acid}}$$

The degree of hydrolysis is determined by the nature of a salt, its concentration, and temperature. The nature of a salt manifests itself in the value of the hydrolysis constant. The dependence on the concentration expresses itself in that the degree of hydrolysis grows with dilution of a solution. Indeed, suppose we have a solution of potassium cyanide. The following equilibrium sets in in it:

$$KCN + H_2O \rightleftharpoons HCN + KOH$$

which the constant

$$K_h = \frac{[HCN][KOH]}{[KCN]}$$

corresponds to.

Let us dilute the solution 10 times. At the first moment, the concentrations of all the substances—KCN, HCN, and KOH—diminish to one-tenth their initial values. As a result, the numerator in the right-hand side of the equation of the hydrolysis constant decreases 100 times, and the denominator only 10 times. But the hydrolysis constant, like any equilibrium constant, does not depend on the concentrations of the substances. Therefore, equilibrium in the solution will be violated. For it to set in again, the numerator of the fraction must grow and the denominator diminish, i.e. a certain amount of the salt must additionally hydrolyze. As a result, the concentrations of HCN and KOH will grow, and that of KCN will drop. Thus, the degree of hydrolysis of the salt will increase.

The influence of the temperature on the degree of hydrolysis follows from Le Chatelier's principle. All neutralization reactions proceed with the liberation of heat (Sec. 88), and hydrolysis with the absorption of heat. Since the yield of endothermic reactions increases with elevation of the temperature, the degree of hydrolysis also grows with elevation of the temperature.

It is evident from the above that to curtail hydrolysis, solutions should be stored with a high concentration and at low temperatures. In addition, the suppressing of hydrolysis is facilitated by acidification (for salts formed by a strong acid and a weak base) or alkalization (for salts formed by a strong base and a weak acid) of the solution.

We now consider the hydrolysis of salts formed by a weak polybasic acid or a weak base of a polyvalent metal. The hydrolysis of such salts proceeds in steps. Thus, the first step of hydrolysis of sodium carbonate proceeds according to the equation

$$Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 + NaOH$$

or in the net ionic form:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

The acid salt hydrolyzes, in turn (the second step of hydrolysis):

$$NaHCO_3 + H_2O \rightleftharpoons H_2CO_3 + NaOH$$

or

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

It can be seen that in hydrolysis in the first step the ion HCO_3^- is formed whose dissociation is characterized by the second dissociation constant of carbonic acid, while in hydrolysis in the second step carbonic acid is formed whose dissociation is characterized by the first dissociation constant. Therefore, the first-step hydrolysis constant $K_{h,1}$ is related to the second dissociation constant of the acid, and the second-step hydrolysis constant $K_{h,2}$ to the first dissociation constant of the acid. This relationship is shown by the expressions

$$K_{h,1} = \frac{K_w}{K_{2,acid}}; \quad K_{h,2} = \frac{K_w}{K_{1,acid}}$$

Since the first dissociation constant of an acid is always greater than the second one, the first-step hydrolysis constant is always greater than the second-step one:

$$K_{h,1} > K_{h,2}$$

For this reason, hydrolysis in the first step always proceeds to a greater degree than in the second one. In addition, the ions formed in the first-step hydrolysis (in the example being considered—the OH^- ions) facilitate the shifting of equilibrium in the second step to the left, i.e. also suppress the second-step hydrolysis.

The hydrolysis of salts formed by a weak base of a polyvalent metal proceeds similarly. For example, the hydrolysis of copper(II) chloride proceeds in the first step with the formation of copper chloride hydroxide:

$$CuCl_2 + H_2O \rightleftharpoons CuOHCl + HCl$$

or in the net ionic form:

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+$$

Hydrolysis in the second step occurs to a negligibly small degree:

$$CuOHCl + H_2O \rightleftharpoons Cu(OH)_2 + HCl$$

or

$$CuOH^+ + H_2O \rightleftharpoons Cu(OH)_2 + H^+$$

Especially great is the hydrolysis of salts formed by a weak acid and a weak base. According to the expression given above, the hydrolysis constant in this case is inversely proportional to the product of the dissociation constants of the acid and the base, i.e. its value is especially high. An example is the hydrolysis of aluminium acetate that proceeds to the basic salts—aluminium acetate hydroxide and dihydroxide:

$$Al(CH_3COO)_3 + H_2O \rightleftharpoons Al(OH)(CH_3COO)_2 + CH_3COOH$$
$$Al(OH)(CH_3COO)_2 + H_2O \rightleftharpoons Al(OH)_2(CH_3COO) + CH_3COOH$$

Let us consider the hydrolysis of the cation and the hydrolysis of the anion separately for the given case. These processes are expressed by the net ionic equations

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$$
$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

We see that in the hydrolysis of the cation the H^+ ion is formed, and in the hydrolysis of the anion—the OH^- ion. These ions cannot exist in considerable concentrations; they combine to form molecules of water. The result is the shifting of both equilibria to the right. In other words, the hydrolysis of the cation and the hydrolysis of the anion in this case amplify each other.

The reaction of solutions of salts formed by a weak acid and a weak base depends on the ratio between the dissociation constants of the salt-forming acid and base. If the dissociation constant of the acid is greater than that of the base, the solution is weakly acidic, and if it is smaller, the solution is weakly basic.

If the salt-forming acid and base are not only weak electrolytes, but are also poorly soluble, or unstable and decompose to form volatile products, hydrolysis of the relevant salt often proceeds irreversibly, i.e. is attended by complete decomposition of the salt. For instance, when an aluminium salt, say $AlCl_3$, reacts with sodium carbonate, aluminium hydroxide precipitates, and carbon dioxide evolves:

$$2AlCl_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3\downarrow + 3CO_2\uparrow + 6NaCl$$

or

$$2Al^{3+} + 3CO_3^{2-} + 3H_2O = 2Al(OH)_3\downarrow + 3CO_2\uparrow$$

Acid salts of weak acids also hydrolyze. Here, however, hydrolysis is attended by dissociation of the acid salt anion. For example, in a sodium hydrogen carbonate solution, hydrolysis of the ion HCO_3^- leading to the accumulation of OH^- ions:

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

is attended by dissociation of the HCO_3^- ion, as a result of which the H^+ ion is formed:

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

Thus, an acid salt solution may be either basic (if hydrolysis of the anion predominates over its dissociation), or acidic (in the opposite case). This is determined by the ratio between the hydrolysis constant of the salt and the relevant dissociation constant of the acid. In the example considered above, the hydrolysis constant of the anion exceeds the corresponding dissociation constant of the acid, therefore the solution is weakly basic. When the ratio is opposite (for instance, in the hydrolysis of $NaHSO_3$), the solution is acidic.

The proton theory of acids and bases treats hydrolysis as a particular case of acid-base equilibrium: a proton passes from a water molecule to a given ion or from the given ion to a water molecule. For instance, the hydrolysis of an ammonium ion can be expressed by the equation

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

9

OXIDATION-REDUCTION REACTIONS. FUNDAMENTALS OF ELECTROCHEMISTRY

93. Oxidation of Elements

When an element is in the free state—forms an elementary substance—the motion of the electrons about all the atoms of this substance occurs identically. This holds for all elementary substances regardless of their structure. For example, in a hydrogen molecule, the electrons travel about both atoms to an equal extent—the molecule H_2 is non-polar. For crystals with a covalent bond, the chemical bonds between the atoms are also symmetrical relative to the joined atoms. For metals, the distribution of both the bound and the free electrons is also uniform on an average.

Matters are different in compound substances. The chemical bonds between the atoms of different elements are not symmetrical; polar bonds are generally the rule in molecules of compounds. This non-uniformity in the distribution of the electrons is the greatest in ionic compounds—in the formation of substances with an ionic bond, the valence electrons pass virtually completely from an atom of one element to an atom of another one.

An element whose electrons pass to atoms of another element (completely with an ionic bond or partly with a polar one) is said to be **positively oxidized.** An element to whose atoms electrons from atoms of another element pass is **negatively oxidized** (or **reduced**).

The number of electrons that have passed from one atom of a given positively oxidized element or to one atom of a given negatively oxidized or reduced element is called the **oxidation number** (or **oxidation state**) of the element.

In elementary substances, the oxidation number of an element is always zero. In compounds, some elements always display the same oxidation number, but for most elements it differs in different compounds.

The elements having a constant oxidation number are the alkali metals (+1), the alkaline-earth metals (+2), and fluorine (—1). Hydrogen in most compounds is characterized by an oxidation number of +1, while in metal hydrides (Vol. 2, Sec. 2) and in some other compounds it is —1. The oxidation number of oxygen, as a rule, is —2. The most important exceptions here are the peroxide compounds, where it is —1, and oxygen difluoride OF_2, in which the oxidation number of oxygen is +2. For elements with a changing oxidation number, its value is always simple to find knowing the formula of a given compound and taking into consideration that the sum of the oxidation numbers of all the atoms in a molecule is zero.

Let us determine as an example the oxidation number of carbon in CO, CO_2, CH_4, C_2H_6, and C_2H_5OH. We shall denote it by x. Hence, remembering that the oxidation number of hydrogen is +1 and that of oxygen —2, we get

CO	$x+(-2)=0$	$x=+2$
CO_2	$x+2(-2)=0$	$x=+4$
CH_4	$x+4(+1)=0$	$x=-4$
C_2H_6	$2x+6(+1)=0$	$x=-3$
C_2H_5OH	$2x+6(+1)+(-2)=0$	$x=-2$

To find the oxidation number of elements in compounds, the table of electronegativities of elements (Table 6) can be used. It must be borne in mind here that when a chemical bond forms, the electrons are displaced to the atom of the element with the higher electronegativity. For instance, the relative electronegativity of phosphorus is 2.2, and that of iodine 2.6. Consequently, in the compound PI_3, the shared electrons are displaced to the iodine atoms, and the oxidation numbers of phosphorus and iodine are +3 and —1, respectively. In NI_3, however, the oxidation numbers of nitrogen and iodine are —3 and +1 because the electronegativity of nitrogen (3.07) is higher than that of iodine.

94. Oxidation-Reduction Reactions

All chemical reactions can be divided into two groups. In those of the first group, the oxidation state of all the elements in the reactants remains constant, while in those of the second group, the oxidation state of one or several elements changes.

We can exemplify the reactions of the first group by the neutralization reaction

$$HCl + NaOH = NaCl + H_2O$$

An example of a reaction of the second group is the reaction of a metal with an acid:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

If in the neutralization reaction no element changes its oxidation number, in the second example the oxidation number of the zinc changes from 0 to +2, and of the hydrogen from +1 to 0.

Reactions as a result of which the oxidation numbers of elements change are called oxidation-reduction (redox) reactions.

Oxidation-reduction reactions are of very great importance in biological systems. Photosynthesis, breathing, digestion—all these are chains of oxidation-reduction reactions. In engineering, the significance of redox reactions is also very great. For example, the entire metallurgical industry is based on oxidation-reduction processes during which metals are recovered from natural compounds.

A simple example of an oxidation-reduction reaction is the reaction of formation of an ionic compound from elementary substances, for example, the reaction of sodium with chlorine:

$$2Na + Cl_2 = 2NaCl$$

This reaction, like any heterogeneous one, proceeds in several steps. In one of them, the sodium atoms transform into positively charged ions; the oxidation number of sodium changes from 0 to +1:

$$Na = Na^+ + e^-$$

Such a process—*the losing of electrons attended by an increase in the oxidation number of an element—is called* ***oxidation.***

The electrons lost by the sodium are gained by the chlorine atoms, which transform into negatively charged ions; the oxidation number of the chlorine changes from 0 to —1:

$$Cl_2 + 2e^- = 2Cl^-$$

The gaining of electrons attended by a decrease in the oxidation number of an element is called ***reduction.***

Hence, in the reaction considered above, the sodium is oxidized, and the chlorine is reduced.

A substance containing an element that is oxidized is called a ***reducing agent****, and a substance containing an element that is reduced is called an* ***oxidizing agent****.* Consequently, in the above example, sodium is a reducing agent, and chlorine an oxidizing one.

Inspection of the oxidation-reduction equations shows that one molecule of chlorine when reduced gains two electrons, while the oxidation of one sodium atom is attended by the loss of one electron. The total number of electrons in a system in chemical reactions does not change: *the number of electrons lost by the molecules (atoms, ions) of the reducing agent equals the number of electrons gained by the molecules (atoms, ions) of the oxidizing agent.* Therefore, one molecule of chlorine can oxidize two sodium atoms.

95. Compiling Equations of Oxidation-Reduction Reactions

In Sec. 94, we considered a very simple example of a redox reaction — the formation of a compound from two elementary substances. Usually, the equations of redox reactions are more complicated, and it is often a quite difficult task to balance them. We shall consider a few examples.

Example 1. The reaction between hydrogen iodide and concentrated sulphuric acid. This reaction proceeds as follows:

$$HI + H_2SO_4 \rightarrow I_2 + H_2S + H_2O$$

If we calculate the oxidation number of each element in the reactants and in the products, we shall see that it changes both in the iodine and in the sulphur. In the iodine of HI it is —1, and in free iodine it is 0. The oxidation number of sulphur, on the other hand, changes from +6 (in H_2SO_4) to —2 (in H_2S). Hence, the oxidation number of the iodine increases, and of the sulphur decreases. Consequently, the iodine is oxidized, and the sulphur is reduced.

The equation of the iodine oxidation has a simple form:

$$2I^- = I_2 + 2e^- \text{ (oxidation)}$$

The equation of sulphur reduction is more complicated because both the reactant (H_2SO_4 or SO_4^{2-}) and the product (H_2S) contain other elements in addition to sulphur. In compiling this equation, we shall proceed from the fact that the reaction takes place in an acid aqueous solution, and the ion SO_4^{2-} transforms into the molecule H_2S:

$$SO_4^{2-} \rightarrow H_2S$$

The four oxygen atoms liberated in this process should combine with hydrogen into four molecules of water. Eight hydrogen ions are needed for this. In addition, two hydrogen ions are needed to form a molecule of H_2S. Hence, ten hydrogen ions should react with the SO_4^{2-} ion:

$$SO_4^{2-} + 10H^+ \rightarrow H_2S + 4H_2O$$

The total charge on the ions in the left-hand side of this formula is eight elementary positive charges, while the right-hand side contains only uncharged particles. Since the total charge does not change in the course of the process, eight electrons also participate in the reduction process:

$$SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O \text{ (reduction)}$$

In the above example, the ratio of the number of electrons participating in the reduction process to that liberated in oxidation is 4:1. To obtain the overall equation of the reaction, we have to take this ratio into account when summating the equations of the reduction and oxidation processes, i.e. multiply the reduction equation by four. It is customary practice to indicate the required multipliers to the right of a vertical line when writing the equations:

$$\begin{array}{rl|l} & 2I^- = I_2 + 2e^- & 4 \\ + & SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O & 1 \\ \hline & SO_4^{2-} + 8I^- + 10H^+ = 4I_2 + H_2S + 4H_2O & \end{array}$$

The reaction equation obtained can also be written in the molecular form:

$$H_2SO_4 + 8HI = 4I_2 + H_2S + 4H_2O$$

Example 2. Reaction of aluminium with potassium nitrate in a basic solution. The skeleton equation is:

$$KNO_3 + Al + KOH + H_2O \rightarrow NH_3 + KAlO_2$$

Here the oxidation number changes in the nitrogen and aluminium. Metallic aluminium (its oxidation number is zero) transforms into the ion AlO_2^- in which the oxidation number of the aluminium is +3. To compile the oxidation equation, we shall proceed from the scheme:

$$Al \rightarrow AlO_2^-$$

In a basic solution, the OH^- ion is the source of the oxygen needed for this process to occur. Four hydroxide ions are required to combine one aluminium atom into the AlO_2^- ion:

$$Al + 4OH^- \rightarrow AlO_2^- + 2H_2O$$

The left-hand side of the formula contains four negative charges, and the right-hand side only one. Hence, in the course of the process, three electrons are given up:

$$Al + 4OH^- = AlO_2^- + 2H_2O + 3e^- \text{ (oxidation)}$$

To obtain the reduction equation, we shall proceed from the scheme:

$$NO_3^- \rightarrow NH_3$$

Here in the course of the process, the nitrogen atoms lose oxygen atoms and combine with hydrogen atoms. In a basic solution, this is possible with the participation of water molecules. Three water molecules are needed to combine with three oxygen atoms, and three more water molecules to form a molecule of NH_3:

$$NO_3^- + 6H_2O \rightarrow NH_3 + 9OH^-$$

The total charge of the right-hand side of the formula is nine negative charges, and of the left-hand side—one. Consequently, eight electrons participate in the process:

$$NO_3^- + 6H_2O + 8e^- = NH_3 + 9OH^- \text{ (reduction)}$$

The ratio between the number of electrons liberated in oxidation and the number of electrons gained in reduction is 3:8 in the given example. Hence, to obtain the overall equation of the reaction, we must summate the equations of the oxidation and reduction processes, multiplying the first of them by 8 and the second by 3:

$$
\begin{array}{rl|l}
+ & Al + 4OH^- = AlO_2^- + 2H_2O + 3e^- & 8 \\
 & NO_3^- + 6H_2O + 8e^- = NH_3 + 9OH^- & 3 \\
\hline
 & 8Al + 3NO_3^- + 5OH^- + 2H_2O = 8AlO_2^- + 3NH_3 &
\end{array}
$$

or in the molecular form:

$$8Al + 3KNO_3 + 5KOH + 2H_2O = 8KAlO_2 + 3NH_3$$

Example 3. Catalytic oxidation of ammonia. This reaction is used in the production of nitric acid (see Vol. 2, Sec. 29). It is conducted at a temperature of about 750 °C. The skeleton equation is

$$NH_3 + O_2 \rightarrow NO + H_2O$$

The condensation of water vapour (steam) at 750 °C is impossible. We shall therefore not write the equations of the oxidation and reduction processes as we did for reactions proceeding in an aqueous solution—with the participation of water molecules, hydrogen or hydroxide ions. We shall only count the number of electrons participating in the oxidation and reduction. We shall take into account that the increase in the oxidation number of an element equals the number of lost electrons, and the decrease equals the number of gained electrons.

According to the skeleton equation, the oxidation number changes both in the nitrogen and in the oxygen. In the former, it grows from —3 to +2, and in the latter, it diminishes from 0 to —2. Let us write these changes as formulas, indicating the oxidation numbers of the relevant elements as superscripts. To avoid confusion with the charge of an ion, we shall use Roman numerals for this purpose

$$N^{-III} \rightarrow N^{+II} + 5e^- \text{ (oxidation)}$$

$$O_2^0 + 4e^- \rightarrow 2O^{-II} \text{ (reduction)}$$

The ratio of the number of electrons gained in reduction to the number of electrons lost in oxidation is 4:5. Hence, five molecules of oxygen can oxidize four molecules of ammonia:

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

The reaction equations in the above three examples were compiled in a definite sequence. It can also be adhered to in other cases when compiling the equations of redox reactions. The sequence of operations is as follows:

1. Draw up a skeleton equation indicating the reactants and products.

2. Determine the oxidation numbers of the elements in the substances of the right-hand and left-hand sides of the equation; indicate the elements whose oxidation number changes.
3. Draw up the reduction and oxidation equations; find the ratio of the number of electrons gained in reduction to that lost in oxidation.
4. Summate the oxidation and reduction equations with account taken of the ratio of the number of electrons found in paragraph 3.

96. Most Important Oxidizing and Reducing Agents

What substances can display the properties of oxidizing agents, and what—of reducing agents? We have already mentioned that an oxidizing agent contains an element whose oxidation number decreases, while a reducing agent contains an element whose oxidation number grows in the course of a reaction. Consequently, oxidizing agents will include first of all compounds with the higher, and reducing agents will include compounds with the lower oxidation numbers featuring a given element.

Metals display only a positive oxidation state in their compounds, and their minimum oxidation number is zero. In other words, they have the minimum oxidation number only in the free state. Indeed, all free metals, although to a different extent, are capable of exhibiting only reducing properties. The reducing agents used in practice include aluminium, magnesium, sodium, potassium, and zinc. If a metal can have several oxidation numbers, those of its compounds in which it displays the lowest of them are also reducing agents, as a rule. Examples are the compounds of iron(II), tin(II), chromium(II), and copper(I).

Those compounds of metals can be oxidizing agents in which the oxidation number is high and either equals the number of the group which the metal belongs to or is close to it. Practical use has been found, in particular, by an ammonia solution of silver oxide, an ammonia solution of copper(II) sulphate, mercury(II) chloride, lead dioxide PbO_2, iron(III) chloride, potassium chromate and dichromate (K_2CrO_4 and $K_2Cr_2O_7$), potassium permanganate $KMnO_4$, and manganese dioxide MnO_2.

Non-metals exhibit both positive and negative oxidation states. It is natural that compounds containing non-metals in their higher positive oxidation states can be oxidizing agents, and compounds in which a non-metal displays a negative oxidation state can be reducing agents.

The most important reducing agents are hydrogen, carbon, and carbon monoxide.

Non-metals of the upper part of groups VI and VII of the periodic table are strong oxidizing agents. The strong oxidizing properties of these substances are explained by the high electronegativity of their atoms. Fluorine has the strongest oxidizing properties, but in practice oxygen, chlorine, and bromine are used most frequently as oxidizing agents.

The compounds used as oxidizing agents also include acids. Hydrochloric, sulphuric, and nitric acids have the greatest practical significance. The oxidizing element in hydrochloric acid is hydrogen, in nitric acid it is nitrogen, in dilute sulphuric acid—hydrogen, and in the concentrated acid—sulphur. Hence, the equation of reduction with hydrochloric and dilute sulphuric acids has the form:

$$2H^+ + 2e^- = H_2$$

Nitric acid, depending on its concentration, temperature, and the nature of the reducing agent, can be reduced to different oxidation numbers of the oxygen (see Vol. 2, Sec. 28). One of the usual products of its reduction is nitrogen monoxide NO:

$$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$$

Various products may also be formed in reduction with concentrated sulphuric acid (see Vol. 2, Sec. 16).

One of them is sulphur dioxide:

$$SO_4^{2-} + 4H^+ + 2e^- = SO_2 + 2H_2O$$

Other compounds of non-metals used as oxidizing agents are hydrogen peroxide, the salts of acids in which the acid-forming element exhibits a high oxidation number—chlorates ($KClO_3$), perchlorates ($KClO_4$).

97. Oxidation-Reduction Duality. Intramolecular Oxidation-Reduction

Compounds with the maximum oxidation number of a given element can only play the role of oxidizing agents in redox reactions. The oxidation number can only lower in this case. Conversely, compounds with the minimum oxidation number can only be reducing agents. Here the oxidation number of an element can only grow. If an element is in an intermediate oxidation state, however, its atoms can, depending on the conditions prevailing, either take on or give up electrons. In the first case, the oxidation number of the element will lower, and in the second one it will grow. Consequently, compounds containing elements in intermediate oxidation states have **oxidation-reduction duality**—they are capable of entering into reactions with either oxidizing or reducing agents.

For example, nitrogen forms compounds in which its oxidation number changes from —3 (ammonia and ammonium salts) to +5 (nitric acid and its salts). The nitrogen in ammonia can only be a reducing agent, and that in nitric acid—only an oxidizing agent. Nitrous acid HNO_2 and its salts, in which the oxidation number of nitrogen is +3, however, enter into reactions with both strong oxidizing and strong reducing agents. In the first case, it is oxidized to nitric acid, and in the second, it is usually reduced to nitrogen monoxide NO. We can exemplify the oxidation-reduction duality of nitrous acid by the reactions:

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + 2MnSO_4 + K_2SO_3 + 3H_2O$$

$$2HNO_2 + H_2S = 2NO + S + 2H_2O$$

In addition to nitrous acid, sulphur, iodine, hydrogen peroxide, and a number of other substances have oxidation-reduction duality.

Substances containing an element in an intermediate oxidation state often have another characteristic property. It consists in that in definite conditions such a substance experiences a process in the course of which one part of the element is oxidized and the other part is reduced. This process is known as **autoxidation-autoreduction.** For instance, when chlorine reacts with water, a mixture of hydrochloric and hypochlorous (HOCl) acids is produced:

$$Cl_2 + H_2O = HCl + HOCl$$

Here the chlorine undergoes both oxidation and reduction:

$$Cl_2 + 2H_2O = 2HOCl + 2H^+ + 2e^- \text{ (oxidation)}$$

$$Cl_2 + 2e^- = 2Cl^- \text{ (reduction)}$$

Autoxidation-autoreduction is also called **disproportionation.**

Some compounds in definite conditions (usually when heated) experience **intramolecular oxidation-reduction.** In this process, one constituent part of the substance is an oxidizing agent, and the other is a reducing agent. Examples of intramolecular oxidation-reduction are many processes of thermal dissociation. For instance, when water vapour dissociates:

$$2H_2O = 2H_2 + O_2$$

the oxygen is oxidized (its oxidation number grows from —2 to 0), and the hydrogen is reduced (its oxidation number diminishes from +1 to 0).

Another example is the decomposition of ammonium nitrite employed in the laboratory to obtain pure nitrogen:

$$NH_4NO_2 = N_2 + 2H_2O$$

Here the ion NH_4^+ is oxidized and the ion NO_2^- is reduced to free nitrogen.

98. Chemical Sources of Electrical Energy

We know that in any redox reaction, electrons pass from the reducing agent to the oxidizing one. For example, when a zinc plate is lowered into a copper sulphate solution, the following reaction occurs:

$$Zn + Cu^{2+} = Cu + Zn^{2+}$$

Here the reducing agent—zinc—loses electrons. This half-reaction is

$$Zn = Zn^{2+} + 2e^-$$

The oxidizing agent—the copper ion—gains electrons. The equation of this half-reaction is

$$Cu^{2+} = 2e^- = Cu$$

In the above example, both half-reactions occur at the place of contact of the zinc with the solution so that the electrons pass directly from the zinc atoms to the copper ions. We can conduct this reaction in such a way, however, that the oxidation and reduction half-reactions will be separated in space, and the electrons will pass from the reducing agent to the oxidizing one not directly, but via a conductor of an electric current—through an external circuit. This directed flow of electrons is an electric current. When a redox reaction is conducted in such a way, its energy will be converted into electrical energy that can be used by connecting a consumer of electrical energy (for example, an electrical heating appliance or an electrical lamp) to the external circuit.

Devices used for the direct conversion of the energy of a chemical reaction into electrical energy are called **galvanic** (or **voltaic**) **cells.** They are also known as **chemical sources of electrical energy** or chemical sources of current.

It is customary practice in engineering to apply the name galvanic cell only to a chemical source of current in which virtually irreversible reactions proceed. Such current sources cannot usually be recharged: they are intended for use only once (in one or more stages). Chemical sources of current in which virtually reversible reactions occur are called **accumulators**: they can be recharged and used repeatedly.

The functioning of any galvanic cell is based on the proceeding of a redox reaction in it. The simplest galvanic cell consists of two plates or rods made from different metals and immersed in a solution of an electrolyte. This system makes possible the separation of the redox reaction in space: oxidation occurs on one metal, and reduction on the other. Thus, the electrons are transferred from the reducing agent to the oxidizing one via the external circuit.

Let us consider as an example a copper-zinc galvanic cell operating at the expense of the energy of the reaction between zinc and copper sulphate described above (Fig. 82). This cell (a Jacobi-Daniell cell) consists of a copper plate immersed in a solution of copper sulphate solution (a copper electrode) and a zinc plate immersed in a zinc sulphate solution (a zinc electrode). The two solutions are in contact with each other, but to prevent mixing, they are separated by a partition made from a porous material.

In operation of the cell, i.e. when the circuit is closed, the zinc becomes oxidized: on the surface of its contact with the solution, the zinc atoms transform into ions and after becoming hydrated pass into the solution. The liberated electrons travel through the external circuit to the copper electrode. The entire collection of these processes is depicted schematically by a half-reaction equation, or an **electrochemical equation:**

$$Zn = Zn^{2+} + 2e^-$$

At the copper electrode, reduction of the copper ions takes place. The electrons arriving here from the zinc electrode combine with the copper ions becoming dehydrated and leaving the solution; copper atoms are produced that separate in the form of metal. The corresponding electrochemical equation has the form

$$Cu^{2+} + 2e^- = Cu$$

The net equation of the reaction proceeding in the cell is obtained when the equations of the two half-reactions are summated. Thus, in the operation of a galvanic cell, the electrons from the reducing agent pass to the oxidizing agent through the external circuit, electrochemical processes occur at the electrodes, and the directed motion of the ions is observed in the solution.

The direction of motion of the ions in the solution is due to the electrochemical processes occurring at the electrodes. We have already indicated that at the zinc electrode the cations emerge into the solution, creating an excess positive charge in it, while at the copper electrode the solution, conversely, constantly becomes leaner in cations so that here the solution is charged negatively. The result is the setting up of an electric field in which the cations in the solution (Cu^{2+} and Zn^{2+}) move from the zinc electrode to the copper one, while the anions—SO_4^{2-}—move in the opposite direction. As a

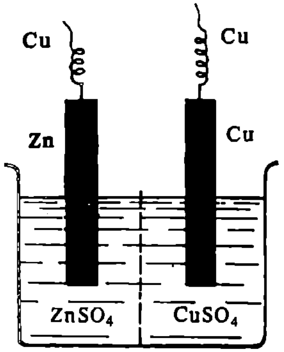

Fig. 82. Copper-zinc galvanic cell

result, the liquid at both electrodes remains electrically neutral. The motion of the electrons and ions in the operation of a copper zinc cell is shown schematically in Fig. 83.

The electrode at which oxidation occurs is called the **anode.** The one at which reduction occurs is called the **cathode.** In the copper-zinc cell, the zinc electrode is the anode, and the copper one—the cathode.

The redox reaction proceeding in a galvanic cell is a complicated process. It includes the electrochemical steps proper (the transformations of atoms, ions, or molecules at the electrodes), the transfer of electrons, and the transfer of ions. All these steps are interlinked and proceed at the same rate. The number of electrons given up by the zinc in unit time equals the number of electrons received during this time by the copper ions. Hence, the rate of a reaction proceeding in a galvanic cell is proportional to the quantity of electricity transferred through the circuit in unit time, i.e. to the current in the circuit.

The electric current flowing in the external circuit of a galvanic cell can do useful work. But the work that can be done at the expense of the energy of a chemical reaction depends on its rate— it is the greatest when the reaction is conducted infinitely slowly, reversibly (see Sec. 67). Consequently, the work that can be done at the expense of the reaction proceeding in a galvanic cell depends on the magnitude of the current taken from it. If we lower the current in the external circuit to an infinitely small value by increasing the resistance of the circuit, the rate of the reaction in the cell will also be infinitely small, and the work will be maximum. The heat evolved in the internal circuit of the cell, on the contrary, will be minimum.

The work of an electric current is expressed by the product of the quantity of electricity *q* flowing through the circuit and the voltage *V*.

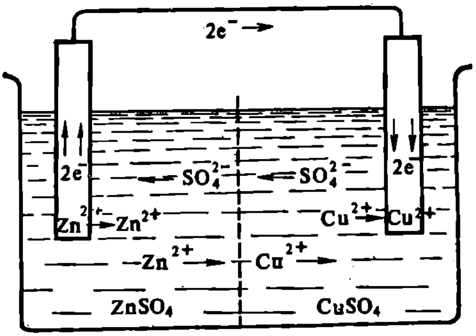

Fig. 83. Motion of ions and electrons in the operation of a copper-zinc galvanic cell

In a copper-zinc cell, when one equivalent of zinc is oxidized and simultaneously one equivalent of copper ions is reduced, a quantity of electricity equal to one faraday (1 F $= eN_A =$ 96 485 coulombs*) where e is the elementary electric charge and N_A is the Avogadro constant) will pass through the circuit. Hence, the useful work W' which a current can do will be

$$W' = FV$$

where F = Faraday's constant, numerically equal to one faraday
V = voltage between the poles of the cell.

But since this work depends on the current, the voltage between the poles of the cell also depends on the current (F is a constant). In the limiting case corresponding to the reversible proceeding of the reaction, the voltage will be maximum. The maximum value of the voltage of a galvanic cell corresponding to the reversible proceeding of the reaction is called the **electromotive force** (e.m.f.) of the given cell.

For this limiting case, the useful work done by the current in a copper-zinc cell when one equivalent of zinc reacts with one equivalent of copper ions is expressed by the equation

$$W'_{\max} = FV_{\max} = FE$$

where $E \equiv V_{\max}$ is the e.m.f. of the cell.

It is clear that when one mole of zinc atoms reacts with one mole of copper ions, the equation becomes

$$W_{\max} = 2W'_{\max} = 2FE$$

In the general case upon the dissolving (or separation) of one mole of a substance whose ions have a charge of z, the maximum useful work is related to the e.m.f. by the equation

$$W_{\max} = zFE$$

At a constant temperature and pressure, the maximum useful work of a reaction equals the change in the Gibbs energy ΔG taken with the reverse sign (see Sec. 67). Hence:

$$\Delta G = -zFE$$

If the concentrations (more exactly, the activities) of the substances participating in a reaction equal unity, i.e. if standard conditions are observed, the e.m.f. of a cell is called its **standard electromotive force** and is designated by the symbol E°. The last equation now becomes:

$$\Delta G^\circ = -zFE^\circ$$

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* In calculations, we shall use the value of this quantity approximated to three significant digits (96 500 C/mol).

With a view to the standard change in the Gibbs energy of a reaction being associated with its equilibrium constant (see Sec. 68) by the expression

$$\Delta G^\circ = -RT \ln K$$

we get an equation relating the standard e.m.f. to the equilibrium constant of a reaction proceeding in a galvanic cell:

$$RT \ln K = zFE^\circ$$

E.m.f.'s can be measured with a high accuracy. These measurements are one of the most accurate ways of finding the standard Gibbs energies and, consequently, the equilibrium constants for oxidation-reduction reactions in solutions.

Redox reactions proceed in a galvanic cell notwithstanding the fact that the oxidizing and reducing agents are not in direct contact with each other. To gain an understanding of how this occurs, of how an e.m.f. appears when the processes of oxidation and reduction are separated in space, let us consider in greater detail the phenomena occurring at the phase interfaces in a galvanic cell.

Direct experiments with the use of radioactive indicators show that if we bring a metal (M) into contact with a solution of its salt, then the metal ions (M^{z+}) pass from the metal phase into the solution and from the solution into the metal. Since the energy state of the ions in these phases is not the same, then at the first moment after contact has been established, the metal ions pass from the metal into the solution and in the reverse direction at different rates. If transition of the ions from the metal phase into the solution predominates, the solution acquires a positive charge, while the metal electrode is charged negatively. As these charges increase, the transition of the cations into the solution having a like charge is hindered so that the rate of this process diminishes. On the other hand, the rate of transition of the cations from the solution onto the negatively charged electrode grows. As a result, the rates of the two processes level out, and equilibrium sets in between the metal and the solution:

$$M^{z+}\ (\text{metal}) \rightleftharpoons M^{z+}\ (\text{solution})$$

The metal electrode is charged negatively, and the solution positively. If, when contact is established between a metal and a solution, the rate of transition of the cations from the metal into the solution was lower than the rate of their transition in the reverse direction, equilibrium also sets in between the electrode and the solution. Here, however, the electrode is charged positively, and the solution negatively.

In the Jacobi-Daniell cell, the corresponding equilibria set in between the zinc electrode and the zinc sulphate solution:

$$Zn^{2+}\ (\text{metal}) \rightleftharpoons Zn^{2+}\ (\text{solution of } ZnSO_4)$$

and also between the copper electrode and the copper sulphate solution:

$$\mathrm{Cu^{2+}\ (metal) \rightleftarrows Cu^{2+}\ (solution\ of\ CuSO_4)}$$

This cell has two other phase interfaces: between the solutions of zinc and copper sulphates, and also between the copper and the zinc (see Fig. 82). The interface between the solutions does not appreciably affect either the magnitude of the e.m.f. or the proceeding of the reaction when the cell is operating. As regards the interface between the metals, electrons can pass through it instead of ions as at a metal-solution interface*. Here too, owing to the different energy state of the electrons in the copper and in the zinc, the initial rates of electron transition from one metal into the other and in the reverse direction are different. In this case, equilibrium also sets in rapidly, however, and the metals also acquire charges of the opposite sign:

$$e^-\ \mathrm{(copper)} \rightleftarrows e^-\ \mathrm{(zinc)}$$

Consequently, when the circuit is open, equilibria set in on the three phase interfaces in the Jacobi-Daniell cell, the phases becoming charged. As a result, the energy state of the electrons at the ends of the open circuit becomes different: on the copper conductor in contact with the zinc electrode the Gibbs energy of the electrons is higher, and on the end connected to the copper electrode it is lower. It is exactly the difference between the Gibbs energies of the electrons at the ends of the circuit that determines the e.m.f. of a given cell.

When the external circuit is closed, the electrons move from the zinc electrode to the copper one. Therefore, equilibria at the phase interfaces are violated. A directed transition of the zinc ions takes place from the metal into the solution, of the copper ions—from the solution into the metal, and of the electrons—from the zinc to the copper. A redox reaction occurs.

In principle, any redox reaction can yield electrical energy. The number of reactions practically used in chemical sources of electrical energy, however, is not great. This is associated with the circumstance that not any redox reaction makes it possible to create a galvanic cell having technically valuable properties (a high and virtually constant e.m.f., the possibility of obtaining high currents, a long lifetime, etc.). In addition, many redox reactions require the use of costly substances.

Unlike the copper-zinc cell, all modern galvanic cells and accumulators use not two, but one electrolyte. Such current sources are considerably more convenient in operation. For example, in lead ac-

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* The diffusion of atoms and ions from a metal into a metal occurs much more slowly and does not virtually affect the establishment of equilibrium at the interface between the metals.

cumulators (see Vol. 2, Sec. 75), a sulphuric acid solution is the electrolyte.

In virtually all the galvanic cells produced at present, the anode is made from zinc, while oxides of less active metals are used as the substance for the cathode.

For a description of the most important galvanic cells see Vol. 2, Sec. 100, and of accumulators see Vol. 2, Secs. 75, 87, and 130.

Chemical sources of electrical energy are used in various branches of engineering. In means of communication (radio, telephone, telegraph) and in electrical measuring apparatus, they are sources of electrical power, on motor vehicles and airplanes they are used for actuating starters and other equipment, on transport and in many other fields they are used in portable lanterns for illumination. With the growing shortage of petroleum products in many countries, greater and greater attention is being given to the development of electric vehicles powered by accumulators.

All conventional chemical current sources are not free of two shortcomings. First, the cost of the substances needed for their operation (for example, lead and cadmium) is high. Second, the ratio of the amount of energy that a cell can give up to its mass is low. The last few decades have seen the conducting of investigations aimed at creating cells whose operation would require the consumption of cheap substances having a low density, similar to liquid or gaseous fuel (natural gas, kerosene, hydrogen, etc.). Such galvanic cells are known as **fuel cells.** Much attention is being given to the fuel cell problem at present, and it can be assumed that in the nearest future fuel cells will find broad application.

99. Electrode Potentials

Every oxidation-reduction reaction consists of oxidation and reduction half-reactions. When a reaction proceeds in a galvanic cell or is conducted by electrolysis, each half-reaction occurs at the corresponding electrode. This is why half-reactions are also called **electrode processes.**

We showed in Sec. 98 that the e.m.f. E of a galvanic cell corresponds to the redox reaction proceeding in this cell. The e.m.f. is related to the change in the Gibbs energy of the reaction ΔG by the equation

$$\Delta G = -zFE$$

In accordance with the division of a redox reaction into two half-reactions, it is customary practice to represent the e.m.f.'s too in the form of the difference between two quantities, each of which corresponds to the given half-reaction. These quantities are known as the **electrode potentials.**

For a copper-zinc cell, the reaction proceeding during its operation:

$$Zn + Cu^{2+} = Zn^{2+} + Cu$$

is divided into two half-reactions:

$$Cu^{2+} + 2e^- = Cu$$

$$Zn = Zn^{2+} + 2e^-$$

Accordingly, the e.m.f. of this element (E) can be represented as the difference between the electrode potentials (φ), one of which (φ_1) corresponds to the first, and the other (φ_2) to the second of the above half-reactions:

$$E = \varphi_1 - \varphi_2$$

The change in the Gibbs energy ΔG_1 that corresponds to the thermodynamically reversible reduction of one mole of copper ions is

$$\Delta G_1 = -2F\varphi_1$$

while the change in the Gibbs energy ΔG_2 corresponding to the thermodynamically reversible oxidation of one mole of zinc atoms is

$$\Delta G_2 = -2F\varphi_2$$

In the general case, the electrode potential φ and a change in the Gibbs energy ΔG equal to

$$\Delta G = -zF\varphi$$

correspond to any electrode process

$$Ox + ze^- = Red$$

where Ox and Red stand for the oxidized and reduced forms, respectively, of the substances participating in the electrode process.

In the following, when dealing with electrode processes, we shall write their equations in the direction of reduction (except, naturally, when we are speaking exactly about oxidation).

Investigation of the potentials of various electrode processes has shown that their magnitudes depend on the following three factors: (1) the nature of the substances participating in the electrode process; (2) the ratio between the concentrations* of these substances, and (3) the temperature of the system. This relationship is expressed by the equation:

$$\varphi = \varphi^\circ + \frac{2.3RT}{zF} \log \frac{[Ox]}{[Red]}$$

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* Strictly speaking, the magnitude of an electrode potential depends on the ratio of the activities (see Sec. 86) and not of the concentrations of substances. In all the following equations, the activity should be substituted for the concentration. But at low concentrations of solutions, the error introduced by substituting the concentration for the activity is not great.

Here φ° is the **standard electrode potential** of a given process—a constant whose physical meaning is considered below; R is the molar gas constant; T is the absolute temperature; z is the number of electrons participating in the process; F is the Faraday constant; [Ox] and [Red] are the products of the concentrations of the substances participating in the process in the oxidized (Ox) and reduced (Red) forms.

The physical meaning of the quantity φ° becomes clear if we consider the case when the concentrations (activities) of all the substances participating in a given electrode process are unity. For this condition, the second addend in the right-hand side of the equation vanishes ($\log 1 = 0$), and the equation becomes

$$\varphi = \varphi^\circ$$

Concentrations (activities) equal to unity are called standard concentrations (activities). Therefore, the potential corresponding to this case is also called the **standard potential.** Thus, *the standard electrode potential is the potential of a given electrode process at concentrations* (more accurately, at activities) *of all the substances participating in it equal to unity.*

Hence, the first addend in the equation of the electrode potential (φ°) takes into account the influence of the nature of the substances on its magnitude, and the second addend $\frac{2.3RT}{zF}\log\frac{[\mathrm{Ox}]}{\mathrm{Red}}$ the influence of their concentrations. In addition, both terms vary with the temperature.

For the customary standard temperature used in electrochemical measurements (25 °C = 298 K), when the values of the constant quantities are introduced [$R = 8.31$ J/(mol·K), $F = 96\,500$ C/mol], the equation becomes

$$\varphi = \varphi^\circ + \frac{2.3 \times 8.31 \times 298}{z \times 96\,500}\log\frac{[\mathrm{Ox}]}{[\mathrm{Red}]} = \varphi^\circ + \frac{0.059}{z}\log\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

To construct a numerical scale of the electrode potentials, it is necessary to assume that the potential of a definite electrode process is zero. The following electrode process has been taken as the standard for constructing such a scale:

$$2\mathrm{H}^+ + 2e^- = \mathrm{H}_2$$

The change in the Gibbs energy associated with the proceeding of this half-reaction in standard conditions is adopted equal to zero. Accordingly, the standard potential of this electrode process is also taken equal to zero. All electrode potentials indicated in this book, and also in the majority of other modern publications, are expressed according to this **hydrogen scale.**

The above electrode process is carried out on a **hydrogen electrode.** The latter is a platinum plate electrolytically coated with spongy platinum and immersed in a solution of an acid through which hydrogen is passed (Fig. 84). The hydrogen dissolves well in the platinum; the hydrogen molecules partly decompose into atoms (the platinum catalyzes this decomposition). Oxidation of the hydrogen atoms or reduction of the hydrogen ions can proceed on the surface of contact of the platinum with the acid solution. The platinum does not virtually participate in the electrode reactions and plays, as it were, the role of a sponge impregnated with atomic hydrogen.

The potential of the hydrogen electrode is reproduced with a very high accuracy. This is exactly why the hydrogen electrode has been taken as the standard in creating a scale of electrode potentials.

Let us establish the form of the general equation of the electrode potential for the hydrogen electrode. For this electrode, $z = 2$, $[\mathrm{Ox}] = [\mathrm{H^+}]^2$, $[\mathrm{Red}] = [\mathrm{H_2}]$. The concentration of the hydrogen dissolved in the platinum is proportional to its partial pressure $p(\mathrm{H_2})$:

$$[\mathrm{H_2}] = kp(\mathrm{H_2})$$

where k is a quantity that is constant at the given temperature. Using the equation of an electrode process (see p. 294) and introducing the constant k into the value of φ°, we get

$$\varphi = \varphi^\circ + 0.059 \log [\mathrm{H^+}] - 0.030 \log p(\mathrm{H_2})$$

The partial pressure of hydrogen $p(\mathrm{H_2})$ is usually kept equal to standard atmospheric pressure, which is conventionally taken as unity. In this case, the last term of the equation obtained vanishes ($\log 1 = 0$). Hence:

$$\varphi = \varphi^\circ + 0.059 \log [\mathrm{H^+}]$$

Since the standard potential of the process being considered is assumed to equal zero, then

$$\varphi = 0.059 \log [\mathrm{H^+}]$$

or since $\log [\mathrm{H^+}] = -\mathrm{pH}$, we finally get

$$\varphi = -0.059\ \mathrm{pH}$$

To find the potential of an electrode process, it is necessary to form a galvanic cell from the electrode being tested and a standard hydrogen electrode and measure its e.m.f. Seeing that the potential of a standard hydrogen electrode is zero, the measured e.m.f. will be the potential of the given electrode process.

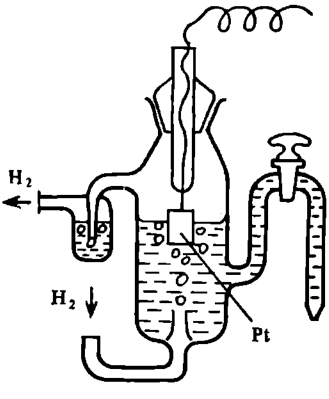

Fig. 84. Hydrogen electrode

A standard hydrogen electrode is not generally used in practice as a reference electrode because this involves considerable complications. More convenient electrodes are employed whose potentials in comparison with the standard hydrogen electrode are known. The e.m.f. of the cell should be calculated by the equation

$$E = |\varphi_{ref} - \varphi_x|$$

Here E is the e.m.f. of the cell, φ_{ref} is the known potential of the reference electrode, and φ_x is the potential of the electrode being tested.

Solving the equation with respect to φ_x, we get:
when $\varphi_{ref} > \varphi_x$

$$\varphi_x = \varphi_{ref} - E$$

when $\varphi_{ref} < \varphi_x$

$$\varphi_x = \varphi_{ref} + E$$

The reference electrodes in greatest favour are the silver-silver chloride and the calomel electrodes. The former is a silver wire coated with a layer of AgCl and immersed in a solution of hydrochloric acid or its salt. The following reaction proceeds in it when the circuit is closed:

$$AgCl + e^- = Ag^+ + Cl^-$$

The calomel electrode consists of mercury coated with a suspension of calomel (Hg_2Cl_2) in a solution of KCl. The potentials of these electrodes are reproduced with a high accuracy. Figure 85 shows a circuit with a calomel electrode.

To find the value of the electrode potential, it is necessary to measure not the voltage of the operating cell, but its e.m.f. When measuring the latter, the resistance of the external circuit (i.e. of the measuring device) is very high. Virtually no reaction proceeds in the cell. Thus, the electrode potentials correspond to the reversible occurring of processes or, which is the same, to the state of electrochemical equilibrium at the electrodes.

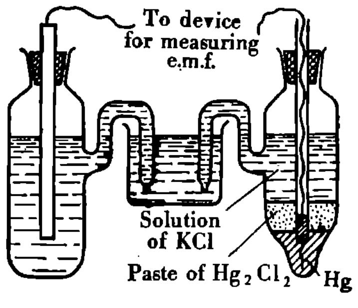

Fig. 85. Circuit for measuring an electrode potential:
at the left is the electrode whose potential is to be measured; at the right is the calomel electrode; at the middle is a connecting vessel

Consequently, electrode potentials are often called **equilibrium electrode potentials** or simply **equilibrium potentials**.

Let us now consider the form which the general equation of the electrode potential will acquire in the most important cases.

1. The electrode process is expressed by the equation

$$M^{z+} + ze = M$$

where M stands for the atoms of a metal, and M^{z+} are its z-charged ions.

This case includes both electrodes of a copper-zinc cell and in general any metal electrode in a solution of a salt of the same metal. Here the metal ions are the oxidized form of the metal, and its atoms are the reduced form. Hence, $[Ox] = [M^{z+}]$, and $[Red] = \text{const}$ because the concentration of the atoms in a metal is a constant quantity at a constant temperature. Including the value of this constant in the quantity φ°, we get:

$$\varphi = \varphi^\circ + \frac{0.059}{z} \log [M^{z+}]$$

For instance, for the process $Ag^+ + e^- = Ag$, we have:

$$\varphi = 0.799 + 0.059 \log [Ag^+]$$

and for the process $Zn^{2+} + 2e^- = Zn$, we get:

$$\varphi = -0.763 + 0.030 \log [Zn^{2+}]$$

2. The electrode process is expressed by the equation:

$$M^{z_2+} + (z_2 - z_1)\, e^- = M^{z_1+}$$

Here both the oxidized (M^{z_2+}) and reduced (M^{z_1+}) forms of the metal are in the solution, and their concentrations are variable quantities. Consequently,

$$\varphi = \varphi^\circ + \frac{0.059}{z_2 - z_1} \log \frac{[M^{z_2+}]}{[M^{z_1+}]}$$

For instance, for the process $Fe^{3+} + e^- = Fe^{2+}$:

$$\varphi = 0.771 + 0.059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

In this and in the cases treated below, the electrode at which the electrode process occurs is made from an inert material. Most often, this material is platinum.

We have considered examples when only ions consisting of one element participated in the electrode processes. Quite often, however, the substance becoming oxidized or reduced consists not of one, but of two or more elements. The oxidizing agent most frequently contains oxygen; here water and the products of its dissociation—hydrogen ions (in an acid solution) or hydroxide ions (in a basic solution) generally participate in the electrode process. Let us see what the equations of the electrode process potentials will be like in such cases.

3. The electrode process is expressed by the equation:

$$O_2 + 4H^+ + 4e^- = 2H_2O$$

This half-reaction (when it proceeds in the direction of reduction) plays a very great part in the corrosion of metals (see Vol. 2, Sec. 82). Oxygen is the most widespread oxidizing agent causing metals to corrode in aqueous solutions.

In the above electrode process, oxygen is reduced with the participation of hydrogen ions to form water. Hence, $[\mathrm{Red}] = [H_2O]^2$, and $[\mathrm{Ox}] = [O_2]\,[H^+]^4$. The concentration of the water in dilute solutions may be considered constant. The concentration of oxygen in a solution is proportional to its partial pressure over the solution $\{[O_2] = kp\,(O_2)\}$. After performing the required transformations and designating the sum of the constant quantities by φ°, we get

$$\varphi = \varphi^{\circ} + 0.059 \log\,[H^+] + \frac{0.059}{4} \log p\,(O_2)$$

For the process being considered, $\varphi^{\circ} = 1.228$ V; hence,

$$\varphi = 1.228 - 0.059\ \mathrm{pH} + 0.015 \log p\,(O_2)$$

At a partial pressure of the oxygen equal to standard atmospheric pressure (which is conventionally taken equal to unity), $\log p\,(O_2) = 0$, and the last equation becomes

$$\varphi = 1.228 - 0.059\ \mathrm{pH}$$

4. For electrode processes represented by more complicated equations, the expressions for the potentials contain a greater number of variable concentrations. Let us consider, for example, the electrode process

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

This half-reaction proceeds (in the direction of reduction) when potassium permanganate reacts with most reducing agents in an acid solution.

The concentrations of all the substances participating in this electrode process (except water) are variable quantities. For this process, $\varphi^{\circ} = 1.507$ V. The equation of the electrode potential has the form

$$\varphi = \varphi^{\circ} + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]} + \frac{8 \times 0.059}{5} \log\,[H^+] =$$

$$= 1.507 + 0.012 \log \frac{[MnO_4^-]}{[Mn^{2+}]} - 0.095\ \mathrm{pH}$$

Examples 3 and 4 show that for electrochemical processes occurring with the participation of water, the hydrogen ion concentration is in the numerator of the logarithmic term of the potential equation. For this reason, the electrode potentials of such processes depend on the pH of the solution and their values grow with an increasing acidity of the solution.

We have already mentioned that the dependence of the electrode potential on the nature of the substances participating in an electrode process is described by the quantity φ°. In this connection, it is customary practice to arrange all electrode processes in a series according to the magnitude of their standard potentials. Table 18 gives the equations of the most important electrode processes and the relevant electrode potentials in the order of increasing values of φ°.

The position of an electrochemical system in this series characterizes its oxidation-reduction ability. By an **electrochemical system** here is meant the collection of all the substances participating in the given electrode process.

The oxidation-reduction ability characterizes an electrochemical system, but the oxidation-reduction ability of a substance (or ion) is also often spoken about. It must be borne in mind, however, that many substances can be oxidized or reduced to different products. For instance, potassium permanganate (the ion MnO_4^-) can, depending on the conditions and first of all on the pH of the solution, be reduced either to the ion Mn^{2+}, or to MnO_2, or to the ion MnO_4^{2-}.

The corresponding electrode processes are expressed by the equations:

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

$$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$$

$$MnO_4^- + e^- = MnO_4^{2-}$$

Since the standard potentials of these three electrode processes are different (see Table 18), the positions of these three systems in the series of φ° are also different. Hence, the same oxidizing agent (MnO_4^-) can occupy several positions in the series of standard potentials.

Elements exhibiting only one oxidation number in their compounds have simple oxidation-reduction characteristics and occupy a small number of positions in the series of standard potentials. They chiefly include the metals of the main subgroups of Groups I-III of the periodic table. On the other hand, many positions in the series of φ° are occupied by the elements that form compounds with different oxidation numbers—non-metals and many metals of the auxiliary subgroups of the periodic table.

The series of standard electrode potentials makes it possible to solve the problem about the direction of spontaneous redox reactions.

Table 18

Electrode Potentials in Aqueous Solutions at 25 °C and at a Partial Pressure of the Gases Equal to Standard Atmospheric Pressure

Electrode process	Equation of electrode potential
$Li^+ + e^- = Li$	$\varphi = -3.045 + 0.059 \log [Li^+]$
$Rb^+ + e^- = Rb$	$\varphi = -2.925 + 0.059 \log [Rb^+]$
$K^+ + e^- = K$	$\varphi = -2.924 + 0.059 \log [K^+]$
$Cs^+ + e^- = Cs$	$\varphi = -2.923 + 0.059 \log [Cs^+]$
$Ca^{2+} + 2e^- = Ca$	$\varphi = -2.866 + 0.030 \log [Ca^{2+}]$
$Na^+ + e^- = Na$	$\varphi = -2.714 + 0.059 \log [Na^+]$
$Mg^{2+} + 2e^- = Mg$	$\varphi = -2.363 + 0.030 \log [Mg^{2+}]$
$H_2 + 2e^- = 2H^-$	$\varphi = -2.251 - 0.059 \log [H^-]$
$Al^{3+} + 3e^- = Al$	$\varphi = -1.663 + 0.020 \log [Al^{3+}]$
$Ti^{2+} + 2e^- = Ti$	$\varphi = -1.630 + 0.030 \log [Ti^{2+}]$
$Mn^{2+} + 2e^- = Mn$	$\varphi = -1.179 + 0.030 \log [Mn^{2+}]$
$Cr^{2+} + 2e^- = Cr$	$\varphi = -0.913 + 0.030 \log [Cr^{2+}]$
$Zn^{2+} + 2e^- = Zn$	$\varphi = -0.763 + 0.030 \log [Zn^{2+}]$
$Cr^{3+} + 3e^- = Cr$	$\varphi = -0.744 + 0.020 \log [Cr^{3+}]$
$[Au(CN)_2]^- + e^- = Au + 2CN^-$	$\varphi = -0.61 + 0.059 \log \frac{[[Au(CN)_2]^-]}{[CN^-]^2}$
$2H^+ + 2e^- = H_2$	$\varphi = -0.059\ pH$
$I_2(c) + 2e = 2I^-$	$\varphi = -0.536 - 0.059 \log [I^-]$
$MnO_4^- + e^- = MnO_4^{2-}$	$\varphi = 0.564 + 0.059 \log \frac{[MnO_4^-]}{[MnO_4^{2-}]}$
$Fe^{3+} + e^- = Fe^{2+}$	$\varphi = 0.771 + 0.059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$
$NO_3^- + 2H^+ + e^- = NO_2 + H_2O$	$\varphi = 0.78 + 0.059 \log [NO_3^-] - 0.118\ pH$
$Hg_2^{2+} + 2e^- = 2Hg$	$\varphi = 0.788 + 0.030 \log [Hg_2^{2+}]$
$Ag^+ + e^- = Ag$	$\varphi = 0.799 + 0.059 \log [Ag^+]$
$Hg^{2+} + 2e^- = Hg$	$\varphi = 0.850 + 0.030 \log [Hg^{2+}]$
$2Hg^{2+} + 2e^- = Hg_2^{2+}$	$\varphi = 0.920 + 0.030 \log \frac{[Hg^{2+}]^2}{[Hg_2^{2+}]}$
$Br_2(lq) + 2e^- = 2Br^-$	$\varphi = 1.065 - 0.059 \log [Br^-]$
$Pt^{2+} + 2e^- = Pt$	$\varphi = 1.188 + 0.030 \log [Pt^{2+}]$
$O_2 + 4H^+ + 4e^- = 2H_2O$	$\varphi = 1.228 - 0.059\ pH$
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	$\varphi = 1.333 + 0.010 \log \frac{[Cr_2O_7^{2-}]}{[Cr^{3+}]^2} - 0.138\ pH$
$Cl_2(g) + 2e^- = 2Cl^-$	$\varphi = 1.359 - 0.059 \log [Cl^-]$
$PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 4H_2O$	$\varphi = 1.449 - 0.030 \log [Pb^{2+}] - 0.118\ pH$
$Au^{3+} + 3e^- = Au$	$\varphi = 1.498 + 0.020 \log [Au^{3+}]$
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	$\varphi = 1.507 + 0.012 \log \frac{[MnO_4^-]}{[Mn^{2+}]} - 0.095\ pH$
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- = PbSO_4 + 2H_2O$	$\varphi = 1.685 + 0.030 \log [SO_4^{2-}] - 0.118\ pH$
$Au^+ + e^- = Au$	$\varphi = 1.692 + 0.059 \log [Au^+]$
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	$\varphi = 1.692 + 0.020 \log [MnO_4^-] - 0.079\ pH$
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	$\varphi = 1.776 + 0.030 \log [H_2O_2] - 0.059\ pH$
$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	$\varphi = 2.010 + 0.030 \log \frac{[S_2O_8^{2-}]}{[SO_4^{2-}]^2}$
$F_2 + 2e^- = 2F^-$	$\varphi = 2.87 - 0.059 \log [F^-]$

As in the general case of any chemical reaction, the determining factor here is the sign of the change in the Gibbs energy of the reaction. If we form a galvanic cell from two electrochemical systems, then in its operation the electrons will pass spontaneously from the negative pole of the cell to the positive one, i.e. from an electrochemical system with a lower value of the electrode potential to a system with a higher value of it. But this signifies that the first system will play the role of a reducing agent, and the second that of an oxidizing agent. Consequently, in a galvanic cell, *an oxidation-reduction reaction can proceed spontaneously in a direction in which the electrochemical system with a higher value of the electrode potential plays the role of an oxidizing agent, i.e. becomes reduced.* Upon the direct reaction of the substances, the possible direction of the reaction will naturally be the same as when it is conducted in a galvanic cell.

If the oxidizing and reducing agents are far from each other in the series of φ°, the direction of the reaction is practically completely determined by their mutual position in the series. For example, zinc ($\varphi^\circ = -0.763$ V) will displace copper ($\varphi^\circ = +0.337$ V) from an aqueous solution of its salt at any practically achievable concentration of the solution. If, on the other hand, the values of φ° for the oxidizing and reducing agents are close to each other, then when solving the problem of the direction in which the reaction will proceed spontaneously, it is also necessary to take account of how the concentrations of the relevant substances affect the electrode potentials. For example, the reaction

$$\mathrm{Hg_2^{2+} + 2Fe^{2+} = 2Hg + 2Fe^{3+}}$$

can proceed spontaneously either from the left to the right or from the right to the left. Its direction is determined by the concentrations of the iron and mercury ions. Two electrochemical systems participate in this reaction:

$$\mathrm{Hg_2^{2+} + 2}e^- \mathrm{= 2Hg} \qquad (1)$$

$$\mathrm{Fe^{3+} +} e^- \mathrm{= Fe^{2+}} \qquad (2)$$

The following potentials correspond to the relevant electrode processes:

$$\varphi_1 = 0.788 + 0.030 \log [\mathrm{Hg_2^{2+}}]$$

$$\varphi_2 = 0.771 + 0.059 \log \frac{[\mathrm{Fe^{3+}}]}{[\mathrm{Fe^{2+}}]}$$

Let us calculate the values of φ_1 and φ_2 at $[\mathrm{Hg_2^{2+}}] = [\mathrm{Fe^{2+}}] = 10^{-1}$ and $[\mathrm{Fe^{3+}}] = 10^{-4}$ mol/1000 g of H_2O:

$$\varphi_1 = 0.788 + 0.030 \log 10^{-1} = 0.788 - 0.030 \approx 0.76 \text{ V}$$

$$\varphi_2 = 0.771 + 0.059 \log \frac{10^{-4}}{10^{-1}} = 0.771 - 3 \times 0.059 \approx 0.59 \text{ V}$$

Thus, with the ratio of the concentrations we have taken, $\varphi_1 > \varphi_2$, and the reaction proceeds from left to right.

Now let us calculate φ_1 and φ_2 for the reverse ratio of the concentrations. Assume that $[Hg_2^{2+}] = [Fe^{2+}] = 10^{-4}$, and $[Fe^{3+}] =$ $= 10^{-1}$ mol/1000 g of H_2O:

$$\varphi_1 = 0.788 + 0.030 \log 10^{-4} = 0.788 - 4 \times 0.030 \approx 0.67 \text{ V}$$

$$\varphi_2 = 0.771 + 0.059 \log \frac{10^{-1}}{10^{-4}} = 0.771 + 3 \times 0.059 \approx 0.95 \text{ V}$$

Consequently, at these concentrations, $\varphi_1 > \varphi_2$, and the reaction proceeds from right to left.

If a redox reaction proceeds with the participation of water and hydrogen or hydroxide ions, then the pH of the solution must also be taken into consideration.

Table 18 includes 38 half-reactions. Combining them with one another, we can solve the problem of the directions of the spontaneous proceeding of $(38 \times 37)/2 = 703$ reactions.

Example. Establish the direction in which the following reaction can proceed:

$$2KBr + PbO_2 + 4HNO_3 = Pb(NO_3)_2 + Br_2 + 2KNO_3 + 2H_2O$$

We shall write the equation of the reaction in the net ionic form.

$$2Br^- + PbO_2 + 4H^+ = Pb^{2+} + Br_2 + 2H_2O$$

In Table 18, we find the standard electrode potentials for the electrochemical systems participating in the reaction:

$$Br_2 + 2e^- = 2Br^- \quad \varphi_1^\circ = 1.065 \text{ V}$$

$$PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 4H_2O \quad \varphi_2^\circ = 1.449 \text{ V}$$

The oxidizing agent is always the electrochemical system with a higher value of the electrode potential. Since here φ_2° is considerably greater than φ_1°, then at virtually any concentrations of the reacting substances the bromide ion will be the reducing agent and will be oxidized by the lead dioxide: the reaction will proceed spontaneously from left to right.

The farther a system is in the series of standard potentials, i.e. the higher its standard potential, the stronger an oxidizing agent is its oxidized form. And, conversely, the earlier a system appears in the series, i.e. the smaller the value of φ°, the stronger a reducing agent is its reduced form. Indeed, among the oxidized forms of systems at the bottom of the series, we find such strong oxidizing agents as F_2, H_2O_2, and MnO_4^-. The strongest reducing agents, on the other hand, are the reduced forms of the systems at the top of the series: the alkali and alkaline-earth metals.

When redox reactions proceed, the concentrations of the reactants diminish, and of the products grow. The result is a change in the magnitudes of the potentials of both half-reactions: the electrode potential of the oxidizing agent drops, and that of the reducing agent grows. When the potentials of both processes become equal to each other, the reaction terminates—a state of chemical equilibrium sets in.

100. Electromotive Series of Metals

If from the entire series of standard electrode potentials we separate only the electrode processes that correspond to the general equation

$$M^{z+} + ze^- = M$$

we get an **electromotive** (or **activity**) **series of metals.** In addition to metals, hydrogen is included in this series, which permits us to see what metals are capable of displacing hydrogen from aqueous solutions of acids. The electromotive series for the most important metals is given in Table 19. The position of a metal in the series characterizes its ability to participate in oxidation-reduction reactions in aqueous solutions in standard conditions. Ions of the metals are oxidizing agents, and the metals in the form of elementary substances are reducing agents. The farther a metal is in the electromotive series, the stronger an oxidizing agent in an aqueous solution are

Table 19

Electromotive Series of Metals

Equation of electrode process	Standard potential φ° at 25 °C, V	Equation of electrode process	Standard potential φ° at 25 °C, V
$Li^+ + e^- = Li$	—3.045	$Co^{2+} + 2e^- = Co$	—0.277
$Rb^+ + e^- = Rb$	—2.925	$Ni^{2+} + 2e^- = Ni$	—0.250
$K^+ + e^- = K$	—2.924	$Sn^{2+} + 2e^- = Sn$	—0.136
$Cs^+ + e^- = Cs$	—2.923	$Pb^{2+} + 2e^- = Pb$	—0.126
$Ca^{2+} + 2e^- = Ca$	—2.866	$Fe^{3+} + 3e^- = Fe$	—0.037
$Na^+ + e^- = Na$	—2.714	$2H^+ + 2e^- = H_2$	0
$Mg^{2+} + 2e^- = Mg$	—2.363	$Bi^{3+} + 3e^- = Bi$	0.215
$Al^{3+} + 3e^- = Al$	—1.663	$Cu^{2+} + 2e^- = Cu$	0.337
$Ti^{2+} + 2e^- = Ti$	—1.630	$Cu^+ + e^- = Cu$	0.520
$Mn^{2+} + 2e^- = Mn$	—1.179	$Hg_2^{2+} + 2e^- = 2Hg$	0.788
$Cr^{2+} + 2e^- = Cr$	—0.913	$Ag^+ + e^- = Ag$	0.799
$Zn^{2+} + 2e^- = Zn$	—0.763	$Hg^{2+} + 2e^- = Hg$	0.850
$Cr^{3+} + 3e^- = Cr$	—0.744	$Pt^{2+} + 2e^- = Pt$	1.188
$Fe^{2+} + 2e^- = Fe$	—0.440	$Au^{3+} + 3e^- = Au$	1.498
$Cd^{2+} + 2e^- = Cd$	—0.403	$Au^+ + e^- = Au$	1.692

its ions. Conversely, the nearer a metal is to the top of the series, the stronger are the reducing properties exhibited by the elementary substance—metal.

The potential of the electrode process

$$2H^+ + 2e^- = H_2$$

in a neutral medium ($pH = 7$) is $-0.059 \times 7 = -0.41$ V (see p. 295). The active metals at the top of the series having a potential that is considerably more negative than -0.41 V displace hydrogen from water. Magnesium displaces hydrogen only from hot water. The metals between magnesium and cadmium do not usually displace hydrogen from water. The surfaces of these metals become covered with oxide films having a protective action*.

The metals between magnesium and hydrogen displace hydrogen from solutions of acids. The surfaces of some metals also become covered with protective films that inhibit the reaction. For example, the oxide film on aluminium makes this metal stable not only in water, but also in solutions of some acids. Lead does not dissolve in sulphuric acid when its concentration is below 80% because the salt $PbSO_4$ formed when lead reacts with sulphuric acid is insoluble and produces a protective film on the surface of the metal. The phenomenon of the deep inhibition of the oxidation of a metal due to the presence of protective oxide or salt films on its surface is called **passivation**, and the state of the metal is called the passive state.

Metals are capable of displacing one another from solutions of salts. The direction of the reaction is determined by their relative position in the electromotive series. When considering specific cases of such reactions, one must remember that active metals displace hydrogen not only from water, but also from any aqueous solution. Consequently, the mutual displacement of metals from solutions of their salts occurs in practice only with metals below magnesium in the series.

The displacement of metals from their compounds by other metals was first studied in detail by N. Beketov**. As a result of his investi-

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* The potentials of metals in water naturally differ from their potentials in standard conditions, in the majority of cases they have a more negative value. But, as a rule, this does not affect the correctness of our conclusions on the ability of metals to displace hydrogen from water.

** **Nikolai Nikolaevich Beketov** (1826-1911) was an eminent Russian scientist—a physicochemist. Beketov's outstanding work is his *Investigations of Phenomena of the Displacement of Elements by Other Elements* published in 1865. He discovered the ability of aluminium to displace metals from their oxides at an elevated temperature. This discovery later formed the cornerstone of aluminothermics (see Vol. 2, Sec. 78) that found broad application in metallurgy. Beketov carried out numerous thermochemical measurements. He was the first (since 1865) to introduce the teaching of physical chemistry as a separate subject.

gations, he arranged the metals in a "displacement series" according to their chemical activity. This series was the prototype of the electromotive series of metals.

The relative position of some metals in the electromotive series and in the periodic table, at first sight, is not the same. For example, according to its position in the periodic table, the chemical activity of potassium should be greater than that of sodium, and of sodium greater than that of lithium. In the electromotive series, however, lithium is the most active, while potassium occupies a position between lithium and sodium. Zinc and copper as regards their position in the periodic table should have an approximately identical chemical activity, but in the electromotive series, zinc is considerably ahead of copper. The reason for such discrepancies is as follows.

In comparing metals occupying definite positions in the periodic table, the magnitude of the ionization energy of free atoms is taken as a measure of their chemical activity—their reducing power. Indeed, as we pass, for example, down the main subgroup of group I of the periodic table, the ionization energy of atoms diminishes, which is associated with an increase in their radii (i.e., with a greater distance to the outer electrons from the nucleus) and with an increasing screening of the positive charge of the nucleus by intermediate electron layers (see Sec. 31). Consequently, potassium atoms display a greater chemical activity—have stronger reducing properties—than sodium atoms, and sodium atoms display a greater activity than lithium atoms.

When comparing metals in the electromotive series, the measure of their chemical activity is the work of transforming a metal in the solid state into hydrated ions in an aqueous solution. This work can be represented as the sum of three addends: the energy of **atomization**—the transformation of a metal crystal into isolated atoms, the energy of **ionization** of the free atoms of the metal, and the energy of **hydration** of the ions formed. The atomization energy characterizes the strength of the crystal lattice of a given metal. The ionization energy of atoms—the energy needed to detach valence electrons from them—is directly determined by the position of the metal in the periodic table. The energy evolved in hydration depends on the electronic structure of an ion, its charge and radius. Ions of lithium and potassium, having an identical charge, but different radii, will set up different electric fields around themselves. The field set up near small lithium ions will be stronger than that near big potassium ions. It is thus clear that lithium ions will become hydrated with the liberation of more energy than potassium ions.

Thus, in the course of the transformation being considered, energy is spent for atomization and ionization, and energy is evolved in hydration. When the summary expenditure of energy is smaller, the entire process will occur more readily, and the given metal will be closer to the top of the electromotive series. But of the three components of the overall energy balance, only one—the ionization energy—is directly determined by the position of the metal in the periodic table. Consequently, there are no grounds to expect that the relative position of metals in the electromotive series will always correspond to their position in the periodic table. For instance, the total expenditure of energy for lithium is lower than for potassium, and accordingly lithium is ahead of potassium in the electromotive series.

For copper and zinc, the outlay of energy for the ionization of free atoms and its gain in the hydration of ions are close. But metallic copper forms a stronger crystalline lattice than zinc, which can be seen by comparing the melting points of these metals: zinc melts at 419.5 °C, while copper melts only at 1083 °C. Consequently, the energy spent for the atomization of these metals is appreciably different. As a result, the overall expenditure of energy for the entire process is much greater for copper than for zinc, and this explains the relative positions of these metals in the electromotive series.

When passing over from water to non-aqueous solvents, the relative position of metals in the electromotive series may change. The reason is that the solvation energy of ions of different metals changes differently from solvent to solvent.

Particularly, copper ions solvate very energetically in certain organic solvents. The result is that for such solvents copper is ahead of hydrogen in the electromotive series and displaces it from solutions of acids in these solvents.

Hence, unlike the periodic table of elements, the electromotive series of metals does not reflect a general law on the basis of which it would be possible to give a diverse characteristic of the chemical properties of metals. The electromotive series characterizes only the oxidation-reduction ability of the electrochemical system "metal-metal ion" in strictly definite conditions: the values given in it relate to an aqueous solution, a temperature of 25 °C, and a concentration (activity) of the metal ions equal to unity.

101. Electrolysis

By **electrolysis** is meant the collection of processes occurring when a direct current passes through an electrochemical system consisting of two electrodes and a melt or solution of an electrolyte.

An example of electrolysis is the electrolysis of molten magnesium chloride. When a current passes through molten $MgCl_2$, the magnesium cations under the action of the electric field travel towards the negative electrode. Here they react with the electrons arriving via the external circuit and are reduced:

$$Mg^{2+} + 2e^- = Mg$$

The chloride anions travel to the positive electrode and, giving up their excess electrons, are oxidized. The primary process is the electrochemical step proper—the oxidation of the chloride ions:

$$2Cl^- = 2Cl + 2e^-$$

and the secondary process is the combination of the chlorine atoms formed into molecules:

$$2Cl = Cl_2$$

Summating the equations of the processes occurring at the electrodes, we get the overall equation of the redox reaction proceeding in the electrolysis of molten $MgCl_2$:

$$Mg^{2+} + 2Cl^- = Mg + Cl_2$$

This reaction cannot proceed spontaneously; the energy needed for it is received from an external source of current.

As in a chemical source of electrical energy, the electrode at which reduction occurs is called the cathode, and the one at which oxidation occurs is called the anode. But in electrolysis, the cathode is charged negatively, and the anode positively, i.e. the distribution of the signs of the electrode charges is opposite to what is observed in the operation of a galvanic cell. The reason is that the processes occurring in electrolysis are in principle the reverse ones of those occurring in the operation of a galvanic cell. *In electrolysis, a chemical reaction takes place at the expense of the energy of an electric current supplied from outside, whereas in the operation of a galvanic cell, the energy of the chemical reaction proceeding spontaneously in it transforms into electrical energy.*

When dealing with the electrolysis of aqueous solutions, we must never forget that in addition to the electrolyte ions, every aqueous solution contains ions that are the products of dissociation of water, namely, H^+ and OH^-. In the electric field, the hydrogen ions migrate to the cathode, and the OH^- ions to the anode. Thus, both electrolyte and hydrogen cations may become discharged at the cathode. Similarly, both electrolyte anions and hydroxide ions may become discharged at the anode. In addition, water molecules may also undergo electrochemical oxidation or reduction.

The electrochemical processes that occur at the electrodes in electrolysis depend first of all on the relative values of the electrode potentials of the relevant electrochemical systems. Of several possible processes, the one associated with the minimum expenditure of energy will be carried out. This signifies that oxidized forms of electrochemical systems having the highest electrode potential will be reduced at the cathode, and reduced forms of systems having the lowest electrode potential will be oxidized at the anode. The material of the electrode has an inhibiting action on the proceeding of some electrochemical processes. Such cases will be given special mention below.

In considering **cathode processes** occurring in the electrolysis of aqueous solutions, we shall limit ourselves to the most important case—cathode reduction leading to separation of the elements in the free state. Here account must be taken of the magnitude of the potential in the process of hydrogen ion reduction. This potential depends on the concentration of the hydrogen ions (see p. 295) and for neutral solutions (pH = 7) it is $\varphi = -0.059 \times 7 = -0.41$ V. Therefore, if the cation of an electrolyte is a metal whose electrode potential is considerably more positive than -0.41 V, the metal will separate from a neutral solution of such an electrolyte at the cathode. In the electromotive series, such metals are near hydrogen (beginning approximately with tin) and after it. Conversely, if a metal having a potential considerably more negative than -0.41 V is the cation of an electrolyte, the metal will not be reduced, but hydrogen will be liberated. Such metals include the ones at the top of the electromotive series, approximately up to titanium. Finally, if the potential of a metal is close to the value -0.41 V (metals in the middle part of the series—Zn, Cr, Fe, Cd, Ni), then depending on the concentration of the solution and the conditions of electrolysis* both reduction of the metal and the liberation of hydrogen are possible. Often the joint deposition of the metal and liberation of hydrogen are observed.

The electrochemical liberation of hydrogen from acid solutions occurs owing to the discharge of the hydrogen ions. For neutral or alkaline media, it is the result of the electrochemical reduction of water:

$$2H_2O + 2e^- = H_2 + 2OH^-$$

Thus, the nature of the cathode process in the electrolysis of aqueous solutions is determined first of all by the position of the relevant metal in the electromotive series. In a number of cases, the pH of the solution, the concentration of the metal ions, and other conditions of electrolysis are of great importance.

In considering **anode processes**, we must remember that the material of the anode may become oxidized in the course of electrolysis. In this connection, electrolysis with an inert anode and electrolysis with an active anode are distinguished. An anode is called **inert** if its material does not become oxidized in electrolysis. An anode is called **active** if its material may become oxidized in the course of electrolysis. Most frequently, graphite, carbon, and platinum are used as the materials for inert anodes.

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* The most important conditions of electrolysis include the current density, the temperature, and the composition of the solution. The current density is defined as the ratio of the current to the working surface area of an electrode.

The electrochemical oxidation of water with the liberation of oxygen occurs **at an inert anode** in the electrolysis of aqueous solutions of alkalies, oxyacids and their salts, and also hydrogen fluoride and fluorides. Depending on the pH of the solution, this process goes on differently and can be expressed by different equations. For an alkaline medium, the equation is

$$4OH^- = O_2 + 2H_2O + 4e^-$$

and for an acid or a neutral one, it is

$$2H_2O = O_2 + 4H^+ + 4e^-$$

In the above cases, the electrochemical oxidation of water is the most advantageous process from the energy viewpoint. Oxygen-containing anions are either not capable of becoming oxidized, or their oxidation occurs at very high potentials. For instance, the standard potential of oxidation of the ion SO_4^{2-}

$$2SO_4^{2-} = S_2O_8^{2-} + 2e^-$$

is 2.010 V, which considerably exceeds the standard potential of oxidation of water (1.228 V). The standard potential of oxidation of the ion F^- has a still higher value (2.87 V).

In the electrolysis of aqueous solutions of acids not containing oxygen and their salts (except for HF and fluorides), the anions are discharged at the anode. Particularly, in the electrolysis of solutions of HI, HBr, HCl and their salts, the corresponding halogen is liberated at the anode. We must note that the liberation of chlorine in the electrolysis of HCl and its salts contradicts the mutual position of the systems

$$Cl_2 + 2e^- = 2Cl^- \qquad (\varphi^\circ = 1.359\ V)$$

and

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (\varphi^\circ = 1.228\ V)$$

in the series of standard electrode potentials. This anomaly is connected with the considerable overvoltage (see Sec. 104) of the second of these two electrode processes—the material of the anode has an inhibiting action on the process of oxygen liberation.

With an **active anode**, the number of competing oxidizing processes grows to three: the electrochemical oxidation of water with the liberation of oxygen, discharge of the anion (i.e. its oxidation), and electrochemical oxidation of the anode metal (the **anode dissolving** of the metal). Of these possible processes, the one will occur that is more profitable from the energy viewpoint. If the metal of the anode is above the other two electrochemical systems in the series of standard potentials, then anode dissolving of the metal will be observed. Otherwise, oxygen will be liberated or the anion will be discharged.

Let us consider some typical cases of electrolysis of aqueous solutions.

The Electrolysis of a $CuCl_2$ Solution with an Inert Anode. Copper is below hydrogen in the electromotive series. Consequently, the discharge of the Cu^{2+} ions and the deposition of metallic copper will occur at the cathode. The chloride ions will discharge at the anode.

The scheme of electrolysis* of a solution of copper(II) chloride is as follows:

$$\mathrm{CuCl_2}$$
$$\text{Cathode} \leftarrow \mathrm{Cu^{2+}} \qquad\qquad 2\mathrm{Cl^-} \rightarrow \text{Anode}$$
$$2\mathrm{Cl^-} = 2\mathrm{Cl} + 2e^-$$
$$\mathrm{Cu^{2+}} + 2e^- = \boxed{\mathrm{Cu}} \qquad\qquad 2\mathrm{Cl} = \boxed{\mathrm{Cl_2}}$$

Electrolysis of a K_2SO_4 Solution with an Inert Anode. Since potassium is much higher than hydrogen in the electromotive series, the liberation of hydrogen and the accumulation of OH^- ions will occur at the cathode. The liberation of oxygen and the accumulation of H^+ ions will occur at the anode. At the same time, K^+ ions will arrive at the cathode space, and SO_4^{2-} ions at the anode space. Thus, the solution will remain electrically neutral in all its parts. An alkali will accumulate in the cathode space, however, and an acid in the anode space.

The scheme of electrolysis of a potassium sulphate solution is:

$$2\mathrm{K_2SO_4}$$
$$\text{Cathode} \leftarrow 4\mathrm{K^+} \qquad\qquad 2\mathrm{SO_4^{2-}} \rightarrow \text{Anode}$$
$$4\mathrm{H_2O} + 4e^- = \boxed{\begin{matrix}4\mathrm{K^+}\\ 4\mathrm{OH^-}\end{matrix}} + 4\mathrm{H} \qquad\qquad 2\mathrm{H_2O} = \boxed{\begin{matrix}2\mathrm{SO_4^{2-}}\\ 4\mathrm{H^+}\end{matrix}} + 2\mathrm{O} + 4e^-$$
$$4\mathrm{H} = \boxed{2\mathrm{H_2}} \qquad\qquad 2\mathrm{O} = \boxed{\mathrm{O_2}}$$

Electrolysis of an $NiSO_4$ Solution with a Nickel Anode. The standard potential of nickel (—0.250 V) is somewhat higher than —0.41 V. Hence, in the electrolysis of a neutral solution of $NiSO_4$, discharge of the Ni^{2+} ions and deposition of the metal will mainly occur at the cathode. The opposite process—oxidation of the metal—occurs at the anode because the potential of nickel is much lower than the potential of oxidation of water and, moreover, than the potential of oxidation of the SO_4^{2-} ion. Hence, in the given case, electrolysis consists in dissolving of the anode metal and its deposition at the cathode.

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* In this and the following schemes, the boxes contain the formulas of the substances that are the products of electrolysis.

The scheme of electrolysis of a nickel sulphate solution is

$$\begin{array}{ccc} & NiSO_4 & \\ \text{Cathode} \leftarrow Ni^{2+} & & SO_4^{2-} \rightarrow \text{Anode} \\ Ni^{2+} + 2e^- = \boxed{Ni} & & Ni = \boxed{\begin{array}{c} SO_4^{2-} \\ Ni^{2+} \end{array}} + 2e^- \end{array}$$

This process is used for the electrical purification of nickel (electrolytic refining, see Sec. 103).

102. Laws of Electrolysis

Electrolysis was first studied quantitatively in the thirties of the 19th century by the outstanding British scientist M. Faraday* who established the following laws of electrolysis:

1. *The mass of a substance formed in electrolysis is proportional to the amount of electricity that has passed through the solution.*

This law follows from the essence of electrolysis. We have already mentioned that an electrochemical process—the reaction of the ions or molecules of the electrolyte with the metal electrons—occurs at the place of contact of the metal with the solution, so that the electrolytic formation of a substance is a result of this process. It is quite obvious that the amount of a substance obtained at an electrode will always be proportional to the number of electrons passing through the circuit, i.e. to the amount of electricity.

2. *In the electrolysis of different chemical compounds, equal amounts of electricity result in the electrochemical transformation of equivalent amounts of substances.*

Assume, for example, that an electric current consecutively passes through solutions of hydrochloric acid, silver nitrate, copper(II) chloride, and tin(IV) chloride (Fig. 86). After a certain time, the

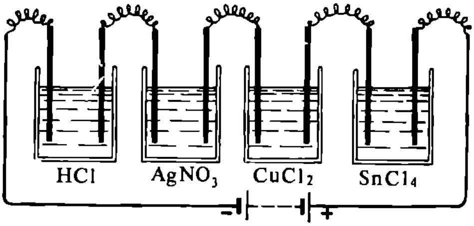

Fig. 86. Arrangement illustrating Faraday's law

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* **Michael Faraday** (1791-1867) was one of the most eminent British physicists and chemists. The major part of his works relate to the field of electricity. He established the laws of electrolysis, and discovered the phenomenon of electromagnetic induction. He was the first to obtain a number of gases (chlorine, ammonia, etc.) in the liquid state. He discovered benzene and isobutylene.

amounts of the electrolysis products are determined. It is found that in the time during which one gram of hydrogen, i.e. one mole of atoms is liberated from a solution of hydrochloric acid, the masses of the metals indicated below will be deposited from the other solutions:

	Electrolyte		
	$AgNO_3$	$CuCl_2$	$SnCl_4$
Mass of metal deposited at cathode, g	107.9	31.8	29.7
Atomic mass of metal	107.87	63.55	118.69

Comparing the deposited masses of the metals with their atomic masses, we find that one mole of silver atoms, one-half mole of copper atoms, and one-fourth mole of tin atoms are deposited. In other words, the amounts of substances formed at the cathode equal their equivalents. The same result is obtained by measuring the amounts of the substances liberated at the anode. Thus, in each of the first, third and fourth cells, 35.5 g of chlorine are liberated, and in the second cell 8 g of oxygen. It is not difficult to see that here too the substances are liberated in amounts equal to their equivalents.

In considering the second law of electrolysis from the viewpoint of the electron theory, it is not difficult to understand why substances are liberated in chemically equivalent amounts in electrolysis. Let us take as an example the electrolysis of copper(II) chloride. When copper is deposited from the solution, each of its ions receives two electrons from the cathode, and at the same time two chloride ions give up electrons to the anode, transforming into chlorine atoms. Consequently, the number of deposited copper atoms will always be half the number of liberated chlorine atoms, i.e. the ratio of the masses of the copper and chlorine will equal the ratio of their equivalent masses.

Measurements have established that the amount of electricity causing the electrochemical transformation of one equivalent of a substance is 96 485 (approximately 96 500) coulombs. This amount of electricity is called the **faraday** or **Faraday's constant** and is designated by the symbol F.

The second law of electrolysis gives a direct way of determining the equivalents of various elements. Calculations associated with electrochemical production processes are based on the same law.

The laws of electrolysis relate to the electrolysis of solutions, melts, and solid electrolytes with purely ionic conductivity.

103. Electrolysis in Industry

Electrolysis finds a very important application in the metallurgical and chemical industries and in electrodeposition.

In the metallurgical industry, electrolysis of molten compounds and aqueous solutions is used to produce metals, and also for electrolytic refining—the purification of metals from harmful impurities and the extraction of valuable components.

The **electrolysis of melts** is used to produce metals having strongly negative electrode potentials, and some of their alloys.

At a high temperature, the electrolyte and the electrolysis products may enter into a reaction with one another, with air, and also with the materials of the electrodes and the electrolyzer. As a result, this scheme of electrolysis, which is simple in principle (for instance, the electrolysis of $MgCl_2$ in the production of magnesium) becomes more intricate.

Usually, not individual molten compounds, but their mixtures are used as the electrolyte. A very important advantage of mixtures is their relatively low melting point allowing electrolysis at a lower temperature.

At present, electrolysis of melts is used to produce aluminium, magnesium, sodium, lithium, beryllium, and calcium. It is virtually not used to produce potassium, barium, rubidium, and cesium owing to the high chemical activity of these metals and their high solubility in the molten salts. In recent years, the electrolysis of molten media has been acquiring some significance for the production of certain refractory metals.

The electrolytic separation of a metal from a solution is called **electrical extraction**. The ore or concentrate (concentrated ore—see Vol. 2, Sec. 78) is treated with definite reagents to transfer the metal into a solution. After purification, the solution is subjected to electrolysis. The metal is deposited at the cathode and in the majority of cases is highly pure. This method is used mainly to produce zinc, copper, and cadmium.

Metals are subjected to **electrolytic refining** for removing impurities from them and for transferring the components contained in them into products convenient to process. The metal to be purified is cast into plates, and they are placed as anodes in an electrolyzer. The passage of a current through the circuit causes the anode metal to dissolve—it passes into solution in the form of cations. The metal cations then become discharged at the cathode and form a compact deposit of pure metal. The impurities in the anode either remain undissolved, settling in the form of **anode mud**, or pass into the electrolyte, whence they are periodically or continuously withdrawn.

Let us consider as an example the electrolytic refining of copper. The main component of the solution is copper sulphate—the most widespread and cheapest salt of this metal. But a solution of $CuSO_4$ has a low electrical conductivity. To increase it, sulphuric acid is added to the electrolyte. Small amounts of additions facilitating the production of a compact deposit of the metal are also introduced into the solution.

The metallic impurities contained in unrefined ("blister") copper can be divided into two groups:

(1) Fe, Zn, Ni, Co. These metals have considerably more negative electrode potentials than copper. Therefore, they are dissolved from the anode together with the copper, but are not deposited at the cathode. They accumulate in the electrolyte, and in this connection the latter is periodically purified.

(2) Au, Ag, Pb, Sn. The noble metals (Au, Ag) do not undergo anode dissolving, and in the course of the process settle near the anode, forming together with other impurities an anode mud that is periodically extracted. Tin and lead, on the other hand, dissolve together with the copper, but form poorly soluble compounds in the electrolyte that precipitate and are also removed.

Copper, nickel, lead, tin, silver, and gold are subjected to electrolytic refining.

Electrodeposition includes electroplating and galvanoplastics. **Electroplating** processes involve the application of other metals on the surface of metal articles by electrolysis to protect the articles from corrosion, to impart hardness to their surfaces, and also for decorative purposes. Among the numerous electroplating processes used in engineering, the most important are chromium plating, zinc plating (galvanization), and nickel plating.

The essence of electroplating is as follows. The well cleaned and degreased component to be protected is immersed in a solution containing a salt of the metal which it is to be coated with, and is connected as the cathode to a direct-current circuit. When a current flows through the circuit, a coat of the protecting metal is deposited onto the component. The best protection is provided by finely crystalline dense deposits. Such deposits also have better mechanical properties.

Galvanoplastics (or **galvanoplasty**) is the name given to processes of obtaining accurate metal copies of relief (embossed) objects by the electrodeposition of metal. Galvanoplastics is used to produce moulds and dies for pressing various articles (phonograph records, buttons, etc.), matrices for stamping leather and paper, printed radio engineering circuits, and stereotype plates. Galvanoplastics was discovered by the Russian academician B. Jacobi (1801-1874) in the thirties of the 19th century.

There are also other kinds of electrochemical treatment of metal surfaces such as the electrical polishing of steel and the oxidation of aluminium and magnesium. The latter consists in anode treatment of the metal in the course of which the structure of the oxide film on its surface is changed in a definite way. The result is improvement of the corrosion resistance of the metal. In addition, the metal acquires an attractive appearance.

In the chemical industry, electrolysis is used to prepare various products. Among them are fluorine, chlorine, sodium hydroxide, highly pure hydrogen, and many oxidizing agents, in particular hydrogen peroxide.

104. Electrochemical Polarization. Overvoltage

When an electrode is at a potential equal to the equilibrium one, electrochemical equilibrium sets in on it:

$$\mathrm{Ox} + ze^- \rightleftharpoons \mathrm{Red}$$

When the potential of the electrode is displaced in the positive or negative direction, oxidation or reduction processes begin to proceed on it. The deviation of the potential of an electrode from its equilibrium value is called **electrochemical polarization** or simply **polarization**.

An electrode can be polarized by connecting it to a direct-current circuit. For this purpose, an electrolytic cell must be formed from an electrolyte and two electrodes—the one being studied and an auxiliary one. By connecting it to a direct-current circuit, we can make the electrode being studied the cathode or (with reverse connection of the cell) the anode. This method of polarization is called polarization from an external source of electrical energy.

Let us consider a simple example of polarization. Assume that a copper electrode is in a 0.1 *m* solution of $CuSO_4$ containing no impurities and no dissolved oxygen. As long as the circuit is not closed, the electrode potential at 25 °C will have an equilibrium value equal to

$$\varphi = 0.337 + 0.030 \log 10^{-1} \approx 0.31 \text{ V}$$

and electrochemical equilibrium will set in at the metal-solution interface:

$$\mathrm{Cu}^{2+} + 2e^- \rightleftharpoons \mathrm{Cu}$$

Let us connect the electrode to the negative pole of the current source—we shall make it the cathode. The surplus of electrons that now appears at the electrode will shift the potential of the electrode in the negative direction and simultaneously violate equilibrium. The electrons will attract copper cations from the solution—a reduction process will occur:

$$\mathrm{Cu}^{2+} + 2e^- = \mathrm{Cu}$$

If we connect the electrode to the positive pole of the current source instead of to the negative one, i.e. make it the anode, then owing to the withdrawal of part of the electrons, the potential of the electrode will shift in the positive direction and equilibrium will also be violated. But now an oxidation process will occur on the electrode because in the course of this process electrons are liberated:

$$\mathrm{Cu = Cu^{2+} + 2}e^-$$

Hence, polarization of the electrode in the negative direction is associated with the going on of a reduction process, and polarization in the positive direction with the going on of an oxidation process. The reduction process is also known as a **cathode process**, and that of oxidation as an **anode process.** In this connection, polarization in the negative direction is called **cathode polarization**, and in the positive one—**anode polarization**.

Another way of polarizing an electrode is to contact it with an electrochemical system whose electrode potential has a more positive or more negative value than that of the electrode being considered.

Let us consider the functioning of a copper-zinc galvanic cell. When the circuit is open, electrochemical equilibria set in on both the copper and zinc electrodes. But the electrode potentials corresponding to these equilibria are different. For 0.1 *m* solutions, they are

$$\varphi\,(\mathrm{Cu/Cu^{2+}}) = 0.337 + 0.030 \log 10^{-1} \approx 0.31\ \mathrm{V}$$

$$\varphi\,(\mathrm{Zn/Zn^{2+}}) = -0.763 + 0.030 \log 10^{-1} \approx -0.79\ \mathrm{V}$$

When the circuit is closed, both electrodes have a polarizing action on each other: the potential of the copper electrode under the influence of the contact with the zinc is displaced in the negative direction, and the potential of the zinc electrode under the influence of the contact with the copper is displaced in the positive direction. In other words, the copper electrode experiences cathode polarization, and the zinc one—anode polarization. The electrochemical equilibria at both electrodes are violated simultaneously, and electrochemical processes begin: a cathode process at the copper electrode and an anode one at the zinc electrode:

$$\mathrm{Cu^{2+} + 2}e^- = \mathrm{Cu}$$

$$\mathrm{Zn = Zn^{2+} + 2}e^-$$

Polarization of an electrode is an essential condition for an electrode process to occur. In addition, its magnitude affects the rate of an electrode process: an increase in the polarization of an electrode is attended by a higher rate of the relevant half-reaction at it.

In addition to the magnitude of the polarization, the rate of electrode processes is affected by other factors. Let us consider the cathode reduction of hydrogen ions. If the cathode is made from platinum, a definite magnitude of cathode polarization is needed to liberate hydrogen at a given rate. When the platinum electrode is replaced with a silver one (other conditions remaining unchanged), greater polarization is needed to produce hydrogen at the previous rate. When the cathode is replaced with a lead one, still greater polarization is needed. Hence, different metals have different catalytic activities with respect to the process of reducing hydrogen ions. The magnitude of the polarization needed for a given electrode process to go on at a definite rate is called the **overvoltage** of the given electrode process. Consequently, the overvoltage of hydrogen liberation on different metals is different.

Table 20 gives, for 1 N solutions, the values of the cathode polarization that must be achieved at an electrode to liberate hydrogen at it at a rate of 0.1 ml a minute from 1 cm^2 of working surface of the electrode.

Table 20

Overvoltage of Hydrogen Liberation on Selected Metals

Electrode metal	Electrolyte	Overvoltage of hydrogen liberation, V	Electrode metal	Electrolyte	Overvoltage of hydrogen liberation, V
Iron	HCl	0.5	Zinc	H_2SO_4	1.0
Copper	H_2SO_4	0.6	Mercury	H_2SO_4	1.2
Silver	HCl	0.7	Lead	H_2SO_4	1.3

The establishment of the relationship between the magnitude of polarization and the rate of an electrode process is a very important method of studying electrochemical processes. The results of measurements are usually represented in the form of **polarization curves**—curves showing how the current density on an electrode depends on the magnitude of polarization. The form of the polarization curve of an electrode process reflects the features of its proceeding. The method of polarization curves is used to study the kinetics and mechanism of oxidation-reduction reactions, the operation of galvanic cells, the phenomena of corrosion and passivation in metals, and various cases of electrolysis.

A great contribution to the development of the kinetics of electrode processes and the theory of overvoltage was made by the Soviet scientist A. Frumkin*.

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* **Aleksandr Naumovich Frumkin** (1895-1976) was an outstanding Soviet electrochemist, an academician, Lenin and State Prize winner. He worked out a quantitative theory of the influence of an electric field on the adsorption of molecules, developed the concept of the structure of a metal-solution interface, and made a considerable contribution to the theory of the e.m.f. of a galvanic cell.

10

DISPERSED SYSTEMS. COLLOIDS

105. The Dispersed State of a Substance. Dispersed Systems

The crystals of any substance, for example sugar or sodium chloride, can be obtained in different sizes—large and small. No matter what the size of crystals is, they all have the same internal structure for a given substance—a molecular or ionic crystal lattice.

When crystals of sugar and sodium chloride are dissolved in water, molecular and ionic solutions are formed, respectively. Thus, the same substance can be in different degrees of comminution: macroscopically visible particles (over 0.2 to 0.1 mm, the resolving power of the human eye), microscopically visible particles (from 0.2-0.1 mm to 400-300 nm*, the resolving power of a microscope when white light is used for illumination), and in the molecular (or ionic) state.

The concept was gradually formed that between the world of molecules and that of microscopically visible particles is a world of comminution of substances with a collection of new properties inherent in this form of organization of matter.

Let us imagine a cube of a substance that we shall cut up parallel to one of its planes, then we shall begin to cut the plates obtained into rods, and the latter into small cubes (Fig. 87). As a result of such dispersion (comminution) of the substance, we get film-, fibre-, and corpuscular dispersed systems. If the thickness of the films, the transverse dimension of the fibres or particles (corpuscles) is less than the resolving power of an optical microscope, they cannot be detected with its aid. Particles that are invisible in an optical microscope are called **colloidal**, and the dispersed state of substances with a particle size from 400-300 nm to 1 nm is called the **colloidal state** of a substance.

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* In this chapter, we shall have to do with the world of small quantities. We remind our readers that in the SI, 1 m (metre) $= 10^2$ cm (centimetre) $= 10^3$ mm (millimetre) $= 10^6$ μm (micrometre, previously called the micron) $= 10^9$ nm (nanometre, previously called the millimicron).

Thus, 1 nm $= 10^{-9}$ m $= 10^{-7}$ cm; 1μm $= 10^{-6}$ m $= 10^{-4}$ cm.

Dispersed systems are heterogeneous. They consist of a continuous phase—the **dispersing medium**, and the comminuted particles of the relevant size or shape—the **dispersed phase**.

Since the dispersed phase is in the form of individual small particles, dispersed systems, unlike heterogeneous ones with continuous phases, are called microheterogeneous, and colloidal dispersed systems are also called ultramicroheterogeneous to stress that the phase interface in these systems cannot be detected in an optical microscope. The colloidal state is the highest dispersed state of a substance.

When a substance is in its surroundings in the form of molecules or ions, such solutions are called true, i.e. homogeneous one-phase solutions.

An essential condition for obtaining dispersed systems is the mutual insolubility of the substance being dispersed and the dispersing medium. For instance, it is impossible to obtain colloidal solutions of sugar or sodium chloride in water, but they can be obtained in kerosene or benzene in which these substances are virtually insoluble.

Dispersed systems are classified according to their dispersity, the state of aggregation of the dispersed phase and the dispersing medium, the intensity of the interaction between them, and the absence or formation of structures in the dispersed systems.

A quantitative characteristic of the dispersity (comminution) of a substance is its **degree of dispersion** (D)—the reciprocal of the size (a) of the dispersed particles:

$$D = \frac{1}{a}$$

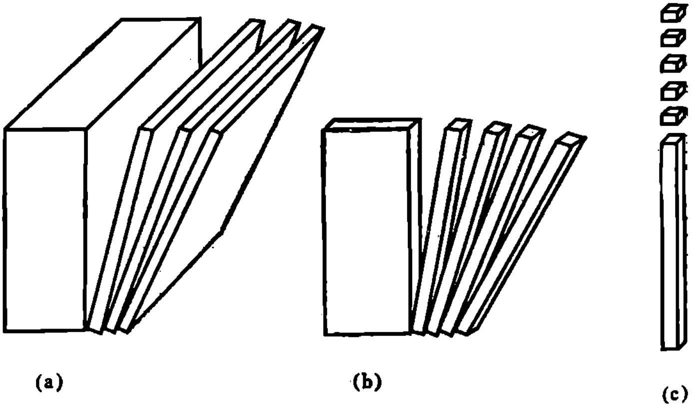

Fig. 87. One-, two-, and three-dimensional dispersion of a substance leads to the formation of film- (a), fibrous- (b), and corpuscular-dispersed (c) systems

Here a is either the diameter of spherical or fibrous particles, or the length of an edge of cubical particles, or the thickness of a film.

The degree of dispersion numerically equals the number of particles that can be densely placed in a row (or in a stack of films) over a length of one centimetre. Table 21 gives the conventionally adopted limits of the dimensions of particles for systems with different particle sizes.

Table 21

Classification of Corpuscular Dispersed Systems by the Degree of Dispersion

System	Comminution of substance	Particle diameter, cm	Degree of dispersion D, cm^{-1}	Number of atoms in particle
Coarsely dispersed	Macroscopic	$1\text{-}10^{-2}$	$1\text{-}10^{2}$	$>10^{18}$
	Microscopic	$10^{-2}\text{-}10^{-5}$	$10^{2}\text{-}10^{5}$	$>10^{9}$
With highest dispersion	Colloidal	$10^{-5}\text{-}10^{-7}$	$10^{5}\text{-}10^{7}$	$10^{9}\text{-}10^{3}$
Molecular and ionic	Molecular and ionic	$10^{-7}\text{-}10^{-8}$	$>10^{7}$	$<10^{3}$

If all the particles of the dispersed phase have the same size, such systems are called **monodispersed** (Fig. 88*a* and *b*). Particles of a dispersed phase having different sizes form **polydispersed** systems (Fig. 88*c*).

With a growth in the dispersity, a greater and greater number of atoms of the substance is in the surface layer at the phase interface in comparison with their number inside the volume of the particles of the dispersed phase. The ratio between the surface area and the volume is the specific (unit) surface $A_{sp} = A/V$, which for spherical particles is

$$A_{sp} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} = \frac{6}{d}$$

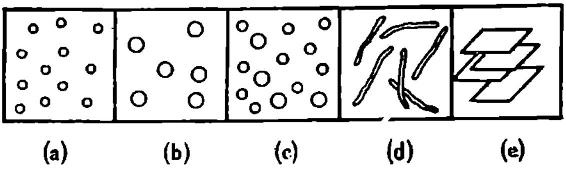

Fig. 88. Freely dispersed systems:
corpuscular- (*a*-*c*), fibrous- (*d*) and film-dispersed (*e*); *a*, *b*—monodispersed; *c*—polydispersed system

where r is the radius of a sphere and d is its diameter, and for cubical particles is

$$A_{sp} = \frac{6l^2}{l^3} = \frac{6}{l}$$

where l is the length of a cube edge.

For instance, the specific surface of a substance comminuted to micrometre cubes is 6×10^4 cm^{-1}. The number of micrometre cubes formed from 1 cm^3 is 10^{12}, and their total surface area ($A = A_{sp}V$) is 6×10^4 cm^2 (6 m^2). Upon further comminution of 1 cm^3 of a substance to cubes of a colloidal size, for example with an edge length of $l = 10^{-6}$ cm (10 nm), their number reaches 10^{18} particles having a total surface area of 6×10^6 cm^2. (600 m^2) and a specific surface of 6×10^6 cm^{-1}.

Consequently, with an increase in the dispersity of a substance, its properties determined by surface phenomena, i.e. by the collection of processes occurring at the phase interface, acquire a greater and greater significance. Hence, the distinctive nature of dispersed systems is determined by the great specific surface of the dispersed phase and the physicochemical interaction of the dispersed phase and the dispersing medium at the phase interface.

The diversity of dispersed systems is due to the fact that the phases forming them can be in any of the three states of aggregation. The letter symbols G (gas), L (liquid) and S (solid) are used for the schematic writing of the state of aggregation of dispersed systems. The first symbol (with the subscript 1) shows the state of the dispersing medium, and the second symbol (with the subscript 2) that of the dispersed phase. The two symbols are separated by a hyphen or an en dash.

Dispersed systems with a gaseous dispersing medium are known as **aerosols**. **Fogs (mists)** are aerosols with a liquid dispersed phase (G_1-L_2), and **dust** and **smoke** are aerosols with a solid dispersed phase (G_1-S_2). Dust is formed in the dispersion of substances, and smoke in the condensation of volatile substances.

Foams are a dispersion of a gas in a liquid (L_1-G_2), the liquid in foams degenerating to thin films separating individual gas bubbles. **Emulsions** are dispersed systems in which one liquid is dispersed as finite droplets in another liquid, the two liquids being immiscible (L_1-L_2). Coarsely dispersed systems of solid particles in liquids (L_1-S_2) are called **suspensions**, and extremely highly dispersed ones are called **colloidal dispersions** or **sols***, or often **lyosols** to emphasize the fact that the dispersing medium is a liquid (from the Greek

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* The term *sol* originates from the Latin *solutio*, which means solution, and was introduced when the radical difference between colloidal dispersions (previously called colloidal solutions) as heterogeneous systems and true solutions had not yet been established.

"lyos"—liquid). If water is the dispersing medium, such sols are known as **hydrosols**, and if an organic liquid is the dispersing medium, they are known as **organosols**.

Gases, liquids, or solids can be dispersed in a solid dispersing medium. The systems S_1-G_2 (solid foams) include foam plastics, foam concrete, pumice, slag, and metals with gas inclusions. Bread, buns, and the like can also be considered as a sort of solid foam. In solid foams, the gaseous phase is in the form of individual closed cells separated by the dispersing medium. Natural pearls exemplify an S_1-L_2 system; they are calcium carbonate in which water is colloidally dispersed.

Of great practical importance are dispersed systems of the type S_1-S_2. They include the most important building materials (for example, concrete), and also metal-ceramic compositions (cermets, Vol. 2, Sec. 115) and crystalline glass-ceramic materials (Sitalls or Pyroceram, Vol. 2, Sec. 68).

Dispersed systems of type S_1-S_2 also include certain alloys, coloured glass, enamels, a number of minerals, in particular some precious and semiprecious stones, and many kinds of volcanic rock in which crystals separated when the magma cooled.

Coloured glass is formed by the dispersion in silicate glass of admixtures of metals or their oxides imparting the relevant colour to the glass. For example, ruby glass contains from 0.01 to 0.1% of gold with a particle size from 4 to 30 μm. The conditions for producing bright red ruby and other coloured glass were already studied by M. Lomonosov. Enamels are silicate glass with inclusions of pigments (SnO_2, TiO_2, ZrO_2) imparting opacity and a colour to them. Precious and semiprecious stones are often metal oxides dispersed in alumina or quartz (for example, ruby is Cr_2O_3 dispersed in Al_2O_3).

Dispersed systems may be **freely dispersed** (Fig. 88) and **cohesively dispersed** (Fig. 89*a-c*) depending on the absence or presence of interaction between the particles of the dispersed phase. Freely dispersed systems include aerosols, lyosols, dilute suspensions, and emulsions. They are fluid. In these systems, the particles of the dispersed phase have no contacts, participate in chaotic thermal motion, and freely

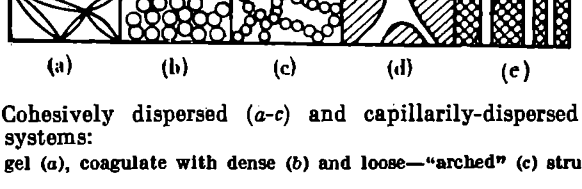

Fig. 89. Cohesively dispersed (*a-c*) and capillarily-dispersed (*d, e*) systems:
gel (*a*), coagulate with dense (*b*) and loose—"arched" (*c*) structure

move under the action of gravity. Cohesively dispersed systems are of a solid nature. They are formed when the particles of the dispersed phase come into contact to form a cohesive structure (a lattice or net). The latter limits the fluidity of the dispersed system and imparts to it the ability to retain its shape. Such structurized colloidal systems are called **gels**. The transition of a sol into a gel occurring as a result of diminishing of the stability of the gel is called **gel formation** (or **gelatination**). A greatly extended and film-lamellar shape of the dispersed particles increases the probability of contacts between them and facilitates the formation of gels at a low concentration of the dispersed phase. Powders, concentrated emulsions and suspensions (pastes), and foams are examples of cohesively dispersed systems. The soil formed as a result of the contact and compaction of the dispersed particles of soil minerals and humus (organic) substances is also a cohesively dispersed system.

A solid body of a substance may be penetrated by pores and capillaries forming **capillarily dispersed systems** (Fig. 89*d*, *e*). They include wood, various membranes and diaphragms, leather, paper, cardboard, and fabrics.

106. State of a Substance at a Phase Interface

All liquids and solids are confined by an external surface at which they are in contact with phases of another composition and structure, for instance, with a vapour, another liquid, or a solid. The properties of a substance in this interphase surface having a thickness of several diameters of an atom or molecule differ from those deeper within the phase. Within the body of a pure substance in the solid, liquid, or gaseous state, any molecule is surrounded by similar ones. At the surface layer, the molecules interact either with a different number of molecules (for example, at the interface of a liquid or solid and its vapour) or with molecules of a different chemical nature (for example, at the interface of two poorly miscible liquids). The greater the difference between the intensities of the intermolecular forces acting in each of the phases, the higher is the potential energy of the interphase surface, known in brief as the **surface energy**.

The work done for the isothermal and reversible formation of a unit of a new phase interface and equal to the change in the Gibbs energy in the relevant process (see Sec. 67) is called the **unit free surface energy** (σ). For the interface of two condensed phases, this quantity is called the **interfacial**, and for the interface of a liquid with its vapour—the **surface tension**.

The surface and interfacial tensions have the dimension of work (we remind our readers that 1 erg = 1 dyn·cm = 10^{-7} J) divided by area (1 $m^2 = 10^4$ cm^2):

$$1\ \text{erg/cm}^2 = 10^{-3}\ \text{J/m}^2$$

These quantities are also sometimes expressed using the dimension of force divided by length (1 erg = 1 dyn·cm and 1 J = 1 N·m):

$$1 \text{ dyn/cm} = 10^{-3} \text{ N/m}$$

The value of σ depends on the nature of the contacting phases, the temperature, and on whether or not solutes have been added.

For most pure liquids at their interface with air saturated with their vapour (a slightly polar medium), the surface tension varies from 1 to 5 $\times 10^{-2}$ J/m^2, while for a strongly polar liquid—water—at 20 °C, we have $\sigma = 7.275 \times 10^{-2}$ J/m^2. With elevation of the temperature, the value of σ diminishes (weakening of the intermolecular interaction), and at the critical temperature when the interface between a liquid and its vapour vanishes, we have $\sigma = 0$.

For molten salts at 400 to 1000 °C, $\sigma \approx 0.15$ J/cm^2. For mercury at room temperature, $\sigma \approx 0.48$ J/m^2. For other metals in the molten state, σ reaches 1 J/m^2 and more.

All spontaneous processes occur in the direction of diminishing of the Gibbs energy (see Sec. 67). Similarly at a phase interface, processes occur spontaneously in the direction of diminishing of the free surface energy equal to the product of its unit value (σ) and the surface area (A). In all systems, the product σA tends to the minimum value possible for the given system with its volume remaining constant. Consequently, dispersed systems are in principle unstable thermodynamically.

If σ is constant, processes occur spontaneously in the direction of diminishing of the total surface area (A), which leads to a decrease in the dispersity, i.e. to consolidation of the particles. This is why the fine droplets coalesce in fogs, rain clouds, and emulsions, and highly dispersed particles consolidate into larger formations. All this leads to destruction of the dispersed systems: fogs and rain clouds precipitate as rain, emulsions become stratified, colloidal dispersions **coagulate**, i.e. separate into a precipitate of the dispersed phase (a **coagulate**, Fig. 89*b*, *c*) and the dispersing medium or, when the dispersed phase has the form of extended particles, they transform into a gel (Fig. 89*a*).

The ability of comminuted systems to retain their inherent degree of dispersion is called their **aggregative stability**. The aggregative instability of the colloidal state of a substance distinguishes it from aggregatively stable coarsely dispersed and molecular systems. The aggregative instability of the colloidal state of a substance underlies the variability of colloidal systems both in time and under the influence of additions of various substances*.

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* A great contribution to the concept of aggregative instability as a qualitative feature of the colloidal state of a substance and to the development of our notions on dispersion stabilizers was made by **Nikolai Petrovich Peskov** (1880-1940), a professor at the Mendeleev Chemical Engineering Institute in Moscow.

If the magnitude of the surface area in a system cannot change, the product σA diminishes spontaneously as a result of a decrease in σ at the phase interface. This is why adsorption processes (see Sec. 109) occur. They consist in a change in the concentration and composition of substances at a phase interface. The general direction of spontaneous processes towards lowering of the free surface energy not only explains why highly dispersed systems are instable, but also shows how to stabilize the dispersity by changing the interphase surface areas (see Sec. 113).

The highly dispersed state of a substance is a qualitatively special form of its existence. Therefore, the field of natural science studying the objective physical and chemical laws of surface phenomena and heterogeneous highly dispersed systems became an independent branch of science known as **colloidal chemistry**.

107. Colloids and Colloidal Dispersions

Particles of colloidal size can have a different internal structure, which appreciably affects both the ways of preparing colloidal dispersions and their properties. Primary particles of colloidal size are divided into the following three types as regards their internal structure.

Type I—**suspensoids** (or **irreversible colloids, lyophobic colloids**). This is the name given to colloidal dispersions of metals, their oxides, hydroxides, sulphides, and other salts. The primary particles of the dispersed phase in colloidal dispersions of these substances do not differ in their internal structure from the relevant compact substance and have a molecular or ionic crystal lattice. Suspensoids are typical heterogeneous highly dispersed systems whose properties are determined by the very greatly developed interphase surface. They differ from suspensions in their higher dispersity. They were named suspensoids because, like suspensions, they cannot exist for a long time in the absence of a dispersion stabilizing agent.They are called irreversible because the precipitates remaining after the evaporation of such colloidal dispersions do not form a sol again upon contact with the dispersing medium. They were called lyophobic (from the Greek "luein"—to dissolve, and "phobos"—fear) because it was assumed that the specific features of colloidal dispersions of this type are due to the very weak interaction between the dispersed phase and the dispersing medium. The concentration of lyophobic sols is not great, usually less than 0.1%. The viscosity of such sols differs insignificantly from that of the dispersing medium.

Lyophobic sols, like dispersed systems in general, in accordance with their intermediate position between the realm of molecules and that of large bodies, can be produced in two ways: by the dispersion, i.e. comminution of large bodies, and by the condensation of substances forming molecular or ionic solutions. Comminution by crushing, grinding, or attrition yields comparatively coarsely dispersed powders (over 60 μm in size). Finer comminution is achieved with the aid of special equipment named colloid mills, or by employing ultrasound.

The condensation method consists in the obtaining of insoluble compounds by reactions of exchange, hydrolysis, reduction, or oxidation. In greatly diluted solutions and in the presence of a small surplus of one of the components, colloidal dispersions are obtained instead of precipitates. Condensation methods also include the preparation of lyosols by changing the solvent. For instance, a colloidal dispersion of rosin can be prepared by pouring its alcohol solution into water, in which rosin is insoluble.

We have revealed in the preceding section that a higher dispersity is attended by a higher free surface energy and a greater inclination to a spontaneous decrease in the dispersity. Hence, to prepare suspensions, emulsions, and colloidal dispersions that will be stable, i.e. keep for a long time, it is necessary not only to achieve the given dispersity, but also to create conditions for its stabilization. This is why stable dispersed systems consist of at least three components: the dispersing medium, the dispersed phase, and a third component—an agent stabilizing the dispersed system.

The stabilizing agent can have either an ionic or a molecular, often a high-molecular, nature. The ionic stabilization of sols of lyophobic colloids is associated with the presence of small concentrations of electrolytes setting up ionic boundary layers between the dispersed phase and the dispersing medium (see Secs. 112 and 113).

High-molecular compounds (proteins, polypeptides, polyvinyl alcohol and others) added to stabilize dispersed systems are called **protective colloids**. Being adsorbed on the phase interface, they form

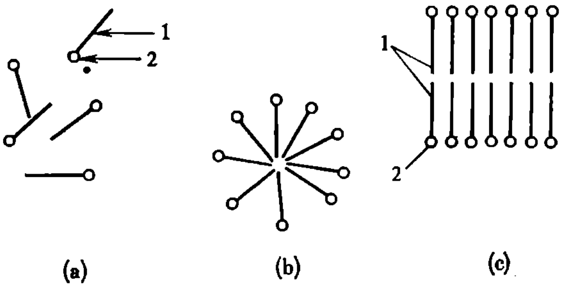

Fig. 90. Solutions of micellar colloids: molecular solution (*a*), colloidal solutions with spherical (*b*) and plate (*c*) micelles.
Diphilic molecule: *1*—hydrocarbon radical; *2*—polar (—COOH, —OH, —NH_2) group

cellular and gel-like structures in the surface layer. These structures form a mechanical barrier that hinders the coalescence of the dispersed phase particles. Structural and mechanical stabilization has a decisive significance for stabilizing suspensions, pastes, foams, and concentrated emulsions.

Type II—**associative,** or **micellar colloids.** They are also called semicolloids. Colloidally dispersed particles of this type are produced at a sufficient concentration of diphilic* molecules of low-molecular substances by their association into molecule aggregations—**micelles**—having a spherical or laminar shape (Fig. 90):

$$\text{Molecular, true solution} \rightleftarrows \text{Micellar, colloidal dispersion (sol)}$$

Micelles are accumulations of regularly arranged molecules retained in place mainly by dispersion forces.

The formation of micelles is characteristic of aqueous solutions of detergents (for example, of soaps—alkaline salts of higher fatty acids) and certain organic dyes with large molecules. These substances dissolve in other media, for instance in ethyl alcohol, with the formation of molecular solutions.

Type III—**molecular colloids.** They are also known as **reversible** or **lyophilic** (from the Greek "philos"—loving) colloids. They include natural and synthetic high-molecular substances having a molecular mass from ten thousand to several millions**. The molecules of these substances have the size of colloidal particles, therefore such molecules are called **macromolecules.**

Dilute solutions of high-molecular compounds are true homogeneous solutions that upon extreme dilution obey the general laws of dilute solutions. Solutions of high-molecular compounds can also be prepared with a high concentration with respect to mass—up to ten and more per cent. But the molar concentration of such solutions is low owing to the high molecular mass of the solute. For instance, a 10% solution of a substance with a molecular mass of 100 000 is only, approximately, a 0.0011 *M* solution.

To obtain solutions of molecular colloids, it is sufficient to bring the dry substance into contact with a suitable solvent. Non-polar macromolecules are dissolved in hydrocarbons (for example, rubber in benzene), and polar macromolecules in polar solvents (for example, certain proteins in water and aqueous solutions of salts). Substances of this type are called reversible colloids because after evaporation of their solutions and the addition of a new portion of solvent, the

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* The adjective **diphilic** is applied to molecules that consist of a hydrocarbon radical having affinity to non-polar solvents, and of a hydrophilic (polar) group having affinity to water.

** For natural and synthetic high-molecular compounds and polymers see Vol. 2, Sec. 63.

dry residue again passes into the solution. The name lyophilic colloids originated from the assumption (which turned out to be erroneous) that strong interaction with the medium is what makes them differ from lyophobic colloids.

The dissolving of macromolecular colloids passes through the stage of swelling, which is a characteristic qualitative feature of substances of this type. In swelling, the solvent molecules penetrate into the solid polymer and move the macromolecules apart. The latter owing to their large size slowly diffuse into the solution, which manifests itself visually in the increase in the volume of the polymer. Swelling can be unlimited, when its final result is the passing of the polymer into the solution, and limited, if swelling does not reach the stage of dissolving of the polymer. Usually polymers with a special "three-dimensional" structure, characterized in that the atoms of the entire substance are joined by valence bonds, undergo limited swelling. The chemical modification of polymers by "cross-linking" their macromolecules in order to diminish the swelling of a polymer is an important step in the production of many materials (the tanning of raw leather, the vulcanization of crude rubber).

Solutions of high-molecular compounds have a considerable viscosity that rapidly grows with an increase in the concentration of the solutions. An increase in the concentration of macromolecular solutions, the addition of substances lowering the solubility of the polymer, and, frequently, lowering of the temperature result in jellification, i.e. the transformation of a greatly viscous, but fluid solution into a non-fluid jelly retaining its shape. Solutions of polymers with greatly extended macromolecules jellify at a low concentration of the solution. For instance, gelatine and agar form jellies and gels in 0.2-1.0% solutions. Dried jellies are capable of swelling again (a significant distinction from gels).

Jellification (gelatination) is an important stage in the production of fibrous materials from polymer solutions. The properties of solutions of high-molecular compounds differ more and more from those of solutions of low-molecular compounds with an increase in their concentration. This occurs as a result of the interaction of individual macromolecules with one another that leads to the formation

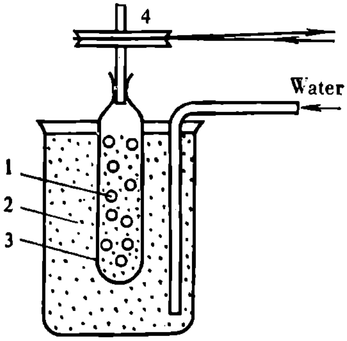

Fig. 91. Dialysis:
1—inner liquid being dialyzed; *2*—outer liquid; *3*—dialyzing membrane (only low-molecular substances pass through its pores); *4*—pulley for rotating membrane with inner solution

of supermolecular structures. The latter have a great influence on the quality of articles (fibres, plastics) made from polymers.

High-molecular compounds, like any other substances, can be obtained in a highly dispersed—colloidal—state in suitable conditions. Such dispersions of polymers in liquids that do not dissolve them, generally in water, are called **latexes.** The particles of the dispersed phase of latexes have a shape close to a spherical one and a size of the order of 10 to 100 nm.

The term "colloids", which means "gluelike" (from the Greek "kolla"—glue, "eidos"—form, shape), was introduced in 1861 when the Scottish chemist Thomas Graham employed dialysis for separating substances (Fig. 91). The method of dialysis is based on the different ability of solution components to diffuse through thin films—membranes (made from cellophane, parchment, nitrocellulose, or acetylcellulose). This method is widely used to purify colloidal dispersions and solutions of high-molecular compounds. Graham called the substances that do not penetrate through membranes in dialysis colloids, and substances capable of dialysis crystalloids because crystalline precipitates were formed when their solutions were evaporated.

The division of substances into crystalloids and colloids was found to be erroneous. P. Weimarn, an Associate Professor at the Petersburg Mining Institute, obtained a number of typical "crystalloids" in the colloidal state. He thus proved (1906) that any substance in suitable conditions can be obtained in the colloidal state.

In the thirties and fourties of the 20th century, the chemical nature of the primary particles forming reversible (lyophilic) colloids was established—they were found to be macromolecules. In this connection, a new branch of chemistry—the physical chemistry of high-molecular compounds—became separated from colloidal chemistry. But because of historical reasons, the common features of the molecular-kinetic properties of lyophilic and lyophobic colloids, the frequent formation of heterogeneous structures in molecular colloids, and also because of the existence of numerous compositions made from high-molecular compounds and highly dispersed systems (for instance, rubber, many paints, lacquers, and varnishes, fibre glass reinforced plastics, and foamed plastics), the subject of colloidal chemistry is interpreted more broadly than is indicated in Sec. 106, namely, as the physical chemistry of the heterogeneous dispersed state of a substance, interphase surfaces, and high-molecular compounds.

108. Dispersion Analysis. Optical and Molecular-Kinetic Properties of Dispersed Systems

Dispersion analysis consists in determining the size of particles and the unit surface area of the dispersed phase and, for polydispersed systems, also in establishing the distribution of the dispersed substance by fractions of different size.

The simplest method of dispersion analysis is sieve or screen analysis consisting in screening the specimen being studied through sieves with definite sizes of their openings. After determining the mass of each of the fractions, we find the distribution of the specimen by fractions of different sizes. Sieve analysis makes it possible to analyse powders up to 60 μm in diameter. The methods of dispersion analysis of systems with a higher dispersity are based on their optical and molecular-kinetic properties.

The interaction of light with a substance depends on the ratio between the wavelength of light and the size of the particles onto which the light beam falls. This interaction follows the laws of geometrical optics (reflection, refraction) if the size of the object is greater than the wavelength of light. If the size of the particles is less than half the wavelength of the incident light, diffusion of the light occurs as a result of its diffraction. The spectrum of visible light is characterized by a wavelength from 760 to 400 nm. Consequently, in molecular and colloidal systems, visible light is scattered, while in transmitted light these solutions are transparent. The scattering of light reaches its highest intensity in colloidal systems for which it is a characteristic feature. The detection in a solution of the path of a ray from a light source when looking at the solution at right angles to the direction of the ray makes it possible to distinguish a colloidal dispersion from a true solution. This optical effect is called the **Tyndall effect** after the British physicist John Tyndall, who studied it in 1860. The same principle underlies the design of an ultramicroscope in which observations are made, unlike an ordinary microscope, at right angles to the direction of the light passing through an object. A flow ultramicroscope designed by B. Deryagin

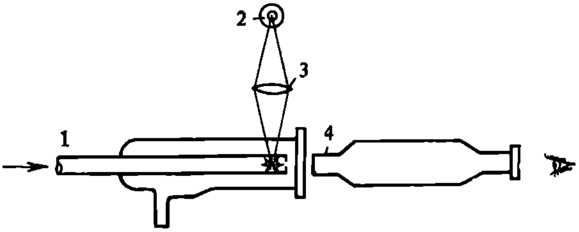

Fig. 92. Flow ultramicroscope designed by Deryagin and Vlasenko: 1—tray; 2—light source; 3—lens; 4—microscope tube

and G. Vlasenko is shown in Fig. 92. This instrument is used to determine the concentration of the dispersed particles in aerosols and colloidal solutions.

The electron microscope invented at the end of the thirties of the 20th century allowed investigators for the first time to see on a fluorescing screen and photograph the shape of colloidal particles, viruses, and many macromolecules including molecules of the larger proteins. The wavelength of the electron beam with a sufficient accelerating potential difference is of the order of 10^{-10} m, which is less than the size of colloidal particles. For this reason, the beam of electrons interacts with colloidal particles according to the laws of geometrical optics*.

Figure 93 shows the limits of applicability of optical methods for studying dispersed systems. Colloidal particles pass through paper filters, but are retained by ultrafilters (membrane filters) that are gels of polymers in the form of films. Knowing the radius of the pores of the ultrafilters, we can assess the size of the colloidal particles.

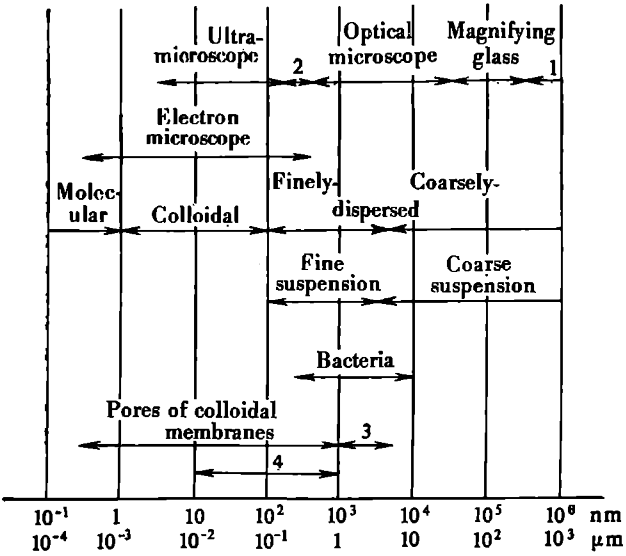

Fig. 93. Limits of dimensions of dispersed system particles and of application of optical methods for determining the dispersity: *1*—eye; *2*—ultraviolet microscope. For comparison, the pore size of paper filters (*3*) and of ultrafilters (*4*) is shown

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* The maximum magnification of an electron microscope reaches 600 000 times, and of an optical microscope only 1500 times.

The properties associated with the chaotic thermal motion of the particles forming a system are called **molecular-kinetic**. The differences in the molecular-kinetic behaviour of molecularly, colloidally, and microscopically dispersed systems depend on the size of the particles forming these systems and are of a quantitative nature.

The molecular-kinetic properties of dispersed systems include Brownian movement, diffusion, and sedimentation.

Brownian movement is the name given to disordered, chaotic—like a swarm of mosquitoes dancing in a sun beam—motion of colloidally and microscopically dispersed particles. This phenomenon was named after the English botanist Robert Brown, who, in 1827, was the first to discover in a microscope continuous oscillating movements of the pollen of plants in its aqueous suspension.

Albert Einstein in 1905 and the Polish physicist Marian Smoluchowski independently of him in 1906 developed the molecular-statistical theory of the Brownian movement and proved that it is a reflection of the invisible thermal, chaotic motion of the molecules of the dispersing medium visible in a microscope. The intensity of Brownian movement becomes more pronounced when the simultaneous collisions of a particle with the molecules of the medium are more unbalanced; it grows with elevation of the temperature, diminishing of the size of the particles and the viscosity of the medium. Brownian movement stops for particles larger than 1 to 3 micrometers. At the end of the first decade of the 20th century, Jean Perrin, in studying the Brownian movement of spherical particles, calculated the Avogadro constant with the aid of the Einstein-Smoluchowski equation. The value he obtained agreed quite well with those found in other ways. This proved the correctness of the molecular-statistical theory of the Brownian movement and confirmed the reality of the existence of molecules in the dispersing medium that are in continuous thermal chaotic motion. At present, observations of the Brownian movement are used for determining the size of dispersed particles.

The rate of **diffusion** at constant temperature and viscosity of the medium depends on the size and shape of the particles. Slow diffusion is a feature distinguishing colloidal systems from true solutions of low-molecular substances.

By **sedimentation** is meant the free settling out of particles in a viscous medium under the action of the gravitational field. The rate of settling out is directly proportional to the acceleration of the Earth's gravitational field (g), the difference between the densities of the particles and the surrounding medium, the square of the radius of the settling-out spherical particles, and inversely proportional to the viscosity of the medium (Stokes's law, 1880).

Only sufficiently large particles settle out. For instance, quartz particles five micrometres in size settle out in water by 3 cm in one hour. The sedimentation of particles with a size of one micrometre and less is prevented by Brownian movement. Consequently, true solutions and colloidal dispersions, including solutions of high-molecular compounds, are stable with respect to sedimentation, while suspensions are not stable.

By letting a suspension settle out under the action of the force of gravity, we determine at definite intervals the mass of the particles that have accumulated in a bowl submerged in the suspension to a definite depth. In this way, we can establish the distribution of the particles by fractions of different size. This method of dispersion analysis of suspensions is called **sedimentation analysis**. It is widely used in studying dispersed systems with particle sizes from 100 to 1 micrometre, particularly soils.

The use of ultracentrifuges in which the acceleration is a million times greater than the acceleration of the force of gravity made it possible to study the sedimentation of proteins and other high-molecular compounds, and also of viruses.

The method of gel permeation (filtration) chromatography proposed by J. Porath and P. Flodin (Sweden) has found broad application in recent years for separating high-molecular substances and determining their molecular mass. The method consists in filtering the solution being studied through columns packed with grains of a swelling three-dimensional polymer (cephadex). The swollen grains of the packing material are "cells" into which only molecules (ions) of a suitable size can penetrate by diffusion. The larger molecules will pass with the filtration stream past the packing grains (Fig. 94). A set of different grades of the packing material with a growing cell (pore) size makes it possible to separate low-molecular substances from high-molecular ones, separate macromolecules, and study the formation of associates in macromolecular solutions.

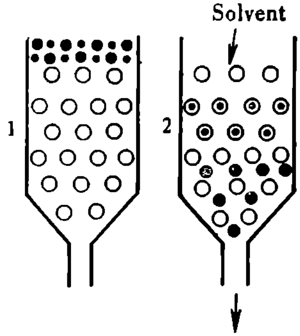

Fig. 94. Gel permeation chromatography:
1—the solution being studied (black particles) is poured into the column with the gel (spherical white particles);
2—after washing of the column with a solvent

109. Sorption and Sorption Processes. Molecular Adsorption

Sorption (from the Latin "sorbere"—to suck) is defined as the process of absorption or adsorption (or both) of one substance (the **sorbate**) by another (the **sorbent**). Depending on the sorption mechanism, there are distinguished adsorption, absorption, chemisorption, and capillary condensation.

Adsorption is defined as the change in the concentration of a substance at a phase interface. Adsorption occurs at any interphase surfaces, and any substances can be adsorbed. Adsorption equilibrium, i.e. the equilibrium distribution of a substance between the boundary layer and the adjoining phases, is dynamic equilibrium and sets in rapidly. Adsorption diminishes with elevation of the temperature.

Quite often, the sorption of one substance by another is not confined to the surface layer, but occurs throughout the entire volume of the sorbent. This is what is called **absorption**. An example of absorption is the dissolving of gases in liquids. The sorption of one substance by another attended by chemical reactions is called **chemisorption**. For instance, the sorption of ammonia or hydrogen chloride by water, of moisture and oxygen by metals with the formation of oxides and hydroxides, and of carbon dioxide by calcium oxide are chemisorption processes. **Capillary condensation** consists in the liquefying of a vapour in microporous sorbents. It occurs because the pressure of the vapour over the concave meniscus of the liquid in the narrow capillaries it wets is lower than the pressure of the saturated vapour over a flat surface of the liquid at the same temperature.

Thus, sorption processes differ in their mechanism. Any sorption process, however, begins with adsorption at the interface of contacting phases, which may be liquid, gaseous, or solid.

As indicated in Sec. 106, all spontaneous processes at phase interfaces occur in the direction of a decrease in the free surface energy. Consequently, positive adsorption leading to a growth in the concentration of a substance in the boundary layer is possible only if it is attended by diminishing of the surface tension.

Let us see how the surface tension of solutions is related to the adsorption at a liquid-gas interface. The surface tension of a solution depends on the nature of the solvent and the solute, on the concentration of the latter, and on the temperature. The relation of the surface tension of a solution at constant temperature to the solute concentration is called the **surface tension isotherm**. A solute either lowers the surface tension of the solvent, when it is known as a **surface-active agent (surfactant)**, or increases the surface tension (a **surface-inactive** agent), or does not affect the magnitude of the surface tension of the solvent (Fig. 95). In aqueous solutions, polar organic compounds (alcohols, acids, amines, phenols) are surfactants. Most of the strong electrolytes are surface-inactive agents.

Surfactants are divided into two large subgroups: (1) truly soluble in water, and (2) micellar colloids. Surfactants of the first subgroup are diphilic molecules with short hydrocarbon radicals, and those of the second group are diphilic molecules with a long hydrocarbon radical only slightly soluble in water.

The difference between the concentrations of the solute in the surface layer and in a similar layer within the solution is called the **surface excess** of this substance and is designated by the Greek letter Γ ("gamma"). Surfactants are positively adsorbed in the surface layer, and, consequently, $\Gamma > 0$ for them because this leads to lowering of the surface tension. Conversely, surface-inactive agents are adsorbed negatively, i.e. their concentration in the surface layer is lower than within the solution ($\Gamma < 0$). The surface tension grows somewhat here because in solutions of strong electrolytes the surface molecules of water are drawn into the solution with a greater force than in pure water.

An example of an adsorption isotherm for a surfactant is shown in Fig. 96. A glance at the figure shows that with an increase in the concentration of the solution, Γ reaches its extreme value (Γ_∞) when the entire surface layer is occupied by the surfactant molecules that have displaced the solvent molecules. In such saturated

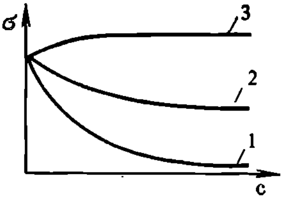

Fig. 95. Surface tension isotherms:

1 and 2—solutions of surfactants with a higher (1) and lower (2) surface activity; 3—solution of surface-inactive agent; σ=surface tension; c=concentration of solution

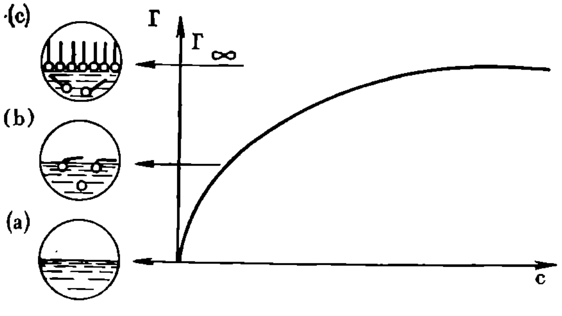

Fig. 96. Isotherm of surface excess (Γ) in solutions of a surfactant.

Structure of surface layer: a—pure solvent; b—unsaturated monomolecular layer of surfactant; c—saturated monomolecular layer of surfactant monomolecular surface layers, the surfactant molecules are oriented identically, with their polar group towards the polar phase (for instance, water), and their non-polar hydrocarbon radical towards the non-polar phase (for example, air), forming a structure resembling a paling.

The surface tension changes and the third component is adsorbed in a similar way at the interface of two immiscible liquids.

The adsorption of gases and vapours on the surface of solids also occurs as a result of diminishing of the free surface energy. Owing to the difficulty of measuring the surface tension of solids, adsorption on them is assessed by directly determining the amount of adsorbed substance. The latter grows with an increasing surface area of the adsorbent. Hence, to carry out adsorption processes, it is very important to create highly porous adsorbents with a developed internal surface that is characterized by the specific surface area, i.e. the surface area per gram of sorbent. The most important porous sorbents are activated carbon and silica gel. The absorbing ability of carbon (charcoal) was noted back in the 18th century. But only in 1915 did N. Zelinsky* develop a way of preparing **activated carbon (charcoal).** He proposed it as universal absorbers of poisonous substances and together with E. Kumant he designed a charcoal gas mask with a rubber mask proper. One of the first ways of activating charcoal was its processing with superheated steam for removing the resinous substances formed in the dry distillation of wood and filling the pores in ordinary charcoal. The modern ways of preparing and studying activated carbon in the Soviet Union were developed by M. Dubinin**. The specific surface area of activated carbon reaches 1000 m^2 per gram. Activated carbon is a hydrophobic adsorbent poorly absorbing water vapour and very well absorbing hydrocarbons.

Great favour has been found for absorbing water vapour by a hydrophilic adsorbent that is an aerogel of dehydrated silicic acid and has been named **silica gel.** Industrial enterprises produce a number of grades of silica gel with different sizes and distribution of the pores.

Unlike the surface of liquids, not all points of the surfaces of solids are equivalent with respect to the adsorptive capacity. At low gas concentrations, adsorption occurs monomolecularly over the most active sections of the adsorbent—its "active centres", which

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* **Nikolai Dmitrievich Zelinsky** (1861-1953), Academician, Hero of Socialist Labour, was the founder of a large school of organic chemists. He is the author of classical works in the field of organic catalysis, and also in the chemistry of petroleum and the preparation of many valuable products from it.

** **Mikhail Mikhailovich Dubinin** (born 1901), Academician, winner of State Prizes, headed a major scientific school in the field of sorption. He made a great contribution to the development of the modern notions on the mechanism of gas and vapour sorption, and also of methods of preparing and studying sorbents.

are individual atoms or groups of atoms on the surface whose force field is the least saturated. In the adsorption of gases at temperatures below their critical temperature, monomolecular adsorption with an increase in the pressure may transform into polymolecular adsorption.

Elevation of the temperature and lowering of the pressure result in desorption of gases and vapours. This is why sorption-desorption methods are widely used in industry for extracting various substances from an air medium, and also for separating gases and vapours.

In the adsorption of solutes from solutions on solid adsorbents, adsorption of the solvents always occurs too to a certain degree. For this reason, adsorption from solutions bears a competitive nature between the absorption of the solutes and solvent. Both dissolved non-electrolytes and electrolytes can be adsorbed. In this connection, molecular and ionic adsorption from solutions is distinguished.

To diminish solvent adsorption, a hydrophobic adsorbent—activated carbon—is customarily used in molecular sorption from aqueous solutions, and a hydrophilic adsorbent—silica gel—in sorption from non-polar solvents (hydrocarbons). Adsorption occurs over the active centres of the adsorbent, frequently monomolecularly and highly selectively. The isotherms of molecular adsorption from solutions, as well as of gases and vapours, have the form of the curve depicted in Fig. 96. Desorption conducted with the aid of liquids is usually called **elution**, and the liquids or solutions used for these purposes are called **eluents**.

Sorption can proceed in static or dynamic conditions. Sorption is called **static** when the sorbate is in the gaseous or liquid phase, is in contact with the stationary sorbent, or is mixed with it. The static activity of a sorbent is characterized by the amount of sorbate per unit of sorbent mass in definite conditions.

Sorption is called **dynamic** when the sorbate is in a mobile liquid or gaseous phase that is filtered through a layer of the sorbent. The dynamic activity of an adsorbent is characterized by the time from the beginning of passing the adsorbate through the apparatus to its breakthrough, i.e. to its appearance after the adsorbent layer (N. Shilov, 1917). At industrial enterprises, sorption-desorption processes, as a rule, are conducted in dynamic conditions because this ensures continuity of the production processes and the possibility of their automation.

110. Ion-Exchange Adsorption

In the adsorption of electrolytes, either cations or anions are mainly adsorbed, and they are replaced with an equivalent amount of ions of the same sign from the adsorbent. The solution remains electrically neutral. Consequently, the adsorption of electrolytes occurs by the equivalent exchange of ions of the same sign, and is therefore called ion-exchange adsorption. The ion-exchange mechanism of electrolyte adsorption was initially noted by agronomists and soil scientists when displacing ions of electrolytes in the soil with others. K. Gedroits* proved (1918) the equivalence of cation exchange in soils and originated the concept of a soil absorbing complex (the highly dispersed organomineral part of the soil) underlying the ability of soils to retain the soluble salts needed by plants in a form accessible for root nutrition.

Inorganic and organic materials capable of exchanging ions are known as ion exchangers. They are divided into **cation exchangers** and **anion exchangers.** The chemical industry produces a variety of synthetic ion exchangers in the form of granular powders, fibres, and membranes.

Organic and inorganic ion exchangers are insoluble in water. They consist of a three-dimensional coherent structure including charge-carrying groups of atoms called potential-determining ions (or co-ions). Ions of the opposite sign are called gegenions (or counter-ions). They are bound to the potential-determining ions of the structure by electrostatic forces, and are therefore capable of exchanging places with other ions. For example, the structure of glass is formed by a three-dimensional lattice of silicon oxide (silica) ions. The voids of this three-dimensional silica lattice contain cations of alkali or alkaline-earth metals retained in place by electrostatic forces and capable of being exchanged for other cations (particularly, for hydrogen ions).

In organic ion exchangers, the three-dimensional coherent structure is formed by a lattice of carbon atoms to which, for example, sulphocarboxy-, or trimethylammonium groups are covalently bound:

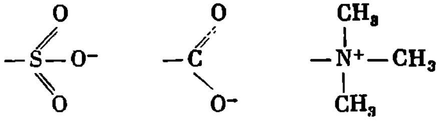

Figure 97 illustrates the exchange of cations on the H^+-form of cation exchanger and the exchange of anions on the OH^--form of anion exchanger.

Ion exchange is a reversible process. We shall schematically write a cation exchanger as R^{x-}, a polyvalent electrolyte with the valence x. Hence, after introduction of the H^+-form of cation exchanger into a solution of an electrolyte, for example NaCl, equilibrium

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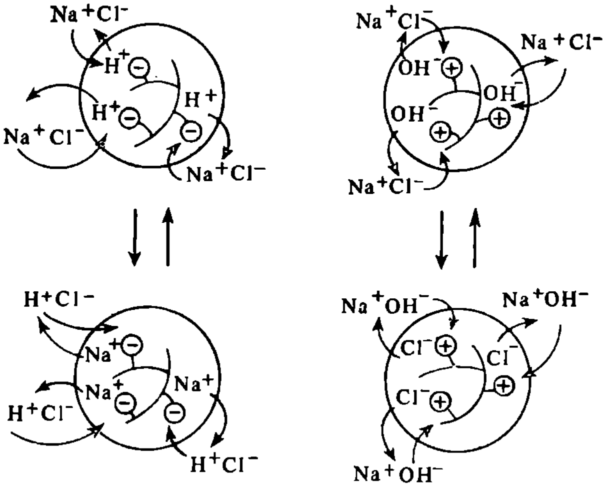
* **Konstantin Kaetanovich Gedroits** (1872-1932), Academician, Lenin Prize winner, was an outstanding soil scientist and agrochemist. He founded the concept of the soil absorption complex and its role in soil fertility, and is the author of many methods of the chemical analysis of soils.

will set in:

$$\underset{\text{cation exchanger}}{R^{x-}xH^+} + \underset{\text{solution}}{xNaCl} \rightleftarrows \underset{\text{cation exchanger}}{R^{x-}(x-y)H^+yNa^+} + \underset{\text{solution}}{(x-y)NaCl + yHCl} \rightleftarrows$$

$$\rightleftarrows \underset{\text{cation exchanger}}{R^{x-}xNa^+} + \underset{\text{solution}}{xHCl}$$

The maximum amount of ions adsorbed in exchange by one gram of ion exchanger is called the **adsorption capacity** or the **exchange capacity***. It reaches 6 to 10 mequiv/g. Ion-exchange equilibrium is determined by the nature of the ion exchanger, the hydration of the ions being exchanged, and their concentration in the phase of the ion exchanger and in the solution. The exchange of ions having a different valence also depends on the magnitude of their charge. A great contribution to developing the theory and application of ion exchange was made by B. Nikolsky**.



(a) (b)

Fig. 97. Ion exchange in grains of a cation exchanger (*a*) and an anion exchanger (*b*).

The potential-determining ions are ionogenic groups chemically bound to the ion exchanger framework: — and +, respectively. The cation exchanger is in the H^+-form, the anion exchanger in the OH^--form; H^+ and OH^- are ions that in an NaCl solution are exchanged for Na^+ and Cl^- ions, respectively

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* The adsorption capacity of soils is related to 100 g of soil and is called the **adsorbing power** of the soil.

** **Boris Petrovich Nikolsky** (born 1900), Academician, Hero of Socialist Labour, Lenin and State Prize winner, heads a major scientific school in the field of ion exchange. He is the author of a thermodynamic substantiation of the ion-exchange theory of the glass electrode.

Ion exchangers are widely used to diminish the hardness of water and desalinate it (see Vol. 2, Sec. 98), and to recover and separate a variety of inorganic and organic ions. Ion exchange is used in the leather, hydrolysis, and pharmaceutic industries for purifying solutions, and also for removing salts from sugar syrups, milk, and wines. Ion exchangers are used to trap the ions of valuable elements from natural solutions and the waste liquors of various production processes. The industrial production of many products of the vital activity of microorganisms (antibiotics, amino acids) became possible or its cost was cut quite considerably owing to the use of ion exchangers. The use of ion exchange allowed chemists to improve the methods of qualitative and quantitative analysis of many inorganic and organic substances.

The substances having ion-exchange properties include certain grades of glasses. Their structure is formed by a silicate lattice and cations electrostatically bound to them that are capable of being exchanged for hydrogen ions of a solution. Such glasses are used to manufacture **glass electrodes** having the properties of a hydrogen electrode (see p. 294). Glass electrodes are used to determine the pH of solutions in conditions when it is difficult or impossible to use a hydrogen electrode (for instance, in the presence of strong oxidizers). Glasses have also been developed whose electrode potential is determined by the concentration of metal ions, for example, of sodium ions.

111. Chromatography

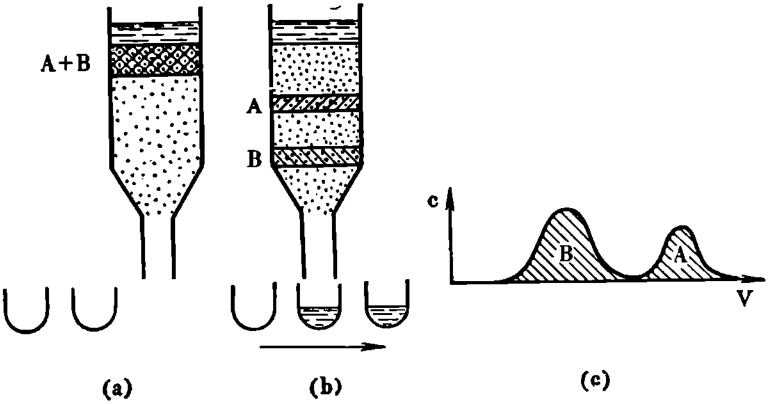
Mikhail Tswett was the first to conceive the idea that adsorption in dynamic conditions improves the separation of complicated mixtures. On the basis of this idea, in 1903, he proposed a new method of analysing such mixtures which he called the **chromatographic method**.

The essence of the method consists in the following. A solution of the mixture being studied is introduced into a "chromatographic column"—a glass tube filled with an adsorbent preliminarily washed and then impregnated with a solvent. The mixture components are adsorbed in the upper part of the column without being separated or being separated only partly; a primary chromatogram is formed (Fig. 98*a*). Next it is "developed". For this purpose, the pure solvent (eluent) is fed into the column. It desorbs the previously adsorbed substances and moves them together with its stream down the column. During the motion along the column, repeated events of adsorption and desorption occur that result in separation of the mixture components in accordance with Tswett's law of adsorption displacement (1910), which consists in the following: if dissolved substances A, B, C, . . . form an adsorption series $A > B > C \ldots$

with respect to their relative affinity to the adsorbent, each member of the adsorption series displaces the following one and, in turn, is displaced by the previous one, that is adsorbed to a greater extent. As a result, a developed chromatogram is formed in the column (Fig. 98*b*). Tswett used this method to separate a mixture of plant leaf pigments on white adsorbents (chalk, calcium oxide, starch, cellulose). The developed chromatogram was formed of bands having different colours. This explains the name of the method proposed by Tswett—**chromatography** ("colour writing", from the Greek "khroma"—colour, and "graphein"—to write).

By continuing the flow of the solvent through the column, the substances being separated are made to emerge from it. They are detected by analysing consecutive portions of the solution flowing out of the column (the eluate). If we construct an emergence curve, i.e. a plot of the dependence of the eluate concentration (c) on the volume (V) of the solution passed through the column, chromatographic peaks on this curve correspond to the emergence of the initial mixture components from the column (Fig. 98*c*). Quite often, complete separation of the components does not occur, and the individual peaks overlap. The construction of emergence curves is the most widespread form of column chromatography because it is associated neither with the colour of the components being separated nor with the colour of the adsorbent.

In 1936, Dubinin carried out the adsorption chromatography of vapours; in the following years new variants of the chromatographic method appeared. At present, chromatography is defined as such physicochemical methods of separating the components of mixtures



(a) (b) (c)

Fig. 98. Development (eluent) chromatography:
a—primary chromatogram, *b*—developed chromatogram; *c*—emergence curve of developing analysis

of gases, vapours, liquids, or solutes that are conducted by sorption in dynamic conditions.

Depending on the predominating physicochemical sorption process determining the separation of the mixture components, we can distinguish adsorption, ion-exchange, and partition chromatography. The components being separated can be in a moving liquid or gaseous phase, while the stationary phase can be either solid or liquid. The grains of the adsorbent or ion exchanger can fill a column (column chromatography) or form a thin dense layer on a glass plate (thin-layer chromatography).

The development and improvement of chromatographic methods of research were due considerably to the rapid rates of development of modern molecular biology and the chemistry of the rare-earth and transuranium elements. Chromatographic methods of extraction and separation of a variety of substances have also been introduced on large industrial scales.

Great significance for analysing very small volumes of solutions (0.01 to 0.1 ml) was acquired by partition paper chromatography. It is based on the fact that a third component is distributed between two immiscible liquids in accordance with a partition coefficient characteristic of this substance. This coefficient is the ratio of the concentrations of the third component in the contacting liquids (the distribution law, see Sec. 76).

To conduct a chromatographic process, it is essential that one layer of the liquid move relative to the other one. In this case, the distribution of the solutes between the two layers of the liquid occurs repeatedly in dynamic conditions. In paper chromatography, one liquid, the more polar one, is sorbed by the fibres of the paper, forming a stationary liquid phase; the second, less polar liquid, wetting the paper fibres, creeps up the paper owing to capillary phenomena.

Figure 99 shows partition paper chromatography ("upflow chromatography"). A drop each of the solution of the mixture being investigated (A + B) and the assumed component of the mixture, the "witness", is applied separately to the starting line of a strip of chromatographic paper (Fig. 99,*I*). The bottom edge of the paper strip is immersed in the solvent. When the front of the solvent almost reaches the top edge of the paper strip after

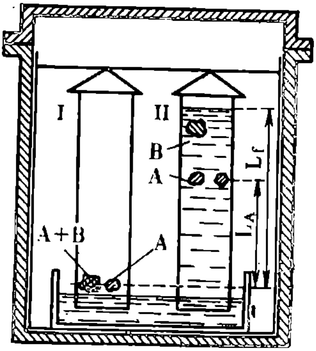


Fig. 99. Upflow partition paper chromatography

travelling the path L_f (Fig. 99,*II*), the components of the initial mixture, if the system of solvents has been properly selected, separate into a number of spots that are determined by the relevant coloured reactions for the expected components and by comparison with the positions of the spots of the "witnesses". The path covered by component A of the initial mixture (L_A) is determined by the distribution coefficient for the given substance. The relative magnitude of this path L_A/L_f denoted by Rf_A (relative front of substance A) is characteristic of every substance in a definite system of solvents.

112. Electrokinetic Phenomena

By electrokinetic phenomena are meant the movement of one phase relative to another in an electric field and the appearance of a potential difference when a liquid flows through porous materials (the streaming potential), or when particles settle (the sedimentation potential). The migration of colloidal particles in an electric field is called **electrophoresis**, and the flow of a liquid through capillary systems under the influence of a potential difference is called **electroosmosis**. Both these phenomena were discovered by F. Reiss, a professor of the Moscow University, in 1809.

Electrokinetic phenomena indicate that an **electrical double layer** appears at a phase interface. It is a thin surface layer of electric charges of opposite signs separated in space. In dispersed systems, an electrical double layer forms ions and dipole molecules. An ionic electrical double layer appears either because of the dissociation of ionogenic groups of a substance in the solid phase, or because of the selective adsorption of ions completing the building up of the crystal lattice of the solid phase. As a result, a structure similar to a capacitor appears at the interface of the solid phase and the solution. Its inner plate is formed by potential-determining ions, and its outer plate by gegenions.

Let us consider the appearance of an electrical double layer by the selective adsorption of ions using as an example the preparation of colloidal particles of AgI in the reaction of $AgNO_3$ and KI in their greatly diluted solutions with a small surplus of the KI.

Ions identical to those forming the crystal lattice or similar to them are preferentially adsorbed on the surface of the crystals. In the present case, the ions I^- will be adsorbed, and the surface of the minute crystals of AgI acquires a negative charge. The interphase potential, or the ε-potential (ε is the Greek letter "epsilon") is the work against the Coulomb forces needed to transfer a unit charge of the opposite sign from the surface of a crystal to infinity.

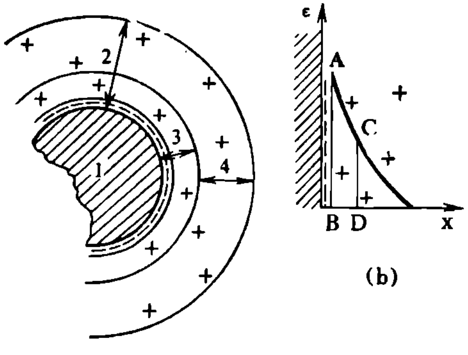
The gegenions (in our case the K^+ ions) are under the action of the electric field of the charged surface and of thermal motion tending to distribute them uniformly in the volume. This leads to the regular dynamic distribution of the gegenions like a cloud whose density diminishes with an increasing distance from the charged surface. The outer boundary of this cloud of gegenions determines the thickness of the electrical double layer (Fig. 100).

Upon a relative displacement of the phases, the boundary of sliding is at a certain distance from the solid surface owing to hydration of the solid surface and the ions. As a result, the electrical double layer divides into a compact (inner) and a diffuse layer (see Fig. 100).

The **inner** (compact) **layer** of an electrical double layer consists of potential-determining ions and part of the gegenions. The **diffuse layer** of the double layer is formed by the remaining gegenions. The rate of movement of the phases in the electric field is determined by the magnitude of the potential on the slipping surface, which is therefore called the **electrokinetic potential** and is briefly designated as the ζ-potential (zeta-potential). This potential is given the sign of the charge of the solid surface.

In a constant external electric field, a colloidal particle moves towards the electrode whose charge sign is opposite to that of the surface of the colloidal particle (Fig. 101*a*). The electroosmotic transfer of the liquid is directed towards the electrode having the same sign as the surface of capillary *C* (Fig. 101*b*). In this case, the hydrated gegenions are mobile in the electric field and carry along the layers of water adjoining them.

The structure of an electrical double layer may change in several



(a)

(b)

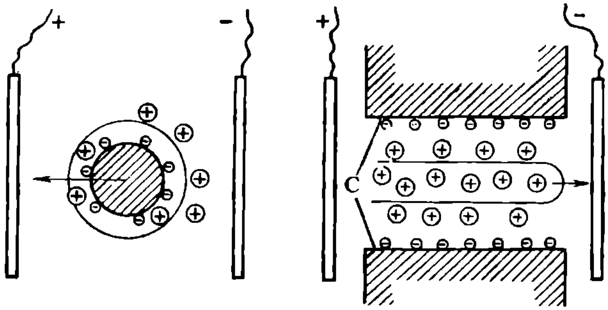
Fig. 100. Structure of a colloidal micelle (*a*) and change in the potential (*b*) in an electrical double layer:

1—nucleus; 2—electrical double layer; 3—its inner layer; 4—its diffuse layer, *AB*—interphase ε-potential, *CD*—electrokinetic ζ-potential; "—"—potential-determining ions, "+"—gegenions directions. At very low concentrations of the electrolytes, as the active centres of the surface become filled with potential-determining ions, the ε-potential grows. Gegenions with a high adsorptivity (for instance, multicharge ions) can penetrate into the adsorption layer in amounts that are more than equivalent to the initial potential-determining ions, producing a change in the sign of the charge of the surface with the relevant rebuilding of the entire electrical double layer (the **recharging of colloids**).

The diffuse layer of an electrical double layer is the most labile and variable. Gegenions are exchanged for other ions of the same sign. An increase in the concentration of a solution results in "displacement" of the gegenions from the diffuse to the compact layer of the double layer. The thickness of the double layer and the magnitude of the zeta-potential diminish. At a certain concentration of the solution (about 0.1 N), all the gegenions become displaced into the inner layer, and the zeta-potential vanishes. In this case, the change in the interphase potential from its maximum value on the surface of the solid phase to zero occurs completely within the limits of the inner layer. Such a state of a colloidal micelle is called the **isoelectric state.**

It follows from the above that electrokinetic phenomena manifest themselves in dilute solutions of electrolytes ($<0.1\ N$). The electrokinetic potential has an order of magnitude of from 0.001 to 0.1 V. Notwithstanding its small value, the zeta-potential plays an appreciable role in the stability of colloidally dispersed systems (see Sec. 113).

Electrokinetic phenomena find a practical application. For instance, various articles are moulded from fine suspensions with the



(a) (b)

Fig. 101. Movement of a colloidal particle in electrophoresis (*a*) and in electroosmotic transfer of a liquid through a capillary (*b*) (*C* is the inner surface of the capillary).
The surfaces of the colloidal particle and of the capillary are charged negatively

aid of electrophoresis, and are then sintered. Electrophoresis is widely used for separating, extracting, and studying biocolloids, especially proteins. A simple version of it, called paper electrophoresis, consists in that a strip of paper is wetted at one spot with the mixture of proteins being investigated, and in the field of a direct electric current the mixture is separated into components according to the magnitude of their charge and, consequently, to the rate of their motion in the field. This method is used to investigate the qualitative and quantitative composition of proteins in blood and of other biological liquids.

Electroosmosis is used to remove moisture from capillary-porous systems and lower the ground-water level in the erection of hydraulic engineering and other structures. The appearance of electric fields in the flow of ground water has found application in geological prospecting for minerals and water sources.

113. Stability and Coagulation of Dispersed Systems

As we have indicated in Sec. 106, a qualitative feature of dispersed systems is their aggregative instability.

The aggregation of primary dispersed particles can be prevented by three factors of dispersed system stability: (1) the kinetic, (2) electrical, and (3) structural-mechanical factors.

An essential condition for the cohesion of two particles of a dispersed phase is their coming close enough for the forces of attraction to manifest themselves. If the frequency of collisions of colloidal particles is low, a dispersed system can be stable (the **kinetic stability factor**). This can occur at a very low concentration of the dispersed particles (for instance, in certain aerosols, or at a very high viscosity of the dispersing medium (for example, in dispersed systems of type S_1-S_2).

Most stable dispersed systems, in addition to the dispersed phase and the dispersing medium, contain a third component that is a dispersion stabilizing agent. Either ions or molecules can be the stabilizing agent. In this connection, two mechanisms of stabilizing dispersed systems are distinguished—the electrical and the molecular-adsorption ones (p. 350).

The **electrical stabilization of dispersed systems** is associated with the appearance of an electrical double layer at the phase interface. Such stabilization is of a paramount significance for preparing stable lyosols and suspensions in a polar medium, for example in water. In any hydrosol, all the colloidal particles have the same sign of their charge. A colloidal micelle as a whole, however, is electrically neutral as a result of the formation of an electrical double layer. Consequently, electrostatic repulsion appears between colloidal particles (the **electrical stability factor**) only when they approach one another sufficiently closely, and overlapping of their ionic atmospheres occurs (Fig. 102). The potential energy of electrostatic repulsion is the greater, the more is the overlapping of the diffuse layers of the electrical double layer of the colloidal particles, i.e. the smaller is the distance (x) between them, and the greater is the thickness of the electrical double layer.

In addition to electrostatic repulsion, colloidal particles, like the molecules of any substance, experience intermolecular forces of attraction among which the greatest role is played by dispersion forces. The dispersion forces acting between individual molecules rapidly diminish with an increasing distance between them. But the interaction of colloidal particles is due to the summation of the dispersion forces of attraction between all the molecules on the surface of contact of the colloidal particles. For this reason, the forces of attraction between colloidal particles diminish at a slower rate and manifest themselves at greater distances than for individual molecules.

The potential energy of interaction (E_p) between colloidal particles is the algebraic sum of the potential energy of electrostatic repulsion ($E_{p,e}$) and that of dispersion attraction ($E_{p,d}$) between them:

$$E_p = E_{p,d} + E_{p,e}$$

If $E_{p,e} > E_{p,d}$ (in absolute value), repulsion predominates over attraction, and the dispersed system is stable. If $E_{p,e} < E_{p,d}$, the colloidal particles colliding in Brownian movement coalesce into larger aggregates, and sedimentation of the latter occurs. The colloidal dispersion **coagulates**, i.e. separates into a coagulate (precipitate) and the dispersing medium.

This is the essence of the theory of electrical stabilization and coagulation of dispersed systems first developed by B. Deryagin* (1937), and later by L. Landau and the Dutch scientists H. Ferwey and J. Overbeek (1948); it is known as the DLFO theory according to the first letters of its authors' surnames.

Figure 103 shows how the quantities $E_{p,d}$ and $E_{p,e}$ depend on

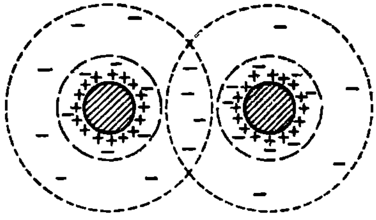


Fig. 102. The overlapping of the ionic atmospheres of two colloidal particles

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* **Boris Vladimirovich Deryagin** (born 1902), a Soviet physicochemist, Associate Member of the USSR Academy of Sciences, is the author of the modern theory of stability and coagulation of colloids, the electrical theory of gluing and adhesion, and of important investigations in the field of aerosols.

the distance between colloidal particles. As is customary practice in physics, the potential energy of attraction is written with a minus sign, and of repulsion with a plus sign. Examination of the figure shows that the resultant energy of interaction (curve *3* in Fig. 103) indicates attraction ($E_p < 0$) between the particles at very small distances and repulsion ($E_p > 0$) at greater distances between them. Of a decisive significance for the stability of dispersed systems is the magnitude of the potential barrier of repulsion ($E_{p,max}$) which, in turn, depends on the course of the curves of $E_{p,d}$ and $E_{p,e}$. At high values of this barrier, a colloidal system is stable. Adhesion of colloidal particles is possible only when they come close enough together. This requires surmounting of the potential barrier of repulsion. At certain low positive values of $E_{p,max}$ (curve *3*), only a few colloidal particles having a sufficiently high kinetic energy can surmount it. This corresponds to the stage of slow coagulation, when only a small fraction of collisions between colloidal particles results in their adhesion. In slow coagulation, a certain diminishing of the total number of colloidal particles occurs in time as a result of the formation of aggregates consisting of two or three primary particles, but no coagulate precipitates. Such coagulation, not attended by a visible change in a colloidal dispersion, is known as **hidden coagulation.** Upon further lowering of the potential barrier, the rate of coagulation, characterized by a change in the number of particles in unit time, increases. Finally, if the potential barrier passes from the region of repulsion to that of attraction (curve *4* in Fig. 103), **rapid coagulation** sets in, when every collision of colloidal particles leads to their adhesion. A coagulate is formed in the colloidal dispersion, and **explicit coagulation** occurs.

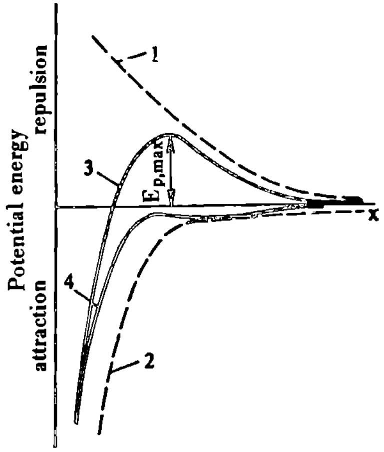

Fig. 103. Potential energy of interaction between two identically charged particles:
1—electrical repulsion ($E_{p,e}$); *2*—dispersion attraction ($E_{p,d}$); *3*—resultant energy of interaction (E_p); *4*—ditto, but with steeper falling of curve *1*; *x*—distance between particles; $E_{p,max}$—potential barrier of interaction of dispersed particles

The potential barrier of repulsion ($E_{p,max}$) appears as a result of summation of the forces of repulsion and attraction acting between colloidal particles. Consequently, all the factors affecting the course of curves *1* and *2* (Fig. 103) lead to a change both in the magnitude of $E_{p,max}$

and in the position of the maximum (i.e. in the distance x corresponding to $E_{p,max}$).

A considerable decrease in $E_{p,max}$ occurs as a result of a change in the potential energy of electrostatic repulsion (i.e. in the course of curve *1*) because of the addition of electrolytes to the colloidal dispersion. An increase in the concentration of any electrolyte is attended by rebuilding of the electrical double layer surrounding the colloidal particles: a greater and greater number of gegenions are displaced from the diffuse layer to the inner layer of the electrical double layer. The thickness of the diffuse layer (layer *4* in Fig. 100), and together with it of the entire electrical double layer (layer *2* in Fig. 100) diminishes. Therefore, the curve of the potential energy of electrostatic repulsion drops more steeply than curve *1* shown in Fig. 103. As a result, the potential barrier of repulsion ($E_{p,max}$) lowers and is displaced in the direction of the smaller distance between colloidal particles. When the electrical double layer is compressed to the thickness of the inner layer (layer *3* in Fig. 100), the entire curve of interaction of the dispersed particles is in the region of attraction (curve *4* in Fig. 103), and rapid coagulation sets in. Such a change in the stability of a colloidal dispersion occurs when any electrolyte is added.

The coagulating action of electrolytes is characterized by the **coagulation threshold**, i.e. the lowest concentration of the electrolyte causing coagulation. Depending on the nature of the electrolyte and the colloidal dispersion, the threshold of coagulation varies from 10^{-5} to 0.1 mole per litre of sol. The charge of the **coagulating ion** of the electrolyte, i.e. of the ion whose charge is opposite in sign to that of a colloidal particle, has the most appreciable influence on the coagulation threshold.

Multiply charged gegenions of the electrolyte have an increased adsorption capacity in comparison with singly charged ones and penetrate into the inner layer of the electrical double layer in large numbers. The coagulation threshold diminishes not in proportion to the magnitude of the gegenion charge, but much more rapidly.

A brilliant confirmation of the DLFO theory was the calculation by Deryagin and Landau (1941) of the relationship between the values of the coagulation thresholds for electrolytes containing ions having different magnitudes of their charge. The coagulation threshold was found to be inversely proportional to the sixth power of the charge of the coagulating ion. Hence, the values of the coagulation thresholds for ions with one, two, three, and four charges should be in the ratio of

$$1 : \left(\frac{1}{2}\right)^6 : \left(\frac{1}{3}\right)^6 : \left(\frac{1}{4}\right)^6 = 1 : 0.016 : 0.0014 : 0.00024$$

which is close to the ratios of the concentrations of the electrolytes observed in the coagulation of various hydrosols. What has been

Table 22

Thresholds of Coagulation (c_c) of Negatively Charged Sol As_2O_3 by Electrolytes

Electrolyte	$c_c \times 10^3$, N	$\frac{(c_c)_x}{(c_c)\ LiCl}$	Electrolyte	$c_c \times 10^3$, N	$\frac{(c_c)_x}{(c_c)\ LiCl}$
LiCl	58.4	1.00	$MgCl_2$	0.717	0.012
NaCl	51.0	0.87	$CaCl_2$	0.649	0.011
KCl	49.5	0.85	$SrCl_2$	0.635	0.011
KNO_3	50.0	0.86	$AlCl_3$	0.093	0.0016

said above is illustrated by the data of Table 22, which gives the equivalent concentrations of electrolytes (c_c) causing the coagulation of a hydrosol of arsenic(III) oxide.

The **molecular-adsorption stabilization of dispersed systems** plays a major role in the stability of dispersions both in aqueous and non-aqueous media. Dispersed systems in non-aqueous media are in principle less stable than in an aqueous one. In a non-polar dispersing medium containing no water, the particles of the dispersed phase are deprived of an electrical charge. The electrical stability factor is absent. Only forces of mutual attraction act between the dispersed particles. The weakening of these forces leading to the stabilization of dispersed systems may occur as a result of the formation around the colloidal particles of adsorption layers consisting of molecules of the dispersing medium and the substances dissolved in it. Such layers weaken the mutual attraction of the dispersed phase particles and set up a mechanical hindrance to their approaching one another.

The stabilization of dispersed systems as a result of the solvation of the dispersed phase by molecules of the dispersing medium is possible both in polar and in non-polar media. For instance, the hydration of particles of clay and silicic acid has an appreciable significance for the stability of suspensions of clays and a sol of silicic acid in an aqueous medium.

The stabilization of dispersed systems is considerably more effective, however, when surfactants and high-molecular compounds adsorbed at the phase interface are added to them. The adsorption layers of the surfactants and the high-molecular compounds, having elasticity and a mechanical strength, prevent the adhesion of the dispersed particles. P. Rehbinder* called the formation of such

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* **Petr Aleksandrovich Rehbinder** (1898-1972), a Soviet physicochemist, Academician, Hero of Socialist Labour, winner of State Prizes, was the founder of a major scientific school in the field of the physical chemistry of dispersed

molecular-adsorption solid-like surface layers the **structural-mechanical** factor of stabilization of dispersed systems. This stabilization mechanism plays the main role in the preparation of extremely stable highly concentrated foams, emulsions, colloidal dispersions, and suspensions not only in non-aqueous, but also in aqueous media. Soaps of the alkali metals, proteins, and starch are used for the structural-mechanical stabilization of dispersions in an aqueous medium, and soaps of the alkaline-earth metals, resins, and rubber are used in non-aqueous media. Such substances are called **protective colloids.**

114. Structure Formation in Dispersed Systems. The Physicochemical Mechanics of Solids and Dispersed Structures

As indicated in Sec. 105, dispersed systems are divided into two large groups: freely dispersed, or non-structurized, and cohesively dispersed, or structurized systems. The latter are formed as a result of contacts appearing between the dispersed particles. The features of these contacts depend on the nature, size, shape, and concentration of the dispersed particles, and also on their distribution by sizes and their interaction with the dispersing medium.

Figure 104 shows schematically the kinds of possible contacts between the particles in structurized dispersed systems. Two kinds of three-dimensional structures sharply differing in their properties are distinguished. Rehbinder called them **coagulation** and **condensation** structures. The main difference between these structures is the different nature of the contact between the particles of the dispersed phase. In coagulation structures, this contact is achieved either through very thin layers of the dispersing medium (Fig. 104*a*) and point contacts (Fig. 104*c*), or with the participation of macromolecules (Fig. 104*b*). Condensation structures appear as a result of adhesion, welding, or intergrowth of the dispersed phase particles at separate parts of the surface (Fig. 104*d*).

Coagulation three-dimensional structures are formed from freely dispersed systems when the dispersion attraction between the particles predominates over the electrostatic repulsion. In this case, the energy of the resultant mutual attraction of the particles is comparable with the energy of their thermal Brownian movement.

In the first stages of coagulation interaction, aggregates of two, three, and sometimes chains of primary dispersed particles appear. The colloidal dispersion retains its fluidity because the develop-

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systems. The ways of controlling the properties of dispersed systems and the processes of their formation and destruction which he developed are closely associated with the solution of major technical problems.

ment of the structure has not reached the formation of a continuous network. A **liquid-like coagulation structure** appears (corresponding to the stage of hidden coagulation, see Sec. 113). In the liquid stream, the aggregates decompose and form again; for each rate of flow there is a corresponding equilibrium amount of aggregates and, consequently, a definite value of their resistance to the liquid flow. For this reason, the appearance of three-dimensional structures in solutions is detected according to the change in the viscosity depending on the rate of flow of the liquid*.

A further growth of the aggregates leads to the formation of a coagulate (sediment) or gel (Fig. 89 on p. 322). A solid-like three-dimensional coagulation structure appears that may be dense or loose.

A dense structure (Fig. 89*b*) appears when the particles of the dispersed phase are packed in the sediment in the most compact way, "sliding" relative to one another. If the primary particles combine into chains, the coagulation structure will be loose—"arched" (Fig. 89*c*). The formation of a gel (Fig. 89*a*) is especially facilitated by an extended shape of the dispersed phase particles, but at higher concentrations, gel formation is also possible with spherical particles if they are disposed to form chains.

Freshly obtained coagulates are often capable of passing again into the state of a sol. Such an isothermal coagulate-sol transition

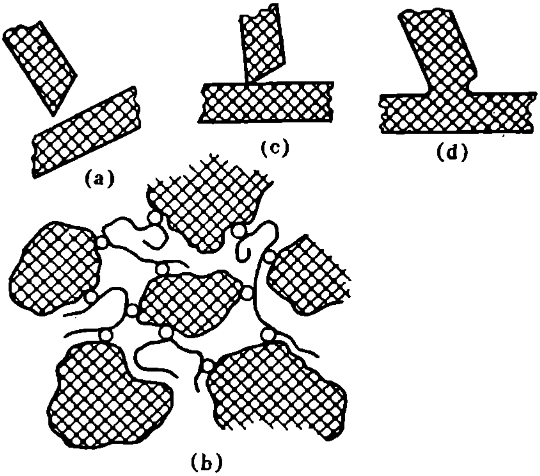

Fig. 104. Kinds of contacts in three-dimensional dispersed structures:
a, *b*—coagulation contacts with low-molecular solvate (*a*) and high-molecular (*b*) layers; *c*—point contacts; *d*—phase contacts

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* For ordinary liquids in the conditions of laminar flow, their viscosity (coefficient of internal friction) does not depend on the rate of flow of the liquid.

is called **peptization**, and the substances inducing it—**peptizin agents**. The latter are stabilizing agents of dispersed systems a may be substances of either an ionic (electrolytes) or molecular nature. The peptizing agents are adsorbed on the surface of the primary particles and weaken the interaction between them. This results in decomposition of the aggregates and transition of the coagulate into the state of a sol. Peptization is often observed when freshly obtained precipitates of metal hydroxides and sulphides are washed with distilled water on a filter. Washing with distilled water diminishes the concentration of the electrolytes, which leads to a change in the structure of the electrical double layer—part of the gegenions pass from the inner layer to the diffuse layer, and the electrokinetic potential of the coagulate particles grows. As a result, the amount of the hydroxide or sulphide precipitate on the filter decreases—it becomes peptized and passes through the filter pores in the form of a sol.

Usually, the ability of coagulates to peptize diminishes with time because of the development of point contacts between the primary particles; strengthening of the coagulation structures occurs. Such a spontaneous change in the properties of colloidal dispersions, coagulates, jellies, and gels is called the **ageing of colloids**. It manifests itself in the aggregation of the dispersed phase particles, in diminishing of their number and the degree of their solvation (hydration for aqueous solutions), and also in diminishing of the interface between phases and of the adsorption capacity.

Coagulation structures have a definite collection of mechanical properties due to the thin layers of the dispersing medium at the sections of contacts between the dispersed phase particles. The cellular lattice of dispersed particles keeps its position at the expense of intermolecular forces, which are not great. For this reason, the strength of coagulation structures is insignificant.

Coagulation structures formed by particles of an extended or laminar shape, and also by chain aggregates, are characterized by **thixotropy** (from the Greek "thiksis"—touching, and "trepein"—to turn). This is the name applied to a reversible demolition of a structure with the transition to the fluid state upon mechanical action, for instance upon shaking, and spontaneous restoration of the structure, "solidification" at rest. Thixotropy can be a useful property. For example, oil paints, being liquefied by mechanical action, do not flow down vertical surfaces as a result of thixotropic structure formation.

Coagulation structures exhibit a structural viscosity, i.e. a change in the viscosity from extremely high values when the structure is not yet destroyed to extremely low values with complete breaking up of the structure and orientation of the particles with their long axis in the direction of flow of the liquid. These extreme values of the viscosity may differ by 10^8 to 10^9 times. Highly concentrated coagulation structures (pastes) are plastic, i.e. their deformation is irreversible.

In the drying of materials having a coagulation structure, the coagulation contacts transform into point ones, the strength of the material rapidly grows, but it loses its plasticity. Watering of such a dried material (for example, paper pulp, dried clay, a ceramic body) results in its wetting with a loss of strength.

The weak interaction between particles in dry dispersed systems causes their pulverization which, particularly, negatively affects the fertility of poorly structurized soils. The poor structure of soils is remedied by introducing organic fertilizers into them. At present, the structure of soils is also improved by introducing synthetic polymers into them, for instance polyacrylamides. Their concentration in the soil should be such that the macromolecules becoming adsorbed on the soil particles will bind several of the latter into a single aggregate (Fig. 104*b*). In a similar way, sands are stabilized and firm soil roads are constructed.

Condensation disperse structures, depending on the mechanism of appearance of the phase contact (Fig. 104*d*) between the particles of the dispersed phase, are divided into two subtypes: (a) a sintered (intergrown) structure, and (b) crystallization structures of solidification.

Condensation sintered (intergrown) structures appear as a result of welding, fusion, sintering, or adhesion of the dispersed particles at their points of contact. Such a structure is obtained in the thermal treatment of a coagulation structure when the particles of the dispersed phase become "welded" at the sites of point contacts. It is characteristic of a number of adsorbents (silica gel, alumogel) that are brittle owing to their loose structure.

At a high density of packing of the dispersed particles, the condensation sintered structures acquire a high strength and frequently a heat resistance. Such structures include compositions of a metal and a refractory metal oxide, for example, sintered aluminium powder. A thin oxide film is deposited on aluminium powder, and the latter is sintered under pressure. The structure of sintered aluminium powder is a lattice of Al_2O_3 film from 10 to 20 nm thick whose cells contain grains of aluminium with the partial contacts between them retained. Thus, condensation structures are continuous lattices of the dispersed phase and the dispersing medium moved into one another without losing their dispersity.

A condensed structure can also be obtained when the dispersed phase condenses from supersaturated vapours, solutions, or melts. Upon the formation and growth of seeds of a new phase, a continuous cellular lattice may be formed from concentrated supersaturated systems by the merging and intergrowth of the growing dispersed phase particles. If these particles are crystals, the appearing structures are called crystallization-condensed structures of solidification.

The formation of crystallization structures in the process of the hydration hardening of mineral binders (aluminate-silicate cements, gypsum, lime) was studied in detail by Rehbinder's school.

A concrete mix consists of cement, aggregates—sand, gravel, crushed stone—and water. The cement grains, which are calcium aluminates and silicates, gradually dissolve, and less soluble crystals of hydrates separate from the supersaturated solution. The hardening of a concrete body consists in the merging and intergrowth of these crystals, which bind the sand, gravel, and crushed stone into a monolithic body. The introduction of surfactants and electrolytes into concrete mixes, and the use of vibrational mechanical action resulted in the development of a new technology for the manufacture of concrete articles having an increased strength and hardness with a simultaneous improvement in the economics of production.

The adhesion of the elements of condensation structures is achieved by the formation of chemical bonds, which is the reason for the considerable strength of these structures. Condensation structures are not thixotropic and are not plastic. They are elastically brittle, irreversibly destroyable structures, unlike the thixotropic reversible coagulation structures.

The field of science studying the physical chemistry of the processes of deformation, destruction, and formation of materials and dispersed structures is called the **physicochemical mechanics of solids and dispersed structures.** It took shape in the middle of the present century owing to the works of Rehbinder and his school as a new field of knowledge bordering on colloidal chemistry, solid state molecular physics, the mechanics of materials, and the technology of their production. The main task of physicochemical mechanics is the creation of materials having the required properties and a structure that is optimal for the uses they are to be put to. Particularly, physicochemical mechanics has the task of improving the strength of materials. This will result in lowering of the mass and increasing of the service life of articles, diminishing of the consumption of materials for their fabrication, thus improving the economical effectiveness of production.

Another task of physicochemical mechanics is closely related to mechanical technology—the processing of metals, minerals, glass, and plastics by crushing, subjecting to pressure, cutting, and drawing—and consists in controlling the relevant processes of deformation, the formation of new surfaces, and dispersion.

In 1928, Rehbinder discovered that the strength of crystals of table salt and calcite decreases noticeably in aqueous solutions of surfactants in comparison with their strength in air. This was the discovery of the effect of adsorption diminishing of the strength and facilitating the deformation of solids called the "Rehbinder effect".

As a result of the adsorption of surfactants at the sites of defects in the crystal lattice (microcracks, seed cracks, grain boundaries in polycrystalline materials), the deformation and destruction of any solid materials are facilitated. The adsorption of surfactants diminishes the surface energy and thus promotes the formation of new surfaces when materials break up.

The effect of the adsorption lowering of the strength and facilitating of the deformation of solids has found widespread use in improving various production processes. The use of this effect allowed engineers to achieve a considerable increase in speeds in the drilling and driving of boreholes in rock, to facilitate the processing of metals by cutting, subjecting to pressure, and drawing, to improve the finish of surfaces in grinding and polishing, and to create better lubricants promoting the running in of machine components.

The strength of real materials owing to defects of their crystalline structure is considerably lower than that of ideal monocrystals. If a material is dispersed to particles whose size is commensurable with the distances between the structure defects, the strength of such highly dispersed particles will be close to that of ideal solids. This gave rise to the idea of increasing the strength of materials by their comminution with the following sintering of the dispersed powders. This idea underlies the production of new materials and articles from them—powder metallurgy and metal ceramics (Vol. 2, Sec. 115).

Broad possibilities of creating new materials open up on the basis of compositions of inorganic substances and polymers of organic compounds. An example is rubber consisting of vulcanized raw rubber (caoutchouc) and carbon black whose mass reaches 50% of that of the rubber. Rubbers having a variety of properties can be produced depending on the proportion of the components and on the distribution of the sulphur and carbon black in the raw rubber. It will be helpful to use this example for stressing the difference between the concepts of substances and materials. Raw rubber, carbon black, and sulphur are substances from which a material having a definite structure—rubber—is formed.

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Problems and Exercises in General Chemistry

N. GLINKA, D.Sc.

This is a training aid in general chemistry for students of higher educational institutions not majoring in the subject. It has been revised quite considerably (the previous twentieth Russian edition was published in 1973) in order to be used in conjunction with the latest twenty first edition of the author's General Chemistry. Each section has a brief theoretical introduction and examples showing how to solve typical problems. Many sections of the book contain questions contributing to a full coverage of the material. All physicochemical quantities are expressed in SI units. The appendices contain all the reference data needed for solving the problems.

The book will be a useful aid for self-education in the fundamentals of chemistry and for students at chemical technical schools.

Cryochemistry

G. SERGEEV, D.Sc.
and V. BATYUK, Cand. Sc.

The book presents an up-to-date review of the technology available to the cryochemist who is interested in its applications to organic, inorganic and organometallic synthesis, homogeneous and heterogeneous reactions, photochemistry, intermolecular interactions, spectroscopy (infrared, Raman, UV, and visible), matrix-isolation techniques, X-ray diffraction studies, etc.

It contains an extensive bibliography (739 references) and will therefore be a useful reference source for chemists, physicists, chemical engineers and spectroscopists working in these fields. It is also suitable as a text for a course on the subject.

Physical Chemistry (in two volumes)

Ya. GERASIMOV, D. Sc (Ed.)

This manual has been written by a body of authors including Ya. Gerasimov, who has also made the general editing.
Volume I sets forth the fundamentals of chemical thermodynamics, the thermodynamics of solutions, the theoty of chemical and heterogeneous equilibrium and of surface phenomena and absorption.
Volume II is devoted to chemical kinetics, catalysis and electrochemistry.
The book is intended for students of chemical faculties of Universities; it will be useful to post-graduates and teachers of physical chemistry.

Selected SI Units

	Quantity	Unit	
		Name	Symbol
Basic Units	Length	metre	m
	Mass	kilogram	kg
	Time	second	s
	Electric current	ampere	A
	Temperature	kelvin	K
	Amount of substance	mole	mol
Derived Units	Force	newton	N (kg·m/s^2)
	Pressure	pascal	Pa (N/m^2)
	Energy, work, amount of heat	joule	J (N·m)
	Power	watt	W (J/s)
	Quantity of electricity	coulomb	C (A·s)
	Electric voltage, electric potential	volt	V (W/A)
	Electrical resistance	ohm	Ω (V/A)
	Electrical conductance	siemens	S (A/V)

Conversion of Selected Non-System Units to SI Units

Quantity	Unit	Conversion factor to SI
Length	micrometre (μm)	1×10^{-6} m
	angstrom (Å)	1×10^{-10} m
Pressure	atmosphere (atm)	1.01325×10^{5} Pa
	millimetre of mercury (mmHg) or torr	133.322 Pa
	bar	1×10^{5} Pa
Energy, work, amount of heat	electron-volt (eV)	1.60219×10^{-19} J
	calorie (cal)	4.1868 J
	kilocalorie (kcal)	4186.8 J

Fundamental Constants

Speed of light in free space	$c = 2.9979246 \times 10^{8}$ m/s
Charge of an electron	$e = 1.602189 \times 10^{-19}$ C
Planck's constant	$h = 6.62618 \times 10^{-34}$ J·s
Avogadro's constant	$N_A = 6.022045 \times 10^{23}$ mol^{-1}
Faraday's constant	$F = 9.64846 \times 10^{4}$ C/mol
Molar gas constant	$R = 8.3144$ J/(mol·K)

About the book

Professor N. Glinka's textbook systematizes the theoretical aspects and includes an extensive collection of reference data tor the course in general chemistry. Great attention is given to the structure of atoms and molecules, the laws of chemical reactions, and oxidation-reduction, processes. The book has been very popular in the Soviet Union and other countries for many years. During the author's life, it saw 12 editions in Russian and was repeatedly published in other languages. The time that has elapsed after the author's death, however required the introduction of appreciable amendments into the book, first of all beause of the deep penetration of chemistry into many branches of the national economy and of the tremendous growth in the volume of the factual material of chemistry. The required revision of the textbook was carried out in its sixteenth Russian eoition (1973).

An additional revision of the book mainly due to the transition to SI1 units of physical quantities and the associated alterations in the terminology was carried out in the nineteenth Russian edition (1977). The present English text has been translated from the 21st Russian edition (1980), and to facilitate work with the book, has been divided into two volumes.

The book is intended for students of higher educational institutions not majoring in chemistry. It will also be very helpful for persons studying the fundamentals of chemistry independently, and for students of chemical technical schools and the senior classes of secondary schools.

General Chemistry

N. L. Glinka